



Topical Review

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

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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 ($k \approx 20 \text{ \AA}^{-1}$) 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.

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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 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

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

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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

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

where \mathbf{k} is the photon wave vector polarized in the \mathbf{e} 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:

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

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:

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

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 .

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

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 $h = 0.25 \text{ \AA}$. In this work, data points at or near the absorption edge were calculated using $h = 0.20 \text{ \AA}$. This was required to reach adequate convergence. At an energy of

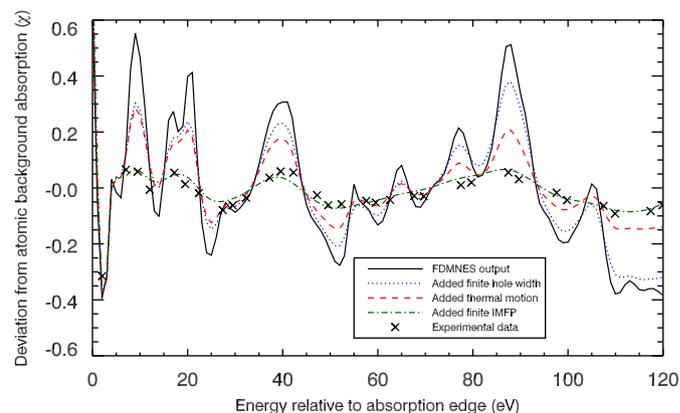


Fig. 1. Oscillatory component (χ) of copper XAFS as determined by the finite difference method. The results of progressively including additional effects are also shown. Firstly the effect of the finite hole width produced by the loss of the photoelectron from the absorbing atom is added. Secondly the 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.

100 eV past the absorption edge, however, $h = 0.15 \text{ \AA}$ was required for convergence. At 200 eV, $h = 0.12 \text{ \AA}$ was needed. The upshot of this rapid increase in cluster density is that the memory requirements, and subsequently the calculation time, balloon for high energy calculations. As stated, past around 300 eV it appears that the standard FDMNES procedure becomes unusable for copper due to severe computational limitations.

The solution to this comes from a simple conceptual understanding of the problem. The number of grid points, and in turn the number of linear equations and memory usage, can be curtailed effectively by reducing the cluster radius. This may seem a poor option given the need for large clusters ($> 8.0 \text{ \AA}$ radius) to achieve convergence at and near the absorption edge. However, this requirement relaxes rapidly as the energy increases, due to inelastic losses.

The inelastic mean free path for most solids diminishes rapidly; from effectively infinite at zero energy, to only a few angstroms within a matter of 50 eV [15]. In copper, the IMFP is believed to drop to as low as 3 \AA at an energy of approximately 10 eV. The rate of increase thereafter is low: around $1\text{--}2 \text{ \AA}$ per 100 eV. As a result, contributions far beyond this distance from the centre of the absorbing cluster are not effectively probed. Further, the convolution width derived from the IMFP increases with energy even despite a slow increase in the IMFP itself. By consideration of the Fourier relationship between XAFS oscillations and atomic displacements mentioned early in this paper, we can see that the high frequency oscillations produced by atoms on the outer edge of the cluster become increasingly insignificant. Therefore we simply remove these components and reduce the cluster size to keep the number of data points manageable.

The rate at which the cluster size can be reduced with energy is naturally dependent upon the material in question. For copper the cluster radius was gradually decreased from 8.3 \AA at the absorption edge to around 7 \AA at 100 eV, and 5 \AA at 200 eV. By 500 eV, the XAFS oscillations had diminished sufficiently to use a cluster radius of 1.0 \AA and an interpoint distance of 0.025 \AA . This yielded a smooth atom-like spectrum for high energies.

