Topical Review

Finite difference method calculations of long-range X-ray absorption fine structure for copper over $k \approx 20 \, \text{Å}^{-1}$

J.D. Bourke, C.T. Chantler *

School of Physics, University of Melbourne, Parkville, Vic 3010, Australia

ARTICLE INFO

ABSTRACT

X-ray Absorption Fine Structure (XAFS) is calculated for copper using the cluster based Finite Difference Method for Near-Edge Structure (FDMNES). This approach is conventionally used to produce high accuracy XAFS theory in the near edge region, however, we demonstrate that it can be readily extended to encompass an energy range of more than 1.5 keV ($k \approx 20 \, \text{Å}^{-1}$) from the K absorption edge.

Such calculations require extensions to FDMNES to account for thermal effects, in addition to broadening effects due to inelastic processes. Extended calculations beyond the range of near-edge structure also require consideration of technical constraints such as cluster sizes and densities. We find that with our approach, we are able to produce accurate theory ranging from the absorption edge to the smooth atom-like region at high energies, with a single consistent model that is free from any fitting parameters.

© 2009 Elsevier B.V. All rights reserved.

X-ray Absorption Fine Structure (XAFS) refers to the complex series of oscillations seen in the photoelectric absorption curve just beyond an absorption edge. These oscillations convey important structural information about the absorbing material, including the relative positions of atoms in the crystal lattice. They are produced by the interference of the wavefunctions of photoelectrons ejected from the absorbing atoms with those returning due to backscattering from surrounding atoms. As a result, XAFS oscillations at high energies are dominated by a Fourier transform of the radial electron density from an absorber [1,2]. At energies close to the absorption edge, however, multiple scattering, many body and polarization effects have a significant impact on the spectrum. Historically, attempts to theoretically model XAFS have required assumptions regarding atomic and crystal potentials that greatly simplify calculations in order to make the problem manageable.

Simplifications such as the muffin-tin approximation common to multiple scattering approaches [3], and models using infinite crystalline lattices [4] can be sufficient for qualitatively accurate results [5]. The speed of such calculations is also of significant benefit in many applications. High accuracy experimental XAFS data, however, shows that these approaches have shortcomings, particularly in the near-edge region (sometimes called the XANES region) [6]. This problem is particularly exacerbated for complex molecular structures such as are common in medical and biological applications. Since one of the most commonly cited

benefits of structural determination via XAFS is its suitability for probing such structures, it is clear that we need an alternative approach.

We therefore employ the Finite Difference Method (FDM), as implemented for XAFS calculations via the package Finite Difference Method for Near-Edge Structure (FDMNES) [7]. This approach has already been demonstrated to give improved results in the near-edge region for complex materials [8]. The principal drawback of FDMNES is its reputed unreliability beyond the near-edge region, where it becomes computationally intensive and is prone to grossly exaggerating the magnitude of absorption peaks. Our previous investigations showed that the latter problem can be overcome by extending FDMNES to account for thermal effects and inelastic processes [9], which enabled us to produce theoretical copper XAFS up to 300 eV from the absorption edge. Our current work deals additionally with the efficiency problem, and enables us to extend our theory to 1.5 keV beyond the absorption edge, thus probing not only all of the XAFS spectrum, but joining the smooth atom-like absorption region beyond. This unlocks the possibility of producing accurate theory for complicated materials across any energy range, with a single consistent approach that requires no fitting parameters or limiting approximations.

FDMNES performs calculations on spherical clusters of atoms in order to produce the photoelectric absorption cross-section [7]. This is given by

$$\sigma = 4\pi^2 \alpha \hbar \omega \sum_{f,g} |M_{gf}|^2 \delta(\hbar\omega - E_f + E_g) \quad (1)$$

* Corresponding author.
  E-mail address: chantler@physics.unimelb.edu.au (C.T. Chantler).

where α is the fine structure constant, $\hbar\omega$ the energy of the incident photon, and E_f, E_g the final and initial state energies. The summation is over the transition matrix amplitudes as given by

$$M_{gf} = \langle \psi_f | \boldsymbol{\varepsilon} \cdot \boldsymbol{r} \left(1 + \frac{i}{2} \boldsymbol{k} \cdot \boldsymbol{r} \right) | \psi_g \rangle \qquad (2)$$

where $\boldsymbol{k}$ is the photon wave vector polarized in the $\boldsymbol{\varepsilon}$ direction, and ψ_g and ψ_f are the initial and final states. The initial state is that of an atomic core orbital, and therefore well known. It is the final state that is calculated using the finite difference method.

This consists of breaking the cluster up into three distinct regions: the region close to atomic cores where the potential is spherically symmetric and the wave function is expressed as a sum of spherical waves, the region beyond the range of the defined cluster where the potential is assumed constant, and the interstitial region between atoms where the FDM itself is employed. The FDM establishes a three dimensional grid with a pre-defined point density, and solves a discretized version of the Schrödinger equation for each grid point. These points are linked by a system of linear equations, and are then matched with the boundaries of the other calculational regions to ensure a continuous wave function. Symmetries in the cluster itself are exploited to reduce the total number of grid points and thus have a profound effect on the efficiency of the calculation.

