

# Finite difference method calculations of X-ray absorption fine structure for copper

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

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

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## Abstract

The finite difference method is extended to calculate X-ray absorption fine structure (XAFS) for solid state copper. These extensions include the incorporation of a Monte Carlo frozen phonon technique to simulate the effect of thermal vibrations under a correlated Debye–Waller model, and the inclusion of broadening effects from inelastic processes. Spectra are obtained over an energy range in excess of 300 eV above the K absorption edge—more than twice the greatest energy range previously reported for a solid state calculation using this method. We find this method is highly sensitive to values of the photoelectron inelastic mean free path, allowing us to probe the accuracy of current models of this parameter, particularly at low energies. We therefore find that experimental data for the photoelectron inelastic mean free path can be obtained by this method. Our results compare favourably with high precision measurements of the X-ray mass attenuation coefficient for copper, reaching agreement to within 3%, and improving previous results using the finite difference method by an order of magnitude.

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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 have long been known to convey important structural information about the absorbing material, most notably the relative positions of atoms in the crystal lattice. This is because they are produced by interference between the outgoing photoelectron wavefunctions from absorbing atoms, and the wavefunctions of photoelectrons that have been backscattered by the surrounding atoms. XAFS oscillations are dominated by a Fourier transform of radial electron density from an absorber [1,2]. Historically, attempts to theoretically model XAFS have primarily centred around assumptions regarding atomic and crystal potentials that greatly simplify calculations at a supposedly minimal cost to the final accuracy of the results.

These assumptions include, most notably, the “muffin-tin” approximation, which refers to the assignment of an effective potential between atoms in a lattice, which is assumed to be constant. This approximation, coupled with assumptions of crystalline symmetry and spherically symmetric potentials near atomic cores, has been shown to produce meaningful results [3] that are commonly regarded as almost a standard in the field. However, recent high accuracy experimental investigations [4] now show significant deviations from the theory produced using muffin-tin approaches [5]. Therefore developments of XAFS are sought that can accurately reproduce fine structure without limiting assumptions that are known to deviate from physical reality.

Dominant methods for modelling XAFS in the literature include the muffin-tin approach, discrete variational methods and the full linear augmented plane-wave approaches. In this work we find that the finite difference method is not only able to treat the complexities of the near-edge region, but can successfully be extended into the central XAFS regime for simple systems.

\* Corresponding author.

E-mail address: [chantler@physics.unimelb.edu.au](mailto:chantler@physics.unimelb.edu.au) (C.T. Chantler).

This Letter does not provide a new structural result for copper, but instead shows that these developments improve agreement between theory and experiment dramatically, with no empirical or other fitting coefficients of any sort. Hence this approach may in the future lead to ab initio methods with minimal free parameters. In the process of developing this, we find that we can provide new determinations of the inelastic mean free path using experimental data. These determinations are largely model-independent.

The approach used for this work is the finite difference method, as implemented by the finite difference method for near edge structure (FDMNES) code developed by Joly [6]. This approach assumes spherical symmetry in the potentials surrounding atomic cores—though for much smaller volumes than with muffin-tin methods—and performs a calculation within an atomic cluster of finite radius. The principle advantage of the finite difference method is that it avoids the muffin-tin approximation by calculating the potential over a grid of points between the atoms using a discretised form of the Schrödinger equation. In an ideal situation, one could calculate potentials over a very dense grid with very small regions of assumed spherical symmetry, and produce a model that accurately represents physical reality.

Computational limitations make this ideal unrealisable. The finite difference method has previously only been considered for “near edge structure” because at energies far from an absorption edge, particularly dense grids are required to give convergent results. This, in turn, leads to extremely long calculations that can take weeks to complete. Also, even when computationally converged, the results from FDMNES far above an absorption edge (i.e. in the XAFS region) show increasingly large deviations from actual spectra. Therefore, FDMNES has so far only been used to produce fine structure calculations within 100 eV of an absorption edge. A recent development of our group pushed this into the intermediate regime [7], but found significant shortcomings at higher energies. Here we will develop techniques to extend the finite difference method to produce realistic results far beyond this range, by accounting for effects of thermal motion and the finite photoelectron inelastic mean free path. These extensions will then be applied to calculations of the XAFS of copper, just beyond a K absorption edge.

