**Advanced EXAFS analysis and considerations: What’s under the hood**

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**X-ray absorption spectroscopy (XAS) experimental setup**

- Sample absorption is given by
  \[ \mu t = \log(I/I) \]
- Reference absorption is
  \[ \mu_{	ext{ref}} t = \log(I/I) \]
- Sample absorption in fluorescence
  \[ \mu = I/I \]

**NOTE:** Because we are always taking relative-change ratios, detector gains don’t matter!

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**X-ray absorption spectroscopy**

- Main features are single-electron excitations.
- Away from edges, energy dependence fits a power law: \( \mu(E) \sim E^{-4} \) (Victoreen).
- Threshold energies \( E_0 \sim 2 \), absorption coefficient \( \mu \sim \mu \).

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**X-ray absorption fine-structure (XAFS) spectroscopy**

- **μ(E) vs. kx**
  - Spectrum: Measured data
  - White line: Unknown instrument
  - pre-edge subtraction
  - post-edge subtraction
  - Data reduction

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**Topics**

1. **Overview**
2. **Theory**
   A. Simple “heuristic” derivation
   B. Polarization: oriented vs spherically averaged (won’t cover)
   C. Thermal effects
3. **Experiment: Corrections and Other Problems**
   A. Sample issues (size effect, thickness effect, glitches) (won’t cover)
   B. Fluorescence mode: Dead time and Self-absorption (won’t cover)
   C. Energy resolution (won’t cover)
4. **Data Analysis**
   A. Correlations between parameters (e.g., mean-free path)
   B. Fitting procedures (After this talk)
   C. Fourier concepts
   D. Systematic errors (won’t cover)
   E. “Random” errors (won’t cover)
   F. F-tests

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**Data reduction: \( \mu(E) \sim \chi(kx) \)**

- **μ(E) vs. kx**
  - **μ(E):** Measured data
  - **White line:** Unknown instrument
  - **pre-edge subtraction**
  - **post-edge subtraction**
  - **Data reduction:**
    - Determine \( E_0 \)
    - Plot \( \mu(E)/E \) vs. \( E \)
How to read an XAFS spectrum

- Peak width depends on back-scattering amplitude $F(k,r)$, the Fourier transform (FT) range, and the distribution width of $g(r)$, a.k.a. the Debye-Waller factors.
- Do NOT read this strictly as a radial-distribution function! Must do detailed fitting!

**How is final state wave function modulated?**

- Assume photoelectron reaches the continuum within dipole approximation:

$$\langle \hat{E} \rangle \langle \hat{E} \rangle^\dagger e^{ikR}$$

- Central atom phase shift $\delta_c(k)$
- Electronic mean-free path $\lambda(k)$

**“Heuristic” derivation**

- In quantum mechanics, absorption is given by “Fermi’s Golden Rule”:

$$\mu = |\langle \psi_i | \hat{V} | \psi_f \rangle|^2$$

$$|\langle \psi_f | \hat{V} | \psi_i \rangle|^2 = \mu_i + \mu_f^* \hat{V}^\dagger \hat{V}$$

$$\hat{V} = \hat{N} + \hat{F}$$

Note, this is the same as saying this is the change in the absorption per photoelectron
How is final state wave function modulated?

• Assume photoelectron reaches the continuum within dipole approximation:
  \( \hat{\psi}(k) = \sum_{j} e^{i k \cdot r_j} \left( \frac{1}{2\sigma} e^{-\frac{(x-x_j)^2}{2\sigma^2}} \right) \) in \( 2\Delta k + 2\delta(\hat{k} + \delta(\hat{k})) \)

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Other factors

• Allow for multiple atoms \( N_j \) in a shell \( j \) and a distribution function function of bondlengths within the shell \( g(r) \)
  \( g(k) = \sum_{j} N_j \left( \frac{1}{2\sigma} e^{-\frac{(x-x_j)^2}{2\sigma^2}} \right) \) in \( 2\Delta k + 2\delta(\hat{k} + \delta(\hat{k})) \)
  where \( g(r) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{r^2}{2\sigma^2}} \) and \( S_2^2 \) is an inelastic loss factor
  \( g(k) = \sum_{j} N_j \left( \frac{1}{2\sigma} e^{-\frac{(x-x_j)^2}{2\sigma^2}} \right) \) in \( 2\Delta k + 2\delta(\hat{k} + \delta(\hat{k})) \)

Requires curved wave scattering, has r-dependence, use full curved wave theory: FEFF
  Assumed both harmonic potential AND \( k \) small: problem at high \( k \) and/or \( \theta \) good to FEFF

Some words about Debye-Waller factors

\( g(\hat{k}) = \sum_{j} N_j \left( \frac{1}{2\sigma} e^{-\frac{(x-x_j)^2}{2\sigma^2}} \right) \) in \( 2\Delta k + 2\delta(\hat{k} + \delta(\hat{k})) \)

- Harmonic approximation: Gaussian
  \( g(r) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{r^2}{2\sigma^2}} \)

\( \sigma_i^2 = \langle (\Delta P_i - \Delta P_i)^2 \rangle = \langle \Delta P_i^2 + \Delta P_i^2 - 2\Delta P_i \Delta P_i \rangle \)

\( \sigma_i^2 = \langle U_i^2 + U_j^2 \rangle - 2\langle U_i U_j \rangle \)

\( U_i^2 \) are the position mean-squared displacements (MSDs) from diffraction

Important: EXAFS measures MSD differences in position (in contrast to diffraction!!)

