Optimization of data end points and taper width in extended absorption fine-structure analysis

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The dependence of deduced interatomic spacing and inner potential on the lower and upper limits of integration, k_1 and k_2, as well as the taper width D, was studied for extended absorption fine structure using sinusoidal model data. The optimal values are achieved when $2(k_1+k_2)R$ or $2(k_2-k_1-D)R$ equals an odd half-integral multiple of π (rather than when $2k_1R$ and $2k_2R$ are integral multiples of π), where R is the spacing. Analytic approximations are used to elucidate numerical computations. Optimization of D is also discussed.

Extended absorption fine-structure (EAFS) techniques, i.e., extended x-ray absorption fine structure and many variants, have become a popular and precise means of determining interatomic spacings.[1,2] A major advantage of EAFS is that the analysis generates the spacing directly from a Fourier transform of the data, as distinguished from the trial-and-error fitting needed for most techniques. The general question we study is what sort of errors are introduced by the selected lower and upper cutoffs of the data. In particular, we consider the analysis procedure introduced by Lee and Beni.[3] They showed that in an ideal case, when the zero of energy for electron propagation in the sample is known, the peak of the magnitude of the Fourier transform and the peak of its imaginary part coincide at the spacing of interest. When analyzing real data, then, an inner potential should be introduced as an adjustable parameter and fine tuned to produce such coincidence. We followed this approach using ideal sinusoidal model data for typical experimental parameters.

Our numerical results found that errors made in deducing spacings due to choice of lower and upper cutoffs were on average 0.6% (0.003 Å for a spacing of 2 Å) but could be more than twice that large. Thus, while negligible for precisions of ± 0.01 Å or lower, these effects could enter at higher precision. As might be expected, the "error" in the inner potential is greatest when the error in deduced spacing is greatest; this error, however, is always below 2 eV and so not remarkable. Our most noteworthy finding is that, contrary to common belief,[4] it is *not* always optimal to start and to end the Fourier transform at nodes of the data. (The choice of nodes does minimize ripples in the real-space spectrum, which could interfere with or obscure peaks due to more-distant neighbor spacings.[5]) In order to understand this behavior, we have obtained an approximate analytic expression, the derivation of which we sketch below. This expression accounts semiquantitatively for the deviations in deduced spacing and inner potential. Given a reasonable guess of the true spacing R, it provides a simple way to optimize the end points. Moreover, we shall show how it can be used to iteratively improve the result when very high precision is needed.

Explicitly, we start with the simple transform integral

$$F(r,u)=\int_{k_1}^{k_2} h(k)\sin[2R(k^2+u)^{1/2}]\exp(-2ikr)\,dk \quad , \tag{1}$$

where u is the inner potential shift from zero and $h(k)$ is a window function having value unity between k_1+D and k_2-D. For our numerical work we used the commonly employed modified Hanning (or Tukey)[6] window, which has the form $\{1-\cos[\pi(k-k_j)/D]\}/2$, $j=1,2$, within D of each end point. To find the peaks of the imaginary part and the magnitude of F, we consider $f\equiv\partial_r F$, where ∂_r denotes the partial derivative with respect to r. The Lee-Beni solution corresponds to the intersection of the curves $f_i(r,u)\equiv \mathrm{Im} f=0$ and $f_s(r,u)\equiv |f|^2=0$. (We use magnitude squared rather than magnitude for calculational convenience.) To find these curves for roots near $\vec{O}=(R,0)$, we generalize Newton's method to a function of two variables, i.e., we Taylor expand to lowest order about $\vec{O}$ and set the result to zero. The curves, of course, are two straight lines:

$$\delta_\alpha\equiv(r_\alpha-R)=a_\alpha+b_\alpha u_\alpha, \quad \alpha=i,s \quad , \tag{2}$$

where $a_\alpha=-f_\alpha(\vec{O})/\partial_r f_\alpha(\vec{O})$, $b_\alpha=-\partial_u f_\alpha(\vec{O})/\partial_r f_\alpha(\vec{O})$, and δ is the error in deduced spacing. To obtain tractable results, we made several approximations. We assumed $2Rk_1$ (and $2Rk_2$) $\gg 1$ so that we could take just the leading terms in these factors. We replaced integrands like $\sin^2(2kR)$ by $\frac{1}{2}$, equivalent to assuming $2R(k_2-k_1)\gg\pi/2$. Finally, we assumed that $D\ll k_1,k_2$. In the Appendix we list our simplified approximate expressions for the components of Eq. (2). The most noteworthy feature of the formulas is that all the partials are monotonic; hence, just $f_i(\vec{O})$ and $f_s(\vec{O})$ will determine the optimal limits.