Fig. 2 shows our calculated absorption spectrum for copper in the XAFS region; from the absorption edge up to around 500 eV. We see good agreement in the peak magnitudes and shapes with the plotted experimental data from Glover et al. [14], Chantler et al. [16], and Wong [17]. Also shown is the calculated atom-like spectrum for copper, which the solid state spectrum approaches in the high energy limit. We note the existence of an offset in

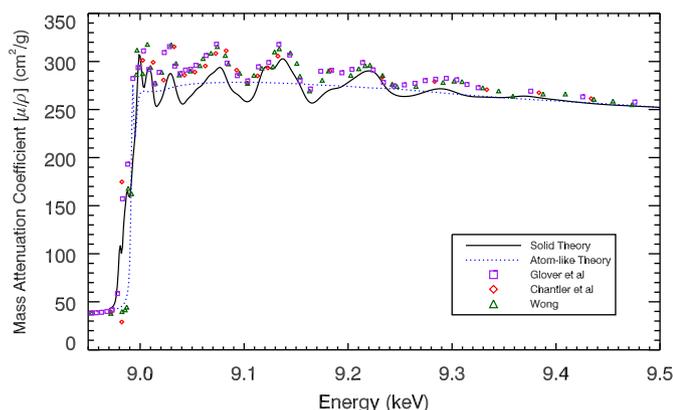


Fig. 2. Calculated absorption spectrum for solid state copper over a range of 500 eV above the K-absorption edge. Also shown are experimental measurements by Glover et al. [14], Chantler et al. [16], and Wong [17]. Good agreement in peak positions and magnitudes is achieved over this range, in spite of an absorption offset common to many XAFS theories [19–21]. Also shown for comparison is a calculated atom-like spectrum for copper.

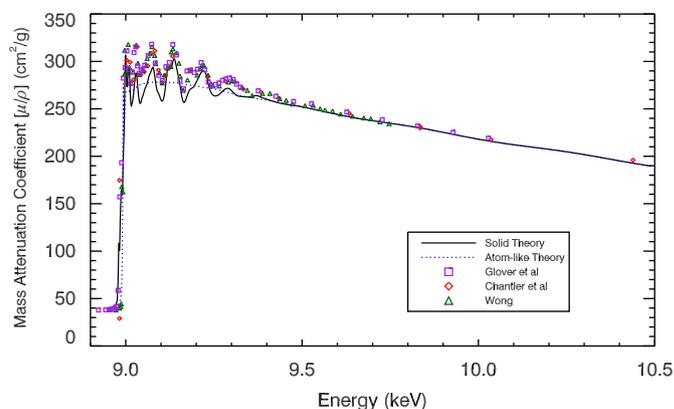


Fig. 3. Calculated absorption spectrum for solid state copper extending to 1.5 keV above the K-absorption edge. Also shown is the absorption curve determined for atom-like copper, and solid state measurements from Glover et al. [14], Chantler et al. [16], and Wong [17]. This extended view shows that the offset phenomenon observed in the near edge region disappears over a sufficiently long energy range.

absorption, particularly in the near edge region. This occurs despite a well defined background function from the FFAST package [18], used to account for absorption due to the photoexcitation of outer shells. The cause of this offset is not understood, however we note that similar offsets have been observed in multiple scattering methods for a variety of materials [19–21].

Fig. 3 shows our results expanded over an energy range of 1.5 keV. This represents a factor of 5 increase in the previous longest energy range of a finite difference method calculation of XAFS. For the first time we can see not only a proof of the applicability of this approach in extended XAFS theory, but can also see that, in a similar way to alternative theories, an offset is observed in the near edge region that disappears as the energy is increased. The extension to 1.5 keV (or $k \approx 20 \text{ \AA}^{-1}$) of this theory opens the door to arbitrary extension to higher energies and k -space due to the convergence towards a smooth atom-like background absorption, which is relatively easy to calculate.

Our results demonstrate the applicability of finite difference method calculations not only to near edge structure, but also to extended X-ray absorption fine structure. This enables a new approach to XAFS theory that is consistent, devoid of any fitting parameters or limiting physical approximations, and can give highly accurate predictions over the entire range of oscillations. The method can also be readily extended to complex molecular structures, with future improvements in computational efficiency expected to further heighten the value of this approach in such systems.

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