In the original implementation of the finite difference method, the thermal motion of atoms was not taken into account, meaning that all calculations were modelling systems at absolute zero temperature (and with no zero point motion). There are two complementary ways of seeing how the addition of thermal motion will affect the absorption spectra: by consideration of the photoelectron interference and through use of Fourier transforms.

If we consider interference, we note that the energy values corresponding to a minimum in the absorption curve also correspond to an electron energy whereby twice the distance between the absorbing and scattering atoms correspond to an integral multiple of the electron’s De Broglie wavelength. Thus at that energy we see constructive interference and hence a low absorption value. If the scattering atom is in thermal motion

then it will be moved slightly from its equilibrium position, resulting in interference that is not totally constructive, and so the peak will be softened. It is clear that the thermal motion will have a greater effect at high energies, where the wavelength of the photoelectrons become small enough to be comparable with the magnitude of the thermal motion. Therefore, although it might be reasonable to ignore thermal effects near an absorption edge, at high energies it is no longer possible to do so.

In terms of Fourier transforms, we note that in the presence of thermal motion the electron densities of the atoms in the lattice will be broadened. If we then take a Fourier transform and observe the XAFS curve, we will see dampening of the oscillations. This can be shown mathematically using the convolution theorem.

The frozen phonon method is an iterative approach that has previously been successfully applied to studies of electron diffraction [8]. It assumes that the electron scattering processes responsible for the existence of XAFS occur on a much shorter timescale than the thermal oscillations of the scattering atoms. Therefore we can claim that each photoelectron will see a static lattice configuration, with each atom perturbed from its equilibrium position by some small amount. Each photoelectron will then see a different configuration, and so the resulting XAFS spectra can be derived using an average taken over calculations using many different lattice configurations. A group of 20 configurations with random perturbations to each atom according to a Gaussian distribution then allows statistical determination of the ensemble result.

The probability  $p(x) dx$  of each atom being perturbed by an amount between  $x$  and  $x + dx$  is given by

$$p(x) dx = \frac{1}{\sqrt{2\pi}\sigma^2} e^{-\frac{x^2}{2\sigma^2}} dx. \quad (1)$$

$\sigma^2$  is then the mean square displacement of the atom from its equilibrium position, which is equivalent to the Debye–Waller factor [9] used in scattering path approaches. The value of this parameter is not simple to evaluate and in this treatment we will make use of a formula first given by Beni and Platzman [10], and corrected by Greeger [9], which gives mean square displacements  $\langle \Delta_j^2 \rangle$  relative to an unmoving central atom. The motion of each atom is correlated to this central atom, but cross-correlation between pairs of non-central atoms is not taken into account in this model.

$$\begin{aligned} \langle \Delta_j^2 \rangle = & \frac{6\hbar}{m\omega_D} \left[ \frac{1}{4} + \left( \frac{T}{\theta_D} \right)^2 D_1 \right] - \frac{6\hbar}{m\omega_D} \left\{ \frac{1 - \cos(q_D r_j)}{2(q_D r_j)^2} \right. \\ & + \left( \frac{T}{\theta_D} \right)^2 \left[ D_1 - \frac{1}{3!} \left( q_D r_j \frac{T}{\theta_D} \right)^2 D_3 \right. \\ & \left. \left. + \frac{1}{5!} \left( q_D r_j \frac{T}{\theta_D} \right)^4 D_5 - \dots \right] \right\}. \quad (2) \end{aligned}$$