For specificity, we take $R=2$ Å and choose $\pi\leq k_1\leq 3\pi/2$ Å^{-1} and $3\pi\leq k_2\leq 7\pi/2$ Å^{-1}, comparable with the limits used in surface extended x-ray-absorption fine structure (SEXAFS) and extended appearance potential fine structure. We step each end point by increments of $\pi/16$. For D we use $\pi/16$, a value smaller than typical choices. We find $b_i\sim -b_s\sim 0.02$: the two lines have similar size slopes in the (r,u) plane with opposite sign. In other words, as u is raised, the peak in the imaginary part moves linearly to greater r while that in the magnitude (squared) moves to smaller r. Solving for the point of intersection of the two lines given by Eq. (2), we see

$$\delta=(a_s b_i-a_i b_s)/(b_i-b_s), \quad u=(a_s-a_i)/(b_i-b_s) \quad . \tag{3}$$

For our data set a_i can be positive or negative but its magni-

tude is always less than about 0.002; a_s is generally an order of magnitude larger (and also can have either sign) so that we can approximate δ by $a_s b_i/(b_i - b_s)$ or roughly $a_s/2$. Referring to Eq. (A3), we see that

$$a_s \propto \cos[2(k_1+k_2)R]\cos[2(k_2-k_1-D)R] \ .$$

Thus $|\delta|$ *will be minimal when either* $2(k_1+k_2)R$ *or* $2(k_2-k_1-D)R$ *approaches a half-integral multiple of* π and will be maximal when they approach integral multiples of π. Hence it is the combination of the two end points rather than either individually that is significant. Furthermore, if k_1 and k_2 are both at nodes of $\sin(2kR)$, then $2(k_1+k_2)R$ will certainly be at an integral multiple of π, while $2(k_2-k_1-D)R$ will be $2DR$ modulo π.

Notice from Eqs. (A1), (A2), and (A3) that this $2DR$ also appears as the argument of the cosine in the prefactor [i.e., $A(R,D)$] of both $a_\alpha's$. The conventional choice for D of a tenth the k range (typically ~ 7 Å^{-1} for SEXAFS or electron-induced equivalents)[2] leads a value of $2DR$ near π for $R \sim 2$ Å. In cases where high precision is desired, one ought to adjust the window width, either decreasing or increasing it so that $D \sim \pi/4R$ or $3\pi/4R$, respectively. This procedure could be pursued iteratively, at each stage inserting one's best estimate of R, although a single iteration would likely be adequate in any realistic application. The end points should also be adjusted to minimize the magnitude of the cosines in $f_s(\vec{0})$. Alternatively, one could focus on the window using $2(k_2-k_1-D)R$, but this latter approach will generally not be so effective since it only eliminates a_s, leaving the residual a_i.

Returning to the less important variable u, we find from Eq. (3) its value at the intersection to be $\sim a_s/(b_i-b_s) = \delta/b_i$ or about 50δ Å^{-2} (for $R=2$ Å), or about 200δ eV. Thus the "error" in the inner potential is of the same sign as that in δ, and is largest when δ is largest. In closing, we remark that our analytic expressions reproduce numerical calculations of δ and u at the Lee-Beni point to within 10–20%, except for cases with $a_s = 0$. (Then the percentage difference can be much larger, but the numbers themselves are about half an order of magnitude smaller than for $a_s \neq 0$). Finally, our work has not treated the role of random noise or of systematic error.

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APPENDIX

We display our analytic approximations for $f \equiv \partial_r F$ and its partials, used in Eq. (2).

Let

$$A(R,D) \equiv (4R)^{-1}\{1/[4RD/\pi)^2-1]\}\cos(2DR) \ . \quad \text{(A1)}$$

Then

$$f_i(\vec{0}) \cong -A(R,D)\left[\left(k_2-\frac{D}{2}\right)\cos(4k_2R-2DR) - \left(k_1+\frac{D}{2}\right)\cos(4k_1R+2DR)\right] \ , \quad \text{(A2)}$$

$$f_s(\vec{0}) \cong A(R,D)(k_2-k_1-D)^2\cos[2(k_1+k_2)R] \times \cos[2(k_2-k_1-D)R] \ , \quad \text{(A3)}$$

$$\partial_r f_i(\vec{0}) \cong [k_2^3 + (k_2-D)^3 - k_1^3 - (k_1+D)^3]/3 \ , \quad \text{(A4)}$$

$$\partial_r f_s(\vec{0}) \cong -(k_2-k_1-D)^4/6 \ , \quad \text{(A5)}$$

$$\partial_u f_i(\vec{0}) \cong -(k_2-k_1-D)R \ , \quad \text{(A6)}$$

$$\partial_u f_s(\vec{0}) \cong R\left\{(k_2-k_1-D)^2 - \tfrac{1}{4}\left[\left(k_2-\frac{D}{2}\right)^2 - \left(k_1+\frac{D}{2}\right)^2\right] \times \ln[k_2(k_2-D)/k_1(k_1+D)]\right\} \ . \quad \text{(A7)}$$

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