Advanced EXAFS analysis and considerations: What's under the hood

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Presented at the *Synchrotron X-Ray Absorption Spectroscopy Summer School ,*
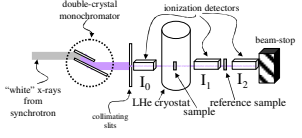June 28-July 1, 2011

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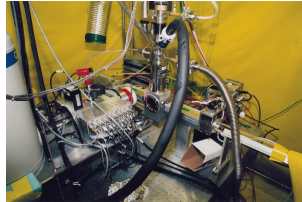
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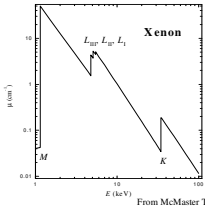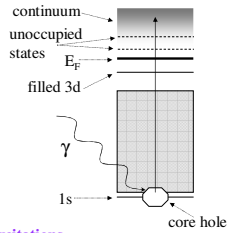## X-ray absorption spectroscopy (XAS) experimental setup

- sample absorption is given by
  $$\mu t = \log_e(I_0/I_1)$$
- reference absorption is
  $$\mu_{REF} t = \log_e(I_1/I_2)$$
- sample absorption in fluorescence
  $$\mu \propto I_F/I_0$$
- NOTE: because we are always taking relative-change ratios, *detector gains don't matter!*
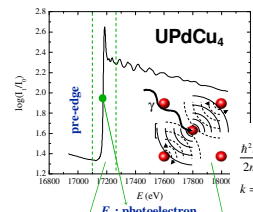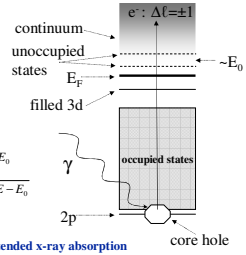
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X-ray absorption spectroscopy

- **Main features are single-electron excitations.**
- **Away from edges, energy dependence fits a power law: $\mu \propto AE^{-3}+BE^{-4}$ (Victoreen).**
- **Threshold energies $E_0 \sim Z^2$, absorption coefficient $\mu \sim Z^4$.**

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X-ray absorption fine-structure (XAFS) spectroscopy

$$\frac{\hbar^2 k^2}{2m_e} = E - E_0$$
$$k = 0.512\sqrt{E - E_0}$$

E_0: photoelectron threshold energy
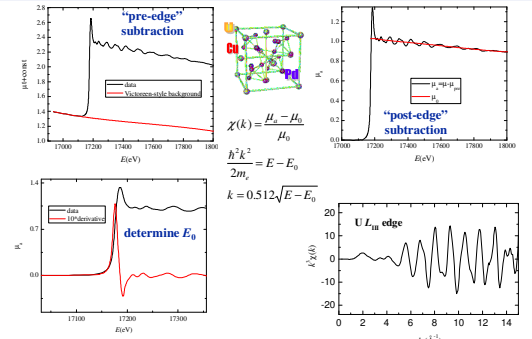
EXAFS region: extended x-ray absorption fine-structure

"edge region": x-ray absorption near-edge structure (XANES)
near-edge x-ray absorption fine-structure (NEXAFS)

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Data reduction: $\mu(E) \rightarrow \chi(k,r)$

$$\chi(k) = \frac{\mu_a - \mu_0}{\mu_0}$$
$$\frac{\hbar^2 k^2}{2m_e} = E - E_0$$
$$k = 0.512\sqrt{E - E_0}$$

"pre-edge" subtraction

"post-edge" subtraction

determine E_0

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How to read an XAFS spectrum

12 U-Cu   4 U-Pd   16 U-Cu

U L_{III} edge

FT of $k\chi(k)$

— data
···· fit

r (Å)

