Self-absorption corrections

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Currently used self-absorption corrections for extended X-ray absorption fine structure and X-ray absorption near-edge structure fluorescence data are briefly reviewed.

1. Introduction

When all of the atoms of interest in a dilute or very thin sample receive the same incident flux of X-rays, the number of fluorescence photons is proportional to the photoelectric part of the X-ray absorption coefficient \( \mu \); see equation (3) in Bridges (2023). However, many samples are not in this limit: the concentration of the atoms of interest may not be low and the sample may be thick. In this case, the penetration of the X-rays into the sample depends on the total absorption coefficient, and if \( \mu \) varies rapidly with energy \( E \), as is the case for X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), the mean absorption depth also changes. Then, if \( \mu \) decreases slightly at some energy, the X-rays penetrate farther into the sample and excite more atoms, and thus the number of fluorescence photons does not decrease as much as expected. This ‘self-absorption’ effect reduces the EXAFS amplitude and can significantly distort the XANES.

Self-absorption has been addressed by several authors over the last few decades (Hayes & Boyce, 1982; Goulon \textit{et al.}, 1982; Tan \textit{et al.}, 1989; Tröger \textit{et al.}, 1992; Brewe \textit{et al.}, 1994; Pfalzer \textit{et al.}, 1999; Booth & Bridges, 2005; Li \textit{et al.}, 2014). Hayes & Boyce (1982) and also Goulon \textit{et al.} (1982) briefly discussed errors from self-absorption effects but did not give an explicit correction function. Tan \textit{et al.} (1989) and Brewe \textit{et al.} (1994) also addressed self-absorption, but took a different approach; they estimated corrections to the amplitude (or coordination number) and the Debye–Waller factor \( \sigma^2 \) when self-absorption was important. Tröger \textit{et al.} (1992) applied a similar approach to that of Goulon \textit{et al.} (1982) for the soft X-ray regime (O K edge) and developed an average correction function to extract the actual EXAFS function \( \chi(k) \) from the experimental function; however, the correction was for thick samples and did not include changes in \( \mu \) from the EXAFS oscillations. Booth & Bridges (2005) extended this calculation to include variable sample thicknesses and also included the effects of the EXAFS oscillations; the latter are important when the EXAFS oscillations are large, such as in ordered materials at low temperatures, for example copper foil. Other approaches have been developed for specialized cases: Li \textit{et al.} (2014) considered self-absorption effects in multilayer systems for which refraction and multiple reflections are included, Brewe \textit{et al.} (1994) considered a glancing
emergent angle geometry and Pfalzer et al. (1999) considered the case of a large solid-angle detector.

Below, the self-absorption correction function is developed following the approach of Booth & Bridges (2005); the geometry and some parameters are given in Fig. 1. Defining \( y = x / \sin \varphi \) and \( z = x / \sin \theta \), and integrating over \( x \), the measured fluorescence intensity \( I_t \) (see Bridges, 2023) is given by

\[
I_t(E) = I_0 \frac{e_\varphi \mu_e}{\sin \varphi} \exp \left[ - \left( \frac{\mu_T}{\sin \varphi} + \frac{\mu_T}{\sin \theta} \right) x \right] dx,
\]

\[
I_x(E) = I_0 \frac{e_\varphi \mu_x}{\mu_T + g \mu_T} \left\{ 1 - \exp \left[ - \left( \frac{\mu_T}{\sin \varphi} + \frac{\mu_T}{\sin \theta} \right) d \right] \right\}, \tag{1}
\]

where the subscript \( e \) refers to the edge of interest, \( \mu_T \) is the total absorption coefficient at the fluorescence energy, \( g = \sin \varphi / \sin \theta \), \( I_0 \) is the incident intensity and \( \mu_T = \mu_b + \mu_e(1 + \chi) \), where \( \mu_b \) is the slowly changing background absorption from other edges/atoms. \( \mu_e \) refers to the average absorption above the edge of interest, which is usually obtained from a spline fit through the EXAFS oscillations. Here, it is assumed that the effects of the finite solid angle of the detector are small enough to be neglected (Booth & Bridges, 2005); however, see Brewe et al. (1994) and Pfalzer et al. (1999) for special cases. The EXAFS function is given by \( \chi \equiv (\mu_e - \mu_b) / \mu_e \) and the experimental value by \( \chi_{\text{exp}} = (I_t - I_0) / I_0 \). Using equation (1) plus some algebra (Booth & Bridges, 2005), \( \chi_{\text{exp}} \) can be written in terms of \( \chi \) as

\[
\chi_{\text{exp}} = \frac{1 - \exp \left[ - (\alpha + \chi \mu_e) \frac{d}{\sin \varphi} \right]}{1 - \exp \left[ - \frac{\alpha d}{\sin \varphi} \right]} \left[ \frac{\alpha(\chi + 1)}{\alpha + \chi \mu_e} \right] - 1, \tag{2}
\]

where \( \alpha = \mu_T / g \mu_T \). At this point the calculation is exact within the assumption of a uniform thickness (plus a uniform distribution of the atom of interest) and a small detector solid angle. The difficulty with it is that \( \chi_{\text{exp}} \) is given as a function of \( \chi \) and cannot be analytically inverted to give \( \chi \) as a function of \( \chi_{\text{exp}} \) for finite sample thicknesses (i.e. \( \alpha d / \sin \varphi < 3 \)) because of the term \( \chi \mu_e d / \sin \varphi \) in the exponent. Note that \( \mu_e / \alpha \) and \( \chi \) is typically less than 0.1. Thus, in most cases

