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Calculation of x-ray refraction from near-edge absorption data only

Chris Jacobsen\textsuperscript{a}, Steve Wang\textsuperscript{b}, Wenbing Yun\textsuperscript{b}, and Sean Frigo\textsuperscript{c}

\textsuperscript{a}Department of Physics \& Astronomy, Stony Brook University, Stony Brook, NY 11794-3800, USA; \textsuperscript{b}Xradia Inc., 4075A Sprig Drive, Concord, CA 94520, USA; \textsuperscript{c}Department of Physics and Astronomy, Northern Arizona University, Flagstaff AZ 86011, USA

ABSTRACT

Near-edge x-ray absorption resonances provide information on molecular orbital structure; these resonances can be exploited in x-ray spectromicroscopy to give sub-50-nanometer resolution images with chemical state sensitivity. At the same time, radiation damage sets a limit to the resolution that can be obtained in absorption mode. Phase contrast imaging may provide another means of chemical state imaging with lower radiation dose. We describe here the use of experimentally measured near-edge absorption data to estimate near-edge phase resonances. This is accomplished by splicing the near-edge data into reference data and carrying out a numerical integration of the Kramers-Kronig relation.

Keywords: Kramers-Kronig, anomalous dispersion, XANES, NEXAFS

1. INTRODUCTION

Beginning with Einstein,\footnote{1} it has long been recognized that the refractive index of x rays in materials is complex and slightly less than unity. It is now common\footnote{2, 3} to write the refractive index as \( n = 1 - \delta - i\beta \), where \( \beta \) is related to the x-ray linear absorption coefficient \( \mu \) by \( \mu = 4\pi\beta/\lambda \). Since x-ray absorption spectra have rich near-edge structure\footnote{4} which can be used for chemical state imaging,\footnote{5} and since the Kramers-Kronig relationship can be used to relate imaginary to real parts of the refractive index,\footnote{6} it is only natural to expect that the phase-shifting, real part of the x-ray refractive index \( \delta \) also has useful near-absorption-edge information.

The phase-shifting, real part of the x-ray refractive index \( \delta \) can be directly measured in several ways. The first estimates were obtained by measurements of refraction from prisms.\footnote{7} Interferometers based on crystal optics\footnote{8} can be used not only for refractive index measurement but also for phase-contrast imaging.\footnote{9} Interference fringes have been used to measure \( \delta \) in connection with Fresnel mirror systems,\footnote{10} and systems loosely based on Young’s double slits.\footnote{11} Dambach \textit{et al.} used the interference of radiation two successive undulators with varying separation distance.\footnote{12} These various approaches are quite successful and it must always be regarded as preferable to directly measure \( \delta \) rather than infer it from measurements of \( \beta \). However, there is an abundance of available data on x-ray \textit{absorption} near-edge structure, but a relative paucity of data on \textit{phase} near-edge structure. Such phase data could be of use in chemical state mapping using any of a variety of phase contrast imaging methods,\footnote{13–20} or for the design of achromatic Fresnel optics,\footnote{21} among other uses.

We describe here the use of only near-edge measurements of the x-ray linear absorption coefficient \( \mu \) to infer the phase-shifting part of the refractive index \( \delta \) using the Kramers-Kronig relation. The method we describe is not new; indeed it is the method used by Henke \textit{et al}. to obtain a standard tabulated set of values of x-ray refractive indices for all naturally-occurring elements,\footnote{2, 3} and several researchers have used detailed absorption spectra over extended energy ranges to refine the determination of \( \delta \).\footnote{22–24} The purpose of this paper is to describe the use of only limited range near-edge absorption data to obtain an approximate measure of the near-edge stucture of \( \delta \), and to comment on its use for phase contrast spectromicroscopy.

Further author information: CJ email Chris.Jacobsen@stonybrook.edu
2. THEORY

The refractive index is well described by modeling atoms as damped, driven harmonic oscillators, where damping corresponds to wave attenuation, the driving force is the incident electromagnetic wave, and the harmonic oscillators correspond to various electronic states. We write an electron’s equation of motion as

\[ m_e \ddot{x} + m_e \gamma \dot{x} + m_e \omega_0^2 x = -eE_0 e^{i\omega t}, \]

where \( e \) is its charge and \( m_e \) its mass, \( \omega \) is the driving frequency, and \( \omega_0 \) is the resonance frequency and \( \gamma \) the damping coefficient of one particular electronic state in the atom. In the limit \( \omega \gg \omega_0 \), this leads to an expression for a complex index of refraction of