3.06 Å
2.93 Å

Envelope = magnitude $[Re^2 + Im^2]^{1/2}$

Real part of the complex transform

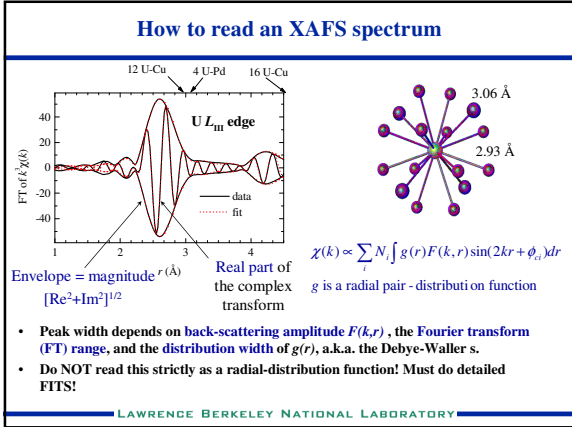$$\chi(k) \propto \sum_i N_i \int g(r) F(k, r) \sin(2kr + \phi_{ci}) dr$$

g is a radial pair - distribution function

- 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 s.
- Do **NOT** read this strictly as a radial-distribution function! Must do detailed **FITS!**

"Heuristic" derivation

- In quantum mechanics, absorption is given by "Fermi's Golden Rule":

$$\mu \sim \left| \langle f | \hat{e} \cdot \hat{r} | i \rangle \right|^2$$

$$|f\rangle = |f_0\rangle + |\Delta f\rangle$$

$$\mu \sim \left| \langle f | \hat{e} \cdot \hat{r} | i \rangle \right|^2 = \left| \langle f_0 + \Delta f | \hat{e} \cdot \hat{r} | i \rangle \right|^2$$
$$= \left| \langle f_0 | \hat{e} \cdot \hat{r} | i \rangle \right|^2 + \langle i | \hat{e} \cdot \hat{r} | f_0 \rangle \langle \Delta f | \hat{e} \cdot \hat{r} | i \rangle$$
$$+ c.c. + h.o.t.$$

γ

$$\chi = \frac{\mu - \mu_0}{\mu_0} = \frac{\Delta \mu}{\mu_0}$$

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:

$$(\hat{e} \cdot \hat{r})^2$$

$\hat{\varepsilon}$

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$$(\hat{e} \cdot \hat{r})^2 \frac{e^{-ikR + i\delta_c(k)}}{kR} e^{-R/\lambda(k)}$$ electronic mean-free path $\lambda(k)$

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$$(\hat{\varepsilon}\cdot\hat{r})^2\,\frac{e^{-ikr+i\delta_c(k)}}{kr}\quad\text{central atom phase shift }\delta_c(k)$$

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$$(\hat{\varepsilon}\cdot\hat{r})^2\,\frac{e^{-ikR+i\delta_c(k)}}{kR}kf(\pi,k)e^{-R/\lambda(k)}\quad\text{complex backscattering probability }f(\pi,k)$$

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$$(\hat{\varepsilon}\cdot\hat{r})^2\,\frac{e^{-ikR+i\delta_c(k)}}{kR}k\big|f(\pi,k)\big|e^{-R/\lambda(k)}\frac{e^{-ik(R-r)+i\delta_c(k)+i\delta_a(k)}}{kR}\quad\begin{array}{l}\text{complex=magnitude and phase:}\\\text{backscattering atom phase shift }\delta_a(k)\end{array}$$

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$$\mathrm{Im}(\hat{\varepsilon}\cdot\hat{r})^2\,\frac{e^{-2ikR+2\delta_c(k)+i\delta_a(k)}}{kR^2}\big|f(\pi,k)\big|e^{-2R/\lambda(k)}\quad\text{final interference modulation per point atom!}$$