\[
\frac{\chi \mu_e d}{\sin \varphi} \ll 1, \tag{3}
\]

and the exponential term in \( \chi \) \( \exp(-\chi \mu_e d / \sin \varphi) \) can be approximated as \( 1 - (\chi \mu_e d / \sin \varphi) \). Equation (2) then becomes a quadratic equation in \( \chi \), with a solution

\[
\chi = \left[ - (\gamma(\alpha - \mu_e(\chi_{\text{exp}} + 1)) + \beta) \right] / 2\beta, \tag{4}
\]

where

\[
\gamma = 1 - \exp \left( - \frac{\alpha d}{\sin \varphi} \right), \quad \beta = \frac{\mu_e \alpha d}{\sin \varphi} \exp \left( - \frac{\alpha d}{\sin \varphi} \right).
\]

The correction factor \( \chi_{\text{exp}} / \chi \) now oscillates in \( k \)-space as a result of the EXAFS oscillations (Booth & Bridges, 2005). An example of the improvement achieved using the above approximation is shown in Fig. 3 of Booth & Bridges (2005) for a 4.6 \( \mu \)m foil. Note that equation (2) can be inverted numerically and hence the approximation (equation 3) can be checked. This correction has been incorporated into several EXAFS packages such as RSXAP (REDUCE and SABCOR; Booth, 2010; Booth & Bridges, 2021) and IFEFFIT (Newville, 2004; Newville & Ravel, 2020). For RSXAP, equation (2) is now inverted numerically.

2. Self-absorption corrections to XANES

The distortion of the XANES from self-absorption is described by the same starting equation as used for EXAFS (equation 1) after background fluorescence contributions have been subtracted. Also, all treatments consider only the infinitely thick limit, for which the exponential term goes to zero. However, remember that the total absorption coefficient \( \mu_T \) is a sum of \( \mu_e \) and \( \mu_b \), where \( \mu_b \) is the background contribution from other absorption processes. Following Haskel (1999), an energy \( E_N \) needs to be chosen above the edge for normalization: it is assumed that this energy is well above the edge and that variations in \( \mu_e \) are small (if not, a point should be chosen on \( \mu_e \), for example at a ‘zero-crossing’ in the EXAFS oscillations). The measured absorption is given by \( I_t(E) / I_0(E) \), the value of this quantity at the normalization energy is \( I_t(E_N) / I_0(E_N) \) and the normalized absorption is given by \( \mu_e(E) / \mu_e(E_N) \). Defining the normalized measured absorption \( X_e \) as \( [I_t(E) / I_0(E)] / [I_t(E_N) / I_0(E_N)] \), \( X_e \) is given by

\[
X_e = \left[ \frac{\mu_e(E)}{\mu_e(E_N)} \right] \frac{\bar{\mu}_e(E)}{\bar{\mu}_e(E_N)} \left[ \frac{\bar{\mu}_b(E)}{\bar{\mu}_b(E_N)} \right] \left[ \frac{B_d + \delta + \frac{\mu(e)}{\mu(e)} \mu(e)}{B_d + \delta + \frac{\mu(e)}{\mu(e)} \mu(e)} \right], \tag{5}
\]

![Figure 1](image-url)

**Figure 1**
The geometry for calculating the fluorescence output into a small solid angle in EXAFS and XANES experiments. Often both \( \varphi \) and \( \theta \) are 45°. The point for absorption is a distance \( x \) below the surface; \( y \) and \( z \) are distances along the incoming and outgoing photon paths. Reproduced from Booth & Bridges (2005). Copyright IOP Publishing. Reproduced with permission. All rights reserved.
where $B = \mu_0 / \mu_c(E_N)$, $\delta = \mu_b(E) / \mu_c(E_N)$ and $\delta' = \mu_b(E_N) / \mu_c(E_N)$. Solving for $\mu_c(E) / \mu_c(E_N)$ and simplifying, one obtains (Haskel, 1999)

$$\frac{\mu_c(E)}{\mu_c(E_N)} = X_c \left[ \frac{1}{1 + \frac{1 - X_c}{B_g + \delta}} \right].$$

Here, it is assumed that $\varepsilon_c(E) / \varepsilon_c(E_N) \simeq 1$, and $\delta \simeq \delta'$ for a small energy range around the edge. Note that equation (6) is normalized ($X_c \simeq 1$) above the edge energy, where self-absorption effects are large. Consequently, the correction factor in equation (6) is $\sim 1.0$ at $E_N$ and decreases as energy decreases towards the bottom of the edge; i.e. the experimental $X_c$ is suppressed the most for energies near the bottom of the edge, where $X_c \simeq 0$. At this point on the edge, the extra correction factor is $1/[1 + 1/(B_g + \delta)]$; as $X_c$ increases, the correction factor approaches 1.0. In contrast, at a white line, particularly for an $L_{III}$ edge, the correction factor must be greater than 1 because $X_c > 1$ and the correction factor is $1/[1 - (X_c - 1)/(B_g + \delta)]$. As long as the correction factor in equation (6) is less than 3–4 this is typically a good approximation, but since it depends on the quality of the data and the choice of $E_N$ it should be checked.

References