\[ n = 1 - \frac{n_a e^2}{2m_e \epsilon_0} \sum_j \frac{f_j}{(\omega_j^2 - \omega^2)^2 + \gamma_j^2 \omega^2} \left[ (\omega^2 - \omega_j^2) + i\gamma_j \omega \right], \]

where \( n_a \) is the volume density of atoms, \( \epsilon_0 \) is the permittivity of free space, and \( \omega_j \) and \( f_j \) are the resonant frequencies and oscillator strengths, respectively, of the \( j \) electronic states of an atom. In the limit of weak damping and driving frequencies \( \omega \gg \omega_j \) for most resonant frequencies, this expression can be simplified as

\[ n \approx 1 - \frac{n_a r_e^2 \lambda^2}{8\pi^2 \epsilon_0 \lambda^2} \frac{1}{2\pi} \sum_j f_j, \]

where \( r_e \) is the classical radius of an electron and \( \lambda \) is the wavelength of the incident radiation. Parameterizing this expression in the form of Eq. 3, we obtain an expression

\[ n = 1 - \delta - i\beta = 1 - K(f_1 + if_2) \]

where \( K \equiv \frac{n_a r_e \lambda^2}{2\pi} \)

in which case we can write

\[ \delta = \frac{r_e \lambda^2}{2\pi} n_a f_1 \]

\[ \beta = \frac{r_e \lambda^2}{2\pi} n_a f_2. \]

For compounds and mixtures, we can instead work with an atom-number-weighted average

\[ n_a f_1 \rightarrow \bar{n}_a f_1 = \sum_k n_{a,k} f_{1,k} \]

\[ n_a f_2 \rightarrow \bar{n}_a f_1 = \sum_k n_{a,k} f_{2,k} \]

for the real and imaginary oscillator densities. We see therefore that we can express the intensity attenuation \( \exp[-2k\beta z] \) and phase advance \( \exp[ik\delta z] \) of x rays in media in terms of a frequency-dependent complex number of atoms per electron \((f_1 + if_2)\).

Values of \( f_2 \) can be obtained from x-ray absorption measurements; in thin film measurements, we have

\[ I_{\text{fluorescence}} \propto -dI/dz = 2k\beta = 2n_a r_e \lambda f_2 \]

so that \( I_{\text{fluorescence}} \propto \lambda f_2 \). If we then assume \( \chi_e \rightarrow 0 \) as \( \omega \rightarrow \infty \), and causality in that charge displacements can lag but not lead the application of an electric field, we can relate the real and imaginary parts of the dielectric permittivity using the Kramers-Kronig relationships (see e.g., 6 and 28). These relations for dielectric permittivity \( \epsilon \) are as follows:

\[ \text{Re}[\epsilon(\omega)] = 1 + \frac{2}{\pi} \text{p} \int_0^\infty \frac{\omega' \text{Im}[\epsilon(\omega')]}{\omega'^2 - \omega^2} d\omega' \]

\[ \text{Im}[\epsilon(\omega)] = -\frac{2\omega}{\pi} \text{p} \int_0^\infty \frac{\text{Re}[\epsilon(\omega') - 1]}{\omega'^2 - \omega^2} d\omega' \]
Figure 1. Complex number of electrons \((f_1 + if_2)\) for carbon and gold as a function of x-ray energy, as tabulated by Henke et al.\textsuperscript{3} Within about 30 eV of x-ray absorption edges, this tabulation is generally not valid due to changes caused by neighboring atoms.

where \(\mathcal{P}\) refers to the principal part of a complex integral. This can be carried over to consideration of refractive indices using \(n \simeq \sqrt{\epsilon(\omega)/\epsilon_0}\). For our purposes, the relationship may be considerably simplified\textsuperscript{2,3} to give

\[
f_1(E) = Z + \frac{2}{\pi} \int_0^\infty \frac{\epsilon f_2(\epsilon)}{E^2 - \epsilon^2} d\epsilon - \Delta f_r
\]

where now \(\epsilon\) is the integration photon energy, \(E = hc/\lambda\) is the determination photon energy, \(\Delta f_r\) is a relativistic correction term that is negligible for soft x-rays, and we have defined \(\kappa\) as

\[
\kappa \equiv \frac{\epsilon}{E^2 - \epsilon^2}
\]

which describes the energy-dependent weighting of \(f_2(\epsilon)\) data in determining \(f_1(E)\). Values of \(f_1\) calculated by Henke, Gullikson et al.\textsuperscript{3} from large-energy-range \(f_2\) data are shown in Fig. 1.