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Other factors

- Allow for multiple atoms N_i in a shell i and a distribution function of bondlengths within the shell $g(r)$

$$\chi(k)=S_0^2\sum_i N_i\int(\hat{\varepsilon}\cdot\hat{r})^2\big|f(\pi,k)\big|e^{-2r/\lambda(k)}g(r)\frac{\sin 2kr+2\delta_c(k)+\delta_a(k)}{kr^2}dr$$

where $\quad g(r)=\dfrac{1}{\sqrt{2\pi}\sigma}e^{-\frac{(r-R_i)^2}{2\sigma^2}}\quad$ and S_0^2 is an inelastic loss factor

$$\chi(k)\approx S_0^2\sum_i N_i(\hat{\varepsilon}\cdot\hat{r})^2\big|f(\pi,k)\big|e^{-2r/\lambda(k)}e^{-2k^2\sigma^2}\frac{\sin 2kr+2\delta_c(k)+\delta_a(k)}{kr^2}$$

Requires curved wave scattering, has r-dependence, use full curved wave theory: FEFF

Assumed both harmonic potential AND $k\sigma\ll1$: problem at high k and/or σ (good to $k\sigma$ of about 1)

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Some words about Debye-Waller factors

$$\chi(k)=S_0^2\sum_i N_i\int(\hat{\varepsilon}\cdot\hat{r})^2\big|f_i(\pi,k)\big|e^{-2r/\lambda(k)}g_i(r)\frac{\sin 2kr+2\delta_c(k)+\delta_i(k)}{kr^2}dr$$

- Harmonic approximation: Gaussian

P_i

P_j

$$g_i(r)=\frac{1}{\sqrt{2\pi}\sigma}e^{-\frac{(r-r_i)^2}{2\sigma^2}}$$

(non-Gaussian is advanced topic: "cumulant expansion")

$$\sigma_{ij}^2=\big\langle(\Delta P_i-\Delta P_j)^2\big\rangle=\big\langle\Delta P_i^2+\Delta P_j^2-2\Delta P_i\Delta P_j\big\rangle$$

$$=\big\langle\Delta P_i^2\big\rangle+\big\langle\Delta P_j^2\big\rangle-2\big\langle\Delta P_i\Delta P_j\big\rangle$$

$$\sigma_{ij}^2=U_i^2+U_j^2-2\phi U_i U_j$$

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

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

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Lattice vibrations and Debye-Waller factors

- isolated atom pair, spring constant κ

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

Classically…

$$E=\frac{1}{2}m_r v^2+\frac{1}{2}\kappa x^2$$

$$<E>=<\frac{1}{2}m_r v^2+\frac{1}{2}\kappa x^2>$$

$$=<\kappa x^2>=\kappa<x^2>=\kappa\sigma^2$$

with $\kappa=m_r\omega^2$

Quantumly…

$$<E>=<n+\frac{1}{2}>\hbar\omega$$

$$<E>\approx k_B T\quad\text{at high }T$$

$$\sigma^2=\frac{<E>}{\kappa}\approx\frac{k_B T}{\kappa}$$

$$\sigma^2=\frac{\hbar\omega}{\kappa}\quad\text{at low }T$$

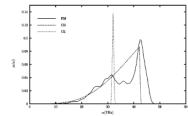LAWRENCE BERKELEY NATIONAL LABORATORY

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:**

$$\sigma_j^2 = \frac{\hbar}{2m_i} \int \frac{d\omega}{\omega} \rho_j(\omega) \coth\left(\frac{\hbar\omega}{2k_B T}\right)$$

where $\rho_j(\omega)$ is the projected density of modes with vibrational frequency ω

$k = 6\pi/6a \quad \lambda = 2.00a \quad \omega_k = 2.00\omega$
$k = 5\pi/6a \quad \lambda = 2.40a \quad \omega_k = 1.90\omega$
$k = 4\pi/6a \quad \lambda = 3.00a \quad \omega_k = 1.70\omega$
$k = 3\pi/6a \quad \lambda = 4.00a \quad \omega_k = 1.41\omega$
$k = 2\pi/6a \quad \lambda = 6.00a \quad \omega_k = 1.00\omega$
$k = 1\pi/6a \quad \lambda = 12.00a \quad \omega_k = 0.52\omega$

FIG. 1. Projected VDOS $\rho_j(\omega)$ for the first shell of Cu calculated using the EM method with $N = 459$ and $k_1 = 27.9$ N/m (solid line), in comparison with CD (long dashed line) and CE (short dashed line) models.