This approach overcomes common problems related to muffin-tin and periodic potentials, but still has shortcomings that become greater as the energy is increased beyond the near-edge region. The first and most significant of these is that there is no explicit account of inelastic losses in the material. Such losses lead to a finite lifetime of the interfering photoelectron, and accordingly an energy uncertainty that requires a Lorentzian convolution of the absorption spectrum. This is complicated slightly by the energy dependence of the electron inelastic mean free path (IMFP), which enforces an energy-dependent convolution.

The principal difficulty here is that the IMFP, which determines the convolution width, is not well established for most materials at low energies. Both theoretical and experimental investigations of the IMFP encounter fatal flaws below 100 eV (or often higher), and as such our choice of IMFP data is sparse and unreliable. Here we seek an *ab initio* approach, which excludes the use of popular "universal curves". We therefore employ the IMFP data determined for copper by Kwei et al. [10], which is calculated using a modified form of the common optical data model [11]. Most optical data model calculations produce good results at high energies; however, we favour this version as it is demonstrably stronger in the near-edge region [12]. We then convert the IMFP $\lambda(E)$ into a convolution width $\Gamma_\lambda(E)$ as follows:

$$\Gamma_\lambda(E) = \frac{\hbar}{\lambda(E)} \sqrt{\frac{2E}{m_e}} \qquad (3)$$

E is both the photoelectron energy and distance from the photoelectric absorption edge, while m_e is the electron mass. We note that, in the absence of a rapid increase of the IMFP with energy, the convolution width increases significantly with energy. Accordingly, high frequency XAFS oscillations are increasingly suppressed at high energies; a fact which will be useful later when considering calculation efficiency issues.

There also exists an energy independent component to the convolution produced by the finite core-hole lifetime. This is readily calculated within FDMNES, however, and is simply added to the IMFP width:

$$\Gamma(E) = \Gamma_\lambda(E) + \Gamma_{hole}(E). \qquad (4)$$

We note that any errors in this hole width are of great significance for the near edge region, but become of little importance past 50 eV in the case of copper. For large Z materials,

the hole width may be significant over much greater energy ranges.

The second energy-dependent addition to FDMNES is due to thermal effects. Since the FDM calculation is done with a cluster of atoms at well defined equilibrium positions, thermal vibration must be added explicitly. Previous investigations using a frozen phonon approach have shown that, for copper, this can be achieved by a simple exponential dampening of the oscillatory component of the absorption spectrum [9]. This is similar to the approach used by multiple scattering models, particularly at high energies where the low order scattering terms dominate. The dampening can be seen as a consequence of Doppler broadening in the photoelectron wave function, and in a sense it is a reverse effect to that of inelastic losses.

The extent of the dampening is determined by the Debye–Waller factor σ^2.

$$\chi(k) \rightarrow \chi(k)e^{-2\sigma^2 k^2} \qquad (5)$$

σ^2 is the mean square displacement of each atom from its equilibrium position, and is approximated analytically elsewhere [13]. Here we use the value for nearest neighbour atoms, as it dominates over the outer atoms' contributions due to IMFP broadening.

An illustration of the magnitude of these energy-dependent corrections is given in Fig. 1. The thermal effect is increasingly significant at high energies, and is the principal determinant of the energy range of observable XAFS. The inelastic mean free path and hole width effects, however, are meaningful right from the absorption edge.

These considerations are sufficient to produce accurate XAFS calculations using the finite difference method up to around 300 eV from the absorption edge in the case of copper. For more complex molecular structures, especially those involving no structural symmetry, the energy limit can be substantially lower due to computational complexity.

The finite difference method considers a finite cluster defined over a grid of points. At high energies, the calculation requires increasingly dense grids in order to converge properly. We consider the problem in terms of the interpoint distance h, for which we conventionally have $h = 0.25$ Å. In this work, data points at or near the absorption edge were calculated using $h = 0.20$ Å. This was required to reach adequate convergence. At an energy of
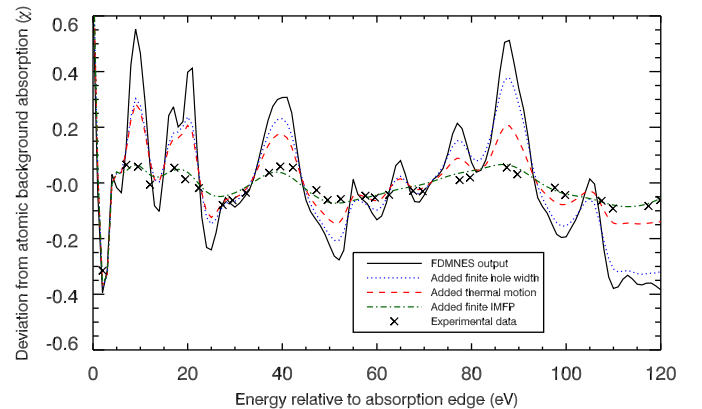
Fig. 1. Oscillatory component (χ) of copper XAFS as determined by the finite difference method. The results of progressively including additional effects are also shown. Firstly the effect of the finite hole width produced by the loss of the photoelectron from the absorbing atom is added. Secondly the oscillations are damped due to the thermal vibrations present in a solid at room temperature. Thirdly the finite IMFP is accounted for via a point-wise convolution with a Lorentzian curve of dynamic width. This shows the relative importance of each extra effect on the final result. Finally, the oscillatory component of the experimental data of Glover et al. [14] is shown for comparison.