Lattice vibrations and Debye-Waller factors

• isolated atom pair, spring constant \( \kappa \)

\( m_i = (1/m_i + 1/m_j)^{-1} \)

Classically...
  \( E = \frac{1}{2} m_i v^2 + \frac{1}{2} \kappa x^2 \)
  \(< E >= \frac{1}{2} m_i v^2 + \frac{1}{2} \kappa x^2 > \)

Quantumly...
  \( \langle E >= \frac{1}{2} \kappa \theta^2 \) at high T
  \( \sigma_i^2 = \frac{\hbar \omega}{\kappa} \) at low T

\( \phi \) term above is +1 if atom motions are perfectly correlated,
0 if they are uncorrelated and -1 if anticorrelated
Some words about Debye-Waller factors

- The general formula for the variance of a lattice vibration is:

\[ \Delta \beta^2 = \langle \frac{1}{2} \beta^2 \rangle - \langle \beta \rangle^2 \]

where \( \beta \) is the projected density of modes with vibrational frequency \( \omega \).

- Einstein model: single frequency
- Correlated-Debye model: quadratic and linear dispersion

\[ \Delta \beta^2 = e \Delta \beta_0 \]

Fitting the data to extract structural information

- Fit is to the standard EXAFS equation using either a theoretical calculation or an experimental measurement of \( F(k) \):

\[ I(k) = N \sum_i N_i \frac{R_i}{k} \left( \frac{r_i}{k} \right)^{2n} \sin(2kR_i + \phi_i) + B \]

- Typically, polarization is spherically averaged, doesn’t have to be
- Typical fit parameters include: \( R_i, N_i, \phi_i, \Delta F_i \)

Many codes are available for performing these fits:

- EXAFSPAK
- FEFFIT
- SCALEPACK
- ATHENA
- GNXAS
- RxCAP

XAFS of uranium-bacterial samples

- XAFS can tell us whether uranium and phosphate form a complex
- U-O\(_{sp} \) are very stiff at 1000 K
- U-O\(_{nb} \) also stiff! Won’t change with temperature
- U-P much lesser \( \Delta \beta \approx 300 \text{ K} \): Enhancement at low \( T \) due to U-O\(_{sp} \)

FEFF: a curved-wave, multiple scattering EXAFS and XANES calculator

- The FEFF Project is lead by John Rohr and is very widely used and trusted
- Calculates the complex scattering function \( F(k) \) and the mean-free path \( l \)

Phase shifts: functions of \( k \)

- \( \sin(2\pi \cdot l \cdot \phi(k)) \): linear part of \( \phi(k) \) will look like a shift in \( k \) slope
  - is about -0.35 Å
  - peak in \( r \) will be shifted by about 0.35 Å
- Both central atom and backscattering atom phase shifts are important

- Can cause CONFUSION: sometimes possible to fit the wrong atomic species at the wrong distance!

- Luckily, different species have reasonably unique phase and scattering functions (next slide)
Species identification: phase and magnitude signatures

First example: same structure, first neighbor

Magnitude signatures then take over

Note Ca (peak at 2.8 Å) and C have nearly the same profile.

But what does this mean? It means that:

Generally should never have $N_{obs}$.

Fit degrees of freedom $\approx N_{obs} - N_{param}$.


More Fourier concepts: Independent data points

Spectral theory indicates that each point in $k$-space affects every point in $r$-space. Therefore, assuming a fit range over $k$ (and $r$):

$\Delta_k = k_1 - k_0$

$r_{max} = \frac{\pi}{2\delta_k} = \frac{k_{max}}{2}\frac{1}{\delta_k} = \left(\frac{\Delta_k}{2}\right) + 1$

$N_{fit} = \frac{1}{2} \Delta_k + 2 + h.o.t.$ "Stern’s rule" EXAFS result

- Fit degrees of freedom $\approx N_{obs} - N_{param}$.
- Generally should never have $N_{obs} > N_{param}$ ($\neq 1$).
- But what does this mean? It means that:

For $N_{obs}$ exceeding $N_{param}$, there are other linear combinations of $N_{obs}$ that produce EXAFTS the same fit function.

More phase stuff: $r$ and $E_0$ are correlated

- When fitting, $\Delta E_0$ generally is allowed to float (vary).
- In theory, a single $\Delta E_0$ is needed for a monovalent absorbing species.
- Errors in $\Delta E_0$ act like a phase shift and correlate to errors in $R^d$.