- **Einstein model: single frequency**
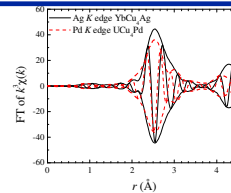- **correlated-Debye model: quadratic and linear dispersion** $\omega_{cD} = c\, k_{cD}$

Poiarkova and Rehr, *Phys. Rev. B* **59**, 948 (1999).

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A "zero-disorder" example: YbCu$_4$X
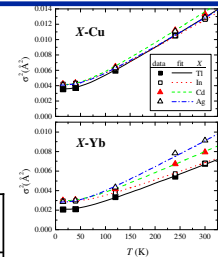
X	S02	Θ_{cD}(K)		σ_{static}^2(Å)		X/Cu interchange
		Cu	Yb	Cu	Yb	
Tl	0.89(5)	230(5)	230(5)	0.0004(4)	0.0005(5)	4(1)%
In	1.04(5)	252(5)	280(5)	0.0009(4)	0.0011(5)	2(3)%
Cd	0.98(5)	240(5)	255(5)	0.0007(4)	0.0010(5)	5(5)%
Ag	0.91(5)	250(5)	235(5)	0.0008(4)	0.0006(5)	2(2)%

$$\sigma_{AB}^2(T) = \sigma_{static}^2 + F(\mu_{AB}, \Theta_{cD})$$

J. L. Lawrence et al., PRB 63, 054427 (2000).

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XAFS of uranium-bacterial samples
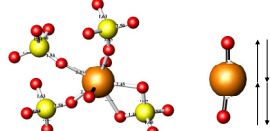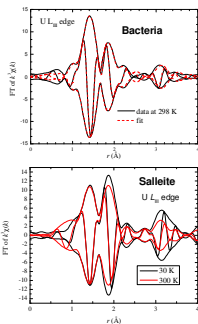
- **XAFS can tell us whether uranium and phosphate form a complex**
- **U-O$_{ax}$ are very stiff Θ_{cD}~1000 K**
- **U-O$_{ax}$-O$_{ax}$ also stiff! Won't change with temperature**
- **U-P much looser Θ_{cD}~300 K: Enhance at low T w.r.t. U-O$_{ax}$-O$_{ax}$!**

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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$_{eff}$**

$$\chi(k) = S_0^2 \sum_i N_i \left|(\hat{\varepsilon} \cdot \hat{r}_i)^2\right| |f_i(\pi, k)| e^{-2r/\lambda(k)} g_i(r) \frac{\sin 2kr + 2\delta_c(k) + \delta_i(k)}{kr^2} dr$$

- **Typically, polarization is spherically averaged, doesn't have to be**
- **Typical fit parameters include: R_i, N_i, σ_i, ΔE_0**
- **Many codes are available for performing these fits:**
  — EXAFSPAK
  — IFEFFIT
    • SIXPACK
    • ATHENA
  — GNXAS
  — RSXAP

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

- **The FEFF Project is lead by John Rehr and is very widely used and trusted**
- **Calculates the complex scattering function F$_{eff}$(k) and the mean-free path λ**
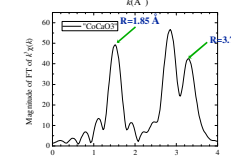
```
TITLE CaMnO3 from Poeppelmeier 1982

HOLE 1  1.0   Mn K edge  ( 6.540 keV), s0^2=1.0
POTENTIALS
*  ipot   z  label
    0   22  Mn
    1    8  O
    2   20  Ca
    3   22  Mn

ATOMS
  0.00000   0.00000   0.00000   0  Mn  0.00000
  0.00000  -1.85615   0.00000   1  O(1) 1.85615
  0.00000   1.85615   0.00000   1  O(1) 1.85615
 -1.31250   0.00000   1.31250   1  O(2) 1.85616
  1.31250   0.00000  -1.31250   1  O(2) 1.85616
  1.31250   0.00000   1.31250   1  O(2) 1.85616
 -1.31250   0.00000  -1.31250   1  O(2) 1.85616
  0.00000   1.85615  -2.62500   2  Ca  3.21495
 -2.62500   1.85615   0.00000   2  Ca  3.21495
 -2.62500  -1.85615   0.00000   2  Ca  3.21495
  0.00000   1.85615   2.62500   2  Ca  3.21495
```