Here  $m$  is the mass of the atom,  $T$  is the temperature of the crystal,  $r_j$  is the equilibrium distance from the central absorbing atom, and  $\theta_D$ ,  $\omega_D$  and  $q_D$  are the Debye temperature, fre-

quency, and wave vector respectively. These are related by

$$\omega_D = \frac{\theta_D k_B}{\hbar}, \quad (3)$$

$$k_D = \left( \frac{6\pi^2}{V} \right)^{1/3}, \quad (4)$$

where  $V$  is the mean volume per atom in the material. The  $D_n$  parameters are given by

$$D_n = \int_0^{\theta_D/T} \frac{x^n}{e^x - 1} dx. \quad (5)$$

These integrals converge slowly, and were evaluated numerically up to  $n = 33$ . Once the value of  $\langle \Delta_j^2 \rangle$  has been defined, we must fit a Gaussian probability distribution. The probability of an atom being perturbed by a magnitude less than some positive value  $|a|$  is given by

$$P(x < |a|) = 2 \int_0^{|a|} p(x) dx = 2 \int_0^{|a|} \frac{1}{\sqrt{4\pi \langle \Delta_j^2 \rangle}} e^{-\frac{x^2}{4\langle \Delta_j^2 \rangle}} dx, \quad (6)$$

where  $0 \leq P(x < |a|) \leq 1$ . A random seed value between 0 and 1 for  $P(x < |a|)$  will yield a value of  $|a|$  with a Gaussian probability curve. Re-arranging gives:

$$P(x < |a|) = \operatorname{erf}\left(\frac{a}{2\sqrt{2}\langle \Delta_j^2 \rangle}\right), \quad (7)$$

$$|a| = 2\sqrt{2}\langle \Delta_j^2 \rangle \operatorname{erf}^{-1}(P(x < |a|)). \quad (8)$$

Therefore  $|a|$  is taken as the displacement of each atom from its equilibrium position.

FDMNES makes use of symmetries within the cluster of interest in order to reduce the scale of the calculation and hence reduce computing time and memory use. However, each *perturbed* cluster in the frozen phonon approach explicitly has no symmetry because the perturbation breaks any site symmetry. Therefore, modest clusters of 3.4 Å radius were used, corresponding to the absorbing atom plus one complete shell of surrounding atoms. This gave 13 atoms in total in the cluster. Such copper cluster sizes have been the subject of recent direct experimental XAFS investigations [11].

Fig. 1 shows a direct mean of the results from 20 perturbed copper cluster configurations. Even with our small cluster sizes, the absorption spectrum for each cluster took several days to calculate using current mid-range computing resources. Qualitatively, the results deviate from those of an unperturbed cluster of the same size by an amount that increases with energy, as expected. This deviation can be well approximated by an exponential dampening of the oscillations, an approach which is similar to that used in multiple scattering calculations of XAFS. This is a valid estimation here given that, at energies far above the absorption edge, the dampening of the oscillations due to thermal motion is dominated over by the effect of the photoelectron inelastic mean free path. It is noted, however, that a more rigorous approach will be required once the mean free path effect is dealt with to sufficient accuracy.

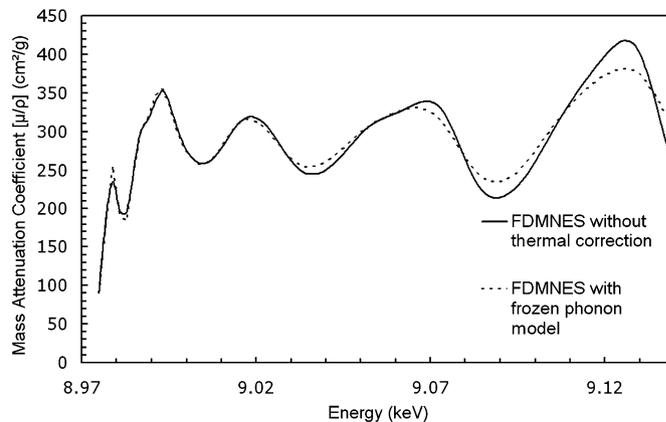


Fig. 1. Effect of correcting the absorption spectrum of copper using the frozen phonon model for thermal motion. The dampening of the absorption peaks can be well approximated by an exponential function to first order.