Examination of Eq. 12 reveals that a correct calculation of \(f_1(E)\) requires knowledge of \(f_2(E)\) over an infinite spectral range. It therefore is useful to examine the energy-dependent weighting term \(\kappa\). This function has the form shown in Fig. 2A, and for determination energies \(E\) within \(\Delta E\) of a particular integrand energy \(\epsilon\) we can determine a limit for \((\Delta E/E) \ll 1\) of

\[
\kappa \simeq -\frac{1}{2} \left( \frac{1}{\Delta E} + \frac{1}{E} \right).
\]

We therefore see that the extrema of \(\kappa\) are at \(\pm 1/(2\Delta E)\), and the cumulative weighting of values of \(f_2(\epsilon)\) over increasing energy regions about \(E\) is shown in Fig. 2B. These figures show how the determination of \(f_1(E)\) at
Figure 2. Properties of the Kramers-Kronig integral. A: the energy-weighting function $\kappa(\epsilon)$ shown for $\Delta E = 0.1$ eV and a center energy of $E = 1000$ eV. B: the integral $\int_{E-\Delta E}^{E+\Delta E} \kappa$ over increasing energy widths $\Delta E$ about a center energy. Data for $f_2(\epsilon)$ over a range of a few tens of electron-Volts about a particular calculation $f_1(E)$ dominate the determination of $f_1(E)$; however, values at more distant energies cannot be ignored. The 90% line refers to the fraction of the integral of $|\int \kappa|$ relative to a ±100 eV integration range; in fact, the integral increases logarithmically as the with changes in the integration energy range.

one energy $E$ is dominated by variations in $f_2(\epsilon)$ at relatively nearby energies $\epsilon \sim E$, but that values of $f_2(\epsilon)$ at more distant photon energies $\epsilon$ must still be considered for obtaining an accurate estimate of $f_1(E)$. In fact, the tabulation by Henke et al. of $f_1(E)$ is based on carrying out the integral of Eq. 12 for data on $f_2(\epsilon)$ over the range $10 \leq \epsilon \leq 30,000$ eV with extrapolation to higher energies, to obtain $f_1(E)$ over the range $50 \leq E \leq 30,000$.

3. CALCULATION METHOD: NEAR-EDGE ABSORPTION SPECTRA

We now wish to consider the calculation of $f_1(E)$ when we have detailed data on $f_2(\epsilon)$ only over a limited near-absorption-edge spectral range. This is often the case in x-ray spectromicroscopy, where energy ranges of no more than about 30 eV will be explored in a spectral image sequence. While more advanced approaches to calculating Kramers-Kronig transforms exist,\textsuperscript{29,30} our approach here will be to splice near-edge data into the Henke data of $f_2(\epsilon)$ for the material in question. Within user-selected energy regions on either side of the absorption edge, a linear ramp is used to make the transition from the Henke data to the experimental data, including adding an offset and

Smoothing: The input data is first Fourier-filtered to smooth it to a specified degree. To do this, the data is first interpolated onto a regular grid with a energy spacing a third of that present in the original data array, and with double the energy span. The data at either end of the original spectrum is then used to fill in constant values on either side of the original spectrum. The spectrum is then Fourier transformed, multiplied by a Hanning filter which goes to zero at the “frequency” corresponding to a specified energy smoothing parameter $\sigma_\epsilon$, and inverse transformed. The resulting spectrum then is then trimmed back from double its span to its original span plus three times $\sigma_\epsilon$ on either side. The result is a spectrum on a finer grid with smoother appearance, and at each end the spectrum approaches a constant value.

Splicing: The smoothed data is now spliced into the data tabulation of Henke et al. of $f_2$ for the material in question. Within user-selected energy regions on either side of the absorption edge, a linear ramp is used to make the transition from the Henke data to the experimental data, including adding an offset and
The boxes show the original data values, and the curve shows the smoothed (with \( \sigma_\epsilon = 0.5 \text{ eV} \)) and spliced version of the data that fits in smoothly with the larger energy range tabulation of Henke et al.\textsuperscript{3} The shaded regions labeled “Ramp” are the regions over which a linear transition was made from the smoothed, scaled version of the original data to the Henke data. Because the “step heights” of the carbon edge in the two data sets are not in agreement, the smoothed and spliced \( f_2 \) data is scaled upwards by about 10\% compared to the original data.