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Phase shifts: functions of *k*
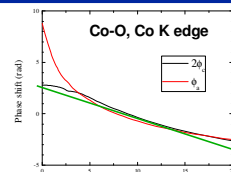
- **sin(2kr+ϕ_{tot}(k)): linear part of ϕ(k) will look like a shift in r slope is about -2x0.35 rad Å, so peak in r will be shifted by about 0.35 Å**
- **Both central atom and backscattering atom phase shifts are important**
- **Can cause CONFUSION:** *sometimes possible to fit the wrong atomic species at the wrong distance!*
- **Luckily, different species have reasonably unique phase and scattering functions (next slide)**

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Species identification: phase and magnitude signatures
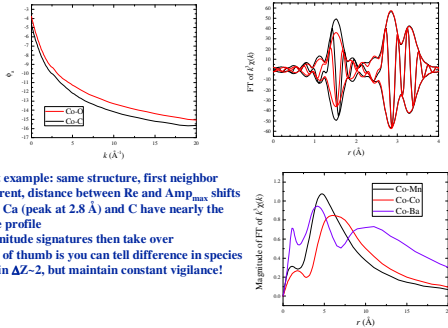
- First example: same structure, first neighbor different, distance between Re and Amp$_{max}$ shifts
- Note Ca (peak at 2.8 Å) and C have nearly the same profile
- Magnitude signatures then take over
- Rule of thumb is you can tell difference in species within $\Delta Z \sim 2$, but maintain constant vigilance!

More phase stuff: r and E_0 are correlated

- When fitting, ΔE_0 generally is allowed to float (vary)
- In theory, a single ΔE_0 is needed for a monovalent absorbing species
- Errors in ΔE_0 act like a **phase shift** and correlate to errors in **R**!

    consider error ε in E_0: $k_{true}=0.512[E-(E_0+\varepsilon)]^{1/2}$
    for small ε, $k=k_0-[(0.512)^2/(2k_0)]\varepsilon$
    eg. at $k=10$Å^{-1} and $\varepsilon=1$ eV, $\Delta r \sim 0.013$ Å

- This correlation is not a problem if k_{max} is reasonably large

- *Correlation between N, S_0^2 and σ is a much bigger problem!*

Information content in EXAFS

- *k*-space vs. *r*-space fitting are *equivalent* if done correctly!
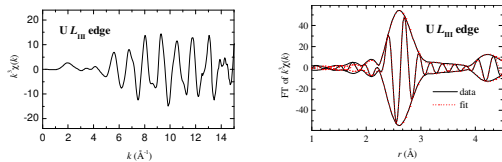
- *r*-range in *k*-space fits is determined by scattering shell with highest *R*
- *k*-space direct comparisons with raw data (i.e. residual calculations) are typically incorrect: must Fourier filter data over *r*-range
- All knowledge from spectral theory applies! Especially, discrete sampling Fourier theory…

Fourier concepts

- highest "frequency" $r_{max}=\pi(2\delta_k)^{-1}$ (Nyquist frequency)
    eg. for sampling interval $\Delta k=0.05$ Å^{-1}, $r_{max}=31$ Å
- for N_{data}, discrete Fourier transform has N_{data} too! Therefore…
    FT resolution is $\delta_R=r_{max}/N_{data}=\pi/(2k_{max})$, e.g. $k_{max}=15$ Å^{-1}, $\delta_R=0.1$ Å
- This is the ultimate limit, corresponds to when a beat is observed in two sine wave δ_R apart. IF YOU DON'T SEE A BEAT, DON'T RELY ON THIS EQUATION!!
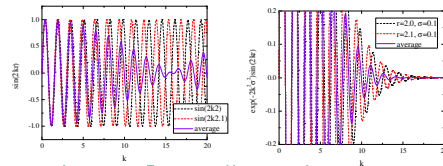
More Fourier concepts: Independent data points