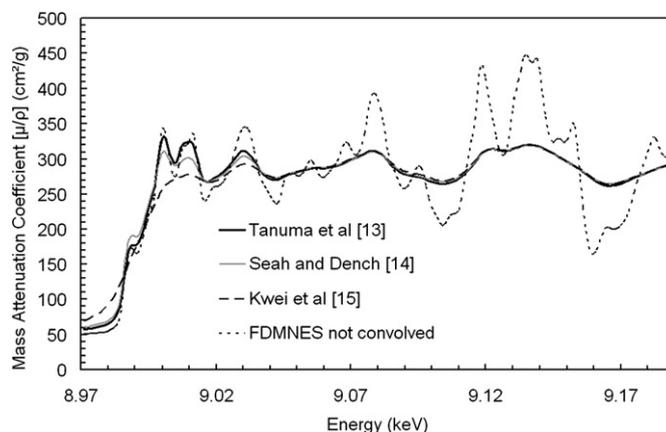


Fig. 2. Comparison between absorption spectra for copper obtained using different values for the photoelectron inelastic mean free path. Values from Seah and Dench are from a general predictive formula, while the values from Tanuma et al. and Kwei et al. use theoretical models combined with experimental optical data. The “FDMNES, not convolved” curve is produced using FDMNES as per Witte et al. [7]. Differing approaches yield large variations in the first few peaks, however the results converge satisfactorily far from the absorption edge.

The finite lifetime of the photoelectron causes uncertainty in its energy and therefore a broadening in the absorption spectrum that is heavily energy dependent. FDMNES incorporates a rudimentary correction based on empirical formulae to account for this effect, however this is unsatisfactory. Rigorous calculations of the inelastic mean free path in a material are necessary for an accurate theory of XAFS.

Current photoelectron inelastic mean free path data is quite varied and it is difficult to acknowledge an accepted standard. While much data has been collected for photoelectron energies above 10 keV, very little is known about inelastic mean free paths for electrons of very low energies [12], making it difficult to obtain an accurate estimate for this effect near to an absorption edge. Different approaches are made for the extension into the momentum space for the dielectric function and for the contribution of inner shells. Fig. 2 shows XAFS spectra for copper, calculated using clusters 8.3 Å in radius and with thermal motion accounted for via an exponential dampening.

Each convolved curve has been broadened according to the inelastic mean free path data from the listed authors (Tanuma et al. [13], Seah and Dench [14], and Kwei et al. [15]). Seah and Dench have calculated mean free path values from a predictive formula based on experimental data collected from a range of different elements. The mean free paths from both Tanuma et al. and Kwei et al. were calculated using theoretical models that made use of experimental optical data for copper. The different tabulations yield broadly similar results far above an absorption edge where thermal dampening is high. There are, however, significant discrepancies in the near edge region.

The photoelectron inelastic mean free path is usually calculated using a relation first put forward by Ritchie [16], linking it to the electron self energy and, in turn, to the dielectric response function of the medium in question. This allows calculation of the mean free path in a free-electron material where the dielectric function is known. In transition metals such as copper, however, there exists a complex band structure. Therefore it is usual to model the dielectric function using a band structure software package such as WIEN2K, or, as in this case, to establish a dielectric function using experimental optical data.

This gives a good approximation of the energy dependence of the dielectric function, but does not guarantee an accurate modelling of the dependence of this function on the electron momentum transfer. Therefore, it is expected that the theory will be less accurate at low electron energies where scattering in the forward direction is not as prevalent [17]. In addition, it is difficult to establish the accuracy of the theory directly due to difficulties in experimental measurements of inelastic mean free paths [18].