Consider error $\varepsilon$ in $E_0$: $k_{min} = 0.512[E-(E_0 + \varepsilon)]^{1/2}$

For small $\varepsilon$: $k_{min} = 0.512^{1/2}[2\delta_k]\varepsilon$.

e.g. at $k = 10\text{Å}^{-1}$ and $\varepsilon = 1$ eV, $\Delta k \approx 0.013$ Å

- This correlation is not a problem if $k_{min}$ is reasonably large.
- Correlation between $N$, $S$, and $\sigma$ is a much bigger problem!

Information content in EXAFS

- $k$-space vs. $r$-space fitting are equivalent if done correctly.

$r$-range in $k$-space fits is determined by scattering shell with highest $R$.

$k$-space direct comparisons with raw data (i.e. residual calculations) are typically incorrect: must Fourier filter data over $r$-range

All knowledge from spectral theory applies! Especially, discrete sampling Fourier theory...

Fourier concepts

- Highest “frequency” $k_{max} = 2\delta_k$ (Nyquist frequency)

e.g. for sampling interval $\Delta k = 0.05$ Å, $k_{max} = 51$ Å

- For $N_{param}$, discrete Fourier transform has $N_{param}$ too! Therefore...

FT resolution is $\delta_r = \frac{1}{\Delta k} = \frac{2\delta_k}{k_{max}}$. Therefore...

- This is the ultimate limit, corresponds to when a beat is observed in two sine wave $\delta_k$ apart. IF YOU DON’T SEE A BEAT, DON’T RELY ON THIS EQUATION!!

- $F(r)$ is $\approx \frac{1}{2\pi} \sum [g(r) \cos(2\pi r)]

$g(r)$ is the real part of $E_0$.

$N_{param}$ is the number of parameters.

Not so Advanced Topic: F-test

- F-test, commonly used in crystallography to test one fitting model versus another

$F = \frac{\langle g_2 \rangle}{\langle g_1 \rangle}$

(if errors approximately cancel)

Alternatively:

$F = \frac{(R_3 - R_1)^2}{\langle g_2 \rangle}$

Like $\chi^2$. F-function is tabulated, is given by incomplete beta function

Advantages over a $\chi^2$-type test:

— don’t need to know the errors!
Statistical tests between models: the F-test

\[ F = \frac{\chi^2_1 / \nu_1}{\chi^2_2 / \nu_2} = \frac{\sum (y_i - y_i^f)^2}{\nu_2} \]

\[ F = \left[ \frac{R_1^2}{R_2^2} \right] (\frac{\alpha}{b}) \]

For tests between data with constant error models that share degrees of freedom, Hamilton test with \( b = \nu_1 - \nu_2 \), where \( \alpha \) is the confidence level and \( I(v_i) \) is an incomplete beta function.

• F-tests have big advantages for data sets with poorly defined noise levels
  — with systematic error, \( R_1 \) and \( R_2 \) increase by constant, reducing the ratio (right direction!)

Unfortunately, systematic errors dominate

Example without systematic error:
\( k_{\text{max}} = 13 \text{ Å}^{-1}, \alpha = 6.19, \theta = 7.19 \)
\( R = 0.31 \)
\( \alpha = 0.999 \rightarrow \text{passes } F \)-test

Example with systematic error at \( R = 2\% \):
\( k_{\text{max}} = 13 \text{ Å}^{-1}, \alpha = 6.19, \theta = 7.19 \)
\( R = 0.31 + 2.0 = 2.31 \)
\( \alpha = 0.79 + 2.0 = 2.79 \)
\( \alpha = 0.86 \rightarrow \text{does not pass} \)

Further reading

• Overview:
• Historically important:
• Theory papers of note:
  — Rehr and Albers, Rev. Mod. Phys. 72, 621 (2008).
• Useful links
  — xaR.org (especially see Tutorials section)
  — http://www.i-x-s.org (International XAS society)
  — http://www.csrri.iit.edu/periodic-table.html (absorption calculator)

F-test example testing resolution in EXAFS:
knowledge of line shape huge advantage

• 6 Cu-Cu at 2.55 Å, 6 at 2.65 Å
• \( k_{\text{max}} = 2.8 \), 15.7 Å
• 1 peak (+cumulants) vs 2 peak fits
• Fits to 18 Å all pass the F-test
• \( S > 50 \) does not pass at 15 Å
• \( S > 20 \) does not pass at 13 Å
• \( S > 4 \) does not pass at ~11 Å

Finishing up

• Never report two bond lengths that break the resolution rule
• Break Stern’s rule only with extreme caution
• Pay attention to the statistics

Further reading

• Glitches:
• Theory vs. experiment:
• Polarized EXAFS:
• Hamilton (F-test):
Further reading

- Correlated-Debye model:
- Correlated Einstein model

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