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

$$\Delta_r = r_2 - r_1 \qquad \Delta_k = k_2 - k_1$$

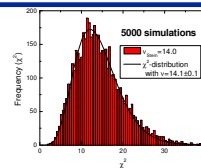$$r_{max} = \frac{\pi}{2\delta_k} \qquad N_k = \frac{k_{max}}{\delta_k}+1 = 2\left(\frac{r_{max}}{\delta_r}+1\right)$$

$$N_{ind} = \frac{2}{\pi}\Delta_r\Delta_k + 2 + h.o.t. \quad \text{"Stern's rule" EXAFS result}$$

- Fit degrees of freedom $\nu=N_{ind}-N_{fit}$ Stern, *Phys. Rev. B* 48, 9825 (1993).
- Generally should never have $N_{fit}>=N_{ind}$ ($\nu<1$)
- But what does this mean? It means that:

    For N_{fit} exceeding N_{ind}, there are other linear combinations of N_{fit} that produce EXACTLY the same fit function

---

not so Advanced Topic: F-test

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

    $$F=(\chi_1^2/\nu_1)/(\chi_0^2/\nu_0)\approx\nu_0/\nu_1\times R_1^2/R_0^2$$
    (if errors approximately cancel)
    alternatively: $F=[(R_1^2-R_0^2)/(\nu_1-\nu_0)]/(R_0^2/\nu_0)$

- Like χ^2, F-function is tabulated, is given by incomplete beta function
- Advantages over a χ^2-type test:
    —don't need to know the errors!

Statistical tests between models: the F-test

$$F = \frac{\chi_1^2/\upsilon_1}{\chi_0^2/\upsilon_0} \qquad R \propto \sqrt{\sum_i (y_i - y_i^f)^2} \qquad F = \frac{(\chi_1^2 - \chi_0^2)/(\upsilon_1 - \upsilon_0)}{\chi_0^2/\upsilon_0}$$

$$F = \left[\left(\frac{R_1}{R_0}\right)^2 - 1\right]\frac{(n-m)}{b}$$

For tests between data with ~constant error models that share degrees of freedom, <u>Hamilton test</u> with $b = \upsilon_1 - \upsilon_0$

$$\alpha = P(F > F_{b,n-m,\alpha}) = 1 - I_{\Re^2}\left[\frac{n-m}{2}, \frac{b}{2}\right]$$

where α is the confidence level and $I_x[y,z]$ 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_0 increase by ~constant, reducing the ratio (right direction!)**

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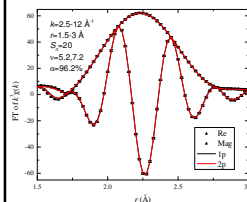## F-test example testing resolution in EXAFS: knowledge of line shape *huge* advantage
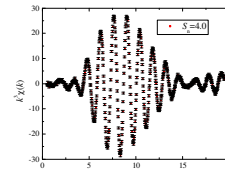
- **6 Cu-Cu at 2.55 Å, 6 at 2.65 Å**
- $k_{max} = \pi/(2\delta_R) = 15.7$ Å^{-1}
- **1 peak (+cumulants) vs 2 peak fits**
- **Fits to 18 Å^{-1} <u>all</u> pass the F-test**
- $S_n = 50$ does not pass at 15 Å^{-1}
- $S_n = 20$ does not pass at 13 Å^{-1}
- $S_n = 4$ does not pass at ~11 Å^{-1}
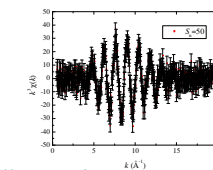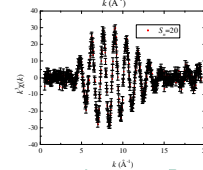
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Unfortunately, systematic errors dominate