With \( f_2(\epsilon) \) prepared in this way, one can calculate \( f_1(E) \) by simple numerical integration of \( \kappa f_2(\epsilon) \) as per Eq. 12 and over a specified range. As a final step, the Henke value of \( f_1 \) at an energy significantly below the absorption edge is compared with the new calculation of \( f_1 \) at the same energy to determine a single additive offset to account for the terms \( Z - \Delta f_r \) in Eq. 12; this offset is then added into the new determination of \( f_1(E) \).

In order to illustrate this procedure, we show its application to experimental measurements of near-edge structure in both \( f_1 \) and \( f_2 \) obtained for an amorphous carbon film by Dambach et al.\textsuperscript{12} By digitizing their plots, values of \( f_2 \) were obtained. The steps of smoothing (with \( \sigma_\epsilon = 0.5 \text{ eV} \)) and splicing the \( f_2 \) data are shown in Fig. 3; as one can see, this procedure alters the step height by about 10\% in this example so that the data can be properly spliced into the tabulation of Henke et al. We then wish to consider calculation of \( f_1(E) \) by numerical integration of Eq. 12. In our example with \( \sigma_\epsilon = 0.5 \text{ eV} \), the quantity \( \kappa f_2(\epsilon) \) was determined on a grid with energy spacing \( \Delta E = \sigma_\epsilon / 3 = 0.17 \text{ eV} \). We then carried out numerical integration of Eq. 12 over several energy ranges. Assuming that the calculation over the full 10–30,000 eV energy range of the Henke data gives the most accurate result, it is particularly important to have the lower energy limit of the calculation extend down to 10 eV; for evaluation of near-edge structure at 290 eV, the upper integration limit needs to be at least 2000 eV in order to closely approach the final result. Adoption of these limits leads to a calculation time on the order of a minute on a standard desktop computer; narrower limits with faster calculation times reproduce the essential near-edge features of \( f_1 \) but with a bias to slightly higher \( f_1 \) values above the absorption edge.

In Fig. 4, we show a comparison of the \( f_1 \) values calculated from Dambach et al.’s near-edge \( f_2 \) data, and their experimentally-determined \( f_1 \) values. Except for a small offset in the \( f_1 \) values as described in the Figure
Figure 4. Comparison of values of \( f_1 \) calculated using the amorphous carbon near-edge \( f_2 \) data of Dambach et al.,\textsuperscript{12} with their experimental measurements of \( f_1 \). In this Figure, we have multiplied the Dambach experimental values of \( f_2 \) by 1.1, and added an offset of \(-0.5\) to their experimental determinations of \( f_1 \), to allow for better visual evaluation of the reproduction of the near-edge variations of \( f_1 \). The true relationship between Dambach’s \( f_2 \) data and our smoothed, spliced version of it is shown in Fig. 3; we believe that the offset that needed to be introduced into the experimental \( f_1 \) values may partly reflect the scaling of the \( f_2 \) data that had to be done in order to splice it into the tabulation of Henke et al.\textsuperscript{3} With those caveats in mind, the calculated \( f_1 \) values agree quite well with the experimentally determined values.

caption, the calculated \( f_1 \) values agree quite well with the experimental measurements. We then show in Fig. 5 the \( f_1 \) values calculated for tyrosine at the carbon absorption edge, and show energies which might be used for differential phase contrast imaging of the aromatic resonance at 285 eV.

4. CONCLUSION

X-ray absorption spectromicroscopy provides rich information on nanoscale chemical speciation in biology, environmental science, and materials science. Absorption of ionizing radiation is damaging, yet one must normally image at absorption resonances in order to sense their presence. By using phase contrast, one might be able to measure changes in \( f_1 \) due to particular molecular resonances by recording changes in phase contrast images between just below the energy of an absorption resonance, and several eV lower (see Fig. 5). Since absorption measurements for determining \( f_2 \) are relatively easy to obtain, while experimental measurements of \( f_1 \) are not as commonly obtained, we have illustrated here specific details of one approach to using the Kramers-Kronig transform to estimate the phase shifting part of the x-ray refractive index from measurements of the absorbing part.

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Figure 5. Calculation of near-carbon-edge values of $f_1$ from measurements of $f_2$ for the amino acid tyrosine obtained by Kaznacheyev et al. The strong absorption resonances associated with the aromatic $\pi^*$ transition at 285.0 eV, and the COOH $\pi^*$ transition at 288.5, produce corresponding resonances in $f_1$. If one were to take phase contrast images at the two energies $E_1$ and $E_2$ shown, one would obtain strong change in phase contrast due to the aromatic $\pi^*$ transition without causing excessive ionizing radiation damage to carbon-rich regions of a specimen.

REFERENCES


