Noise Level and Resolution Effects in EXAFS Spectra

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Abstracts
The effects of uncertainties in intensity measurements (noise levels) and energy space (energy resolution) in EXAFS spectroscopy are presented and discussed. It is shown that poor energy resolution and high noise levels distort EXAFS information in such a way that phase and amplitude transferabilities are lost.

Introduction
In experimental spectroscopic techniques two of the most critical considerations are uncertainties in intensity measurements and energy, or signal-to-noise levels and energy resolution. These considerations are also critical in extended X-ray absorption fine structure (EXAFS) spectroscopy, but their effects are somewhat obscured by the complicated mathematical analyses used in extracting information from EXAFS spectra. Unfortunately, because of this obscurity these effects are often ignored by experimenters, and this has led to a fair amount of concern about the applicability of EXAFS techniques and relative merits of in-house versus synchrotron EXAFS spectrometers. By fairly straightforward analyses of noise and resolution effects and a few examples, we hope to shed some additional light on this controversy and help define limits of applicability and reliability of EXAFS spectroscopy.

Signal-to-noise effects
The linear absorption coefficient, \( \mu_x \), of a material is defined as the log of the ratio of incident and transmitted intensities:

\[
\mu_x = \ln \left( \frac{N_0}{N} \right),
\]

where \( N_0 \) is the number of photons incident on the sample and \( N \) is the number of photons transmitted through the sample. The standard deviation, \( \sigma \), and the relative error, \( \varepsilon \), in a photon counting experiment are simply

\[
\sigma = dN = \sqrt{N},
\]

\[
\varepsilon = \frac{dN}{N} = \frac{1}{\sqrt{N}}.
\]

The problem at hand, then, is to relate the uncertainty in photon counts to the uncertainty in the EXAFS signal. As is customary, we define the EXAFS oscillations as

\[
\chi = \frac{\mu_T}{\mu_0} - 1,
\]

where \( \mu_T \) is the total absorption coefficient, \( \mu_0 \) is the core-level absorption coefficient contribution, and \( \mu_c \) is the 'smooth background' core-level contribution about which \( \chi \) oscillates. (We have normalized the sample thickness, \( x \), to unity.) \( \mu_t \), the pre-edge or non-core-level contributions, and \( \mu_0 \) are usually approximated by slow, smooth functions of \( E \) in data analysis; we shall assume them to have no uncertainties in \( N_0 \) and \( N \). We can rewrite \( \chi \) as

\[
\chi = \frac{\ln N_0 - \ln N - \mu_c}{\mu_0} - 1.
\]

Define \( \delta \chi \) as the uncertainty in the EXAFS oscillations. The uncertainty in \( \chi \) with respect to \( N_0 \) and \( N \) is simply

\[
\delta \chi(N_0, N) = \frac{1}{\mu_0} \left( \frac{1}{\sqrt{N_0}} + \frac{1}{\sqrt{N}} \right).
\]

For simplicity, if the transmission \( T \) is defined as \( T = N/N_0 \), then

\[
\delta \chi(N_0, N) = \frac{1}{\mu_0 \sqrt{N_0}} \left( 1 + \frac{1}{\sqrt{T}} \right).
\]

Haensel (1980) has derived a similar result for the case where \( \mu_T x = 2 \). Equation (6), though, tells us explicitly several things. Firstly, as \( N_0 \) gets large \( \delta \chi \) gets smaller by a reciprocal quadrature relation. Further, if \( \mu_T \approx \mu_c \) or if \( \mu_0 \) is small, \( \delta \chi \) gets larger, as would be expected when a small difference between two large numbers is taken. Finally, if \( N \approx N_0 \), \( \delta \chi \) is minimized, as intuition and basic statistical considerations would predict.

By knowing the automatic composition of a sample, its effective thickness, and using tabulated values of mass absorption coefficients (e.g. International Tables...
for X-ray Crystallography, 1968), \( \mu_0 \) and \( T \) can be approximately calculated. Since (6) relates an uncertainty in the EXAFS to the number of transmitted and incident photons, the number of counts or the time required to achieve the number of counts necessary for adequate signal-to-noise levels is trivially calculable.