Example without systematic error:
$k_{max} = 13$ Å^{-1}, $\upsilon_0 = 6.19$, $\upsilon_1 = 7.19$
$R_0 = 0.31$
$R_1 = 0.79$
$\alpha = 0.999 \rightarrow$ *passes F-test*

Example with systematic error at $R = 2\%$:
$k_{max} = 13$ Å^{-1}, $\upsilon_0 = 6.19$, $\upsilon_1 = 7.19$
$R_0 = 0.31 + 2.0 = 2.31$
$R_1 = 0.79 + 2.0 = 2.79$
$\alpha = 0.86 \rightarrow$ *does not pass*

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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**

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Further reading

- **Overviews:**
  - B. K. Teo, "EXAFS: Basic Principles and Data Analysis" (Springer, New York, 1986).
  - Hayes and Boyce, *Solid State Physics* 37, 173 (1982).
  - "X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES", ed. by Koningsberger and Prins (Wiley, New York, 1988).
- **Historically important:**
  - Sayers, Stern, Lytle, *Phys. Rev. Lett.* 71, 1204 (1971).
- **History:**
  - Lytle, *J. Synch. Rad.* 6, 123 (1999). (http://www.exafsco.com/techpapers/index.html)
  - Stumm von Bordwehr, Ann. Phys. Fr. 14, 377 (1989).
- **Theory papers of note:**
  - Lee, *Phys. Rev. B* 13, 5261 (1976).
  - Rehr and Albers, *Rev. Mod. Phys.* 72, 621 (2000).
- **Useful links**
  - xafs.org (especially see Tutorials section)
  - http://www.i-x-s.org/ (International XAS society)
  - http://www.csrri.iit.edu/periodic-table.html (absorption calculator)

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Further reading

- **Thickness effect:** Stern and Kim, *Phys. Rev. B* 23, 3781 (1981).
- **Particle size effect:** Lu and Stern, *Nucl. Inst. Meth.* 212, 475 (1983).
- **Glitches:**
  - Bridges, Wang, Boyce, *Nucl. Instr. Meth. A* 307, 316 (1991); Bridges, Li, Wang, *Nucl. Instr. Meth. A* 320, 548 (1992);Li, Bridges, Wang, *Nucl. Instr. Meth. A* 340, 420 (1994).
- **Number of independent data points:** Stern, *Phys. Rev. B* 48, 9825 (1993).
- **Theory vs. experiment:**
  - Li, Bridges and Booth, *Phys. Rev. B* 52, 6332 (1995).
  - Kvitky, Bridges, van Dorssen, *Phys. Rev. B* 64, 214108 (2001).
- **Polarized EXAFS:**
  - Heald and Stern, *Phys. Rev. B* 16, 5549 (1977).
  - Booth and Bridges, *Physica Scripta* T115, 202 (2005). (Self-absorption)
- **Hamilton (F-)test:**
  - Hamilton, *Acta Cryst.* 18, 502 (1965).
  - Downward, Booth, Lukens and Bridges, *AIP Conf. Proc.* 882, 129 (2007). http://lise.lbl.gov/chbooth/papers/Hamilton_XAFS13.pdf
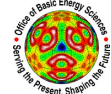
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Further reading

- **Correlated-Debye model:**
  - — Good overview: Poiarkova and Rehr, *Phys. Rev. B* **59**, 948 (1999).
  - — Beni and Platzman, *Phys. Rev. B* **14**, 1514 (1976).
  - — Sevillano, Meuth, and Rehr, *Phys. Rev. B* **20**, 4908 (1979).
- **Correlated Einstein model**
  - — Van Hung and Rehr, *Phys. Rev. B* **56**, 43 (1997).

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