In terms of the current data sets for copper, the available work of Tanuma et al. has greater coverage of low energies than that of Kwei et al. It also uses a more general form of the dispersion equation relating excitation energy and momentum transfer [19]. The inelastic mean free path values from Tanuma et al. give strong relative agreement with our experimental XAFS data, particularly in the near edge region. This is therefore a strong indication of the accuracy of Tanuma's data and the current theoretical approach, and demonstrates some potential for XAFS analysis to assist in the verification of calculated inelastic mean free paths. In particular, our data and FDMNES could be used to determine inelastic mean free paths, invoking assumptions for the hole width and thermal broadening. This might suggest, for example, that the computations of Tanuma et al. are underestimated for energies below about 40 eV, and overestimated for energies between 40–100 eV, with uncertainties or deviations of order 10–20% at the upper energies, as claimed by the authors of these computations.

Fig. 3 shows the final calculated absorption spectrum for copper, inclusive of thermal dampening, and of broadening from the finite photoelectron and core hole lifetimes. The density of the grid has been greatly increased over previous calculations, with the grid spacing reduced from the standard 0.25 Å to 0.17 Å. This reduction is absolutely necessary to extend the results beyond 100 eV, and in fact was found to be important in achieving convergence near the edge as well. Also shown

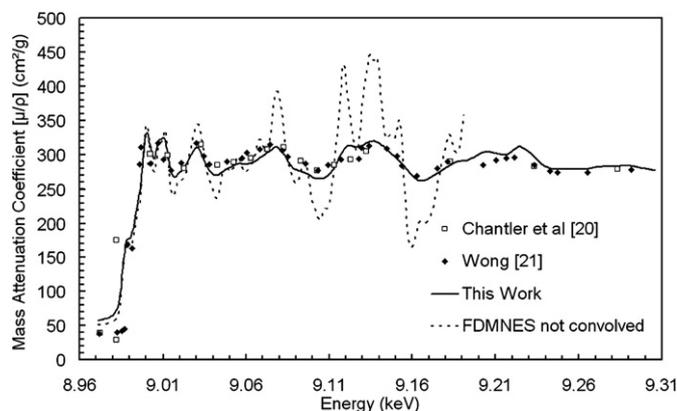


Fig. 3. Comparison between the experimental copper absorption data of Chantler et al. [20] and Wong [21], and theoretical calculations. It can be seen that this work represents a significant improvement over the FDMNES curve produced previously by Witte et al. [7], and greatly extends the approach's range of applicability.

are experimental data sets from the work of Chantler et al. [20] and Wong [21], and a theoretical curve that was produced using FDMNES without modification [7].

Even without our developments, FDMNES gives good predictions of peak positions and of course can be run exhaustively to higher energies. However, there is enormous difficulty predicting relative peak amplitudes, with massive failings seen at high energies. The value of  $\chi_r^2$  for the raw FDMNES curve is 803, as compared to the experimental data of Chantler, which is accurate to within around 0.3%.

The key result of this Letter is that the theory produced with the extended version of the finite difference method, presented here, has a  $\chi_r^2$  of 89.7, an order of magnitude improvement, and is applicable over twice the previous energy range. The dominant contribution to this  $\chi_r^2$  arises from deviations around the first four oscillations of XAFS, and may be due to the inadequacy of the literature values for broadening at low momentum transfers. There may also be theoretical difficulties with the baseline value for the absorption coefficient underlying the XAFS oscillations. On average, this implies that the theory developed here is accurate to 3%.

These results invite more theoretical investigation in all the areas discussed in this Letter, and also suggest that we may use this base theory as a novel approach to deriving experimental values for the inelastic mean free path of the photoelectron. This would be particularly useful in the low energy region where there are significant discrepancies in current experimental and theoretical values. It should be emphasised that this Letter has involved no fitting of any empirical or other coefficients, save for a constant background cross section.

Our results demonstrate strongly the potential applicability of finite difference method calculations for not only near edge structure, but also extended X-ray absorption fine structure. Further improvements in the accuracy of this non-muffin tin theory are anticipated with more dependable values of the photoelectron inelastic mean free path, and a more rigorous approach to the thermal motion of individual atoms within the cluster of interest.

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