The effects of noisy EXAFS data are seen in Figs. 1(a)–(c) and Fig. 2. Fig. 1(a) is a simulated EXAFS spectrum of MnO\(_2\) structure using parameters from Wyckoff (1963) and EXAFS amplitudes and phase parameters from Teo, Lee, Simons, Eisenberger & Kincaid (1977) and Lee, Teo & Simons (1977), respectively. Coordination numbers and distances are given in Table 1. Figs. 1(b) and (c) are the same spectra with noise levels simulated by using a pseudorandom number generator that returns numbers about zero with standard deviation \( \sigma \) (shown on figures). Fig. 2 shows the Fourier transforms of the oscillations, the solid line being the smooth data, the dashed line being the less-noisy data and the dotted line being the more-noisy data. It is apparent from Fig. 2 that the Fourier filter does not completely separate all the high-frequency (noise) components from the structural information but rather tends to distribute them throughout frequency space. Many spurious features appear with decreasing signal-to-noise levels.

### Energy resolution effects

Problems in signal-to-noise ratios can be overcome by patience in photon counting. Also, uncertainties in intensity measurements have an almost intuitive effect on data quality. The effects of energy-resolution effects in EXAFS, though, are somewhat more subtle since information is spread over a broad energy range. Eisenberger & Lengeler (1980) and Lengeler & Eisenberger (1980) have previously addressed resolution problems by examples of experimental spectra, but a straightforward analysis of EXAFS dependence on energy resolution may help clarify several important points.

EXAFS oscillations are approximately sinusoidal in wavevector space, where the wavevector momentum is defined as

\[
k = \left[ \frac{2m_e}{\hbar^2} (E - E_0) \right]^{1/2},
\]

Table 1. Structural parameters for MnO\(_2\) from Wyckoff (1963)

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<th>Backscatterer</th>
<th>( R(\text{Å}) )</th>
<th>( N(\text{atoms}) )</th>
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Fig. 1. Simulated EXAFS spectra using parameters in Table 1. (a) \( \sigma = 0.000 \); (b) \( \sigma = 0.001 \); (c) \( \sigma = 0.005 \).

Fig. 2. Magnitude of Fourier transforms of oscillations in Figs. 1(a)–(c).
where $E$ is the incident photon energy and $E_0$ is the photoelectron threshold energy. Let us assume that the energy-resolution function is symmetric (which it is not) in $E$ space and that the full width at half maximum, $dE$, is proportional to $E$ such that $dE(E) = W E$, where $W$ is the fractional energy resolution. Then

$$\frac{dk}{k} = \frac{E \cdot W}{2(E - E_0)}.$$  \hspace{1cm} (8)

The width of the $k$-space resolution function as a function of $k$ is then

$$dk = \frac{kE W}{2(E - E_0)}.$$  \hspace{1cm} (9)

Equation (9) allows us to generate a family of curves of $dk$ as a function of $k$, parameterizing $E_0$ and $W$. $W$ is found to be on the order of $10^{-3}$ at 10 keV when focusing optics are used (Knapp, Chen & Klippert, 1978; Knapp & Georgopolous, 1980; Hastings, Kincaid & Eisenberger, 1978). Assume again for simplicity that $W = 1.4 \times 10^{-3}$. Fig. 3 shows the resolution in $k$ space using this energy spread. There are three important points illustrated in Fig. 3. Firstly, the resolution is not linear in $k$ space and can thus distort the zero crossings, or frequencies, of the EXAFS oscillations. Secondly, the resolution is hyperbolic, blowing up at low $k$. This is critical to amplitude information since high resolution is most necessary at low $k$ where the amplitude information is the strongest. Nonlinearity of resolution decreases both amplitude and envelope information and makes amplitude transferability at this resolution less reliable. Thirdly, resolution at low $k$ decreases linearly with increasing energy; higher atomic-number elements with larger threshold energies also have larger radii, and since larger interatomic distances are reflected by higher-frequency EXAFS oscillations, reliable structural information becomes difficult to achieve. These difficulties are obviated at unfocused synchrotron facilities, where the energy resolution $W$ is typically $1.5 \times 10^{-4}$, an order of magnitude better than shown in Fig. 3.

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References


