Studies of fundamental photoexcitation and photoelectron-scattering processes

J. D. Bourke*

School of Physics, University of Melbourne, Australia. *Correspondence e-mail: jaybourne@gmail.com

The processes of photoelectric excitation and subsequent photoelectron scattering are the fundamental building blocks of the X-ray absorption fine-structure (XAFS) phenomenon, being chiefly responsible for the complex material-dependent structure in the X-ray absorption spectrum. Tracking the behaviour of the excited photoelectron is therefore the principal consideration of any XAFS theory, as the XAFS signal itself is facilitated by the elastic scattering of the electron, while the strength of the signal is attenuated by inelastic scattering events. This chapter is chiefly concerned with the quantitative impact of inelastic photoelectron scattering on an XAFS spectrum, and particularly the use of XAFS measurements in deriving experimental values for the electron inelastic mean free path (IMFP), a convenient parameterization of the inelastic scattering cross section for a given electron energy. Here, an overview is provided of the current methods for extracting IMFP data from XAFS, with a discussion of how recent results compare with those of more traditional experimental approaches. The impact of the experimental findings on current understanding of the fundamental theory used to describe low-energy electron transport is dealt with, and subsequent extensions to the quantum dielectric theory of inelastic scattering are discussed.

1. Introduction

Since its popularization in the early 1970s, XAFS has been widely utilized as an effective, non-invasive and nondestructive means of interrogating a vast array of material parameters of interest to chemistry, biology and materials science. The ability to robustly determine structural parameters, valence states, oxidation levels and an array of thermal and electronic properties is a great boon to materials analysis and design, with widespread applications that have led to the publication of thousands of papers per annum and, indeed, much of this extensive handbook.

Typically, the extraction of these parameters requires both high-precision measurement techniques and sophisticated analytical software that commonly incorporates a robust theoretical approach to quantify the various physical processes at play in the X-ray–electron interaction that gives rise to XAFS. In other words, the underlying physics is taken as known, while the key properties of the material being studied are the variables that are to be determined.

This dynamic is currently somewhat different when it comes to the topic of inelastic electron scattering, which we quantify here in terms of the electron inelastic mean free path (IMFP). The IMFP is defined as the mean distance between successive inelastic scattering events of a particular electron moving with a given energy $E$. Theoretical determinations of the IMFP for a given material are typically highly robust and accurate for keV energies, being largely dependent upon aggregate electron densities and often calculable using significant
approximations (Tanuma et al., 1988) coupled with broad-based electronic sum rules (Smith & Shiles, 1978). At the energies of interest to XAFS, however, and especially for energies below 100 eV and in the XANES region, the prevailing theoretical models possess significant shortcomings (Bourke & Chantler, 2012). Ergo, in this sphere XAFS has a significant role to play not only in the experimental determination of practical material properties, but in the guidance and development of our basic theoretical understanding of the fundamental interaction properties of electrons within condensed matter.

In this chapter, we cover the basic mechanisms by which inelastic scattering and photoelectron lifetime effects influence XAFS, how these compare with other experimental apparatus which may be used to extract electron IMFPs, and how XAFS-based IMFP determinations have uniquely impacted theoretical modelling of single- and bulk-electron transportation modelling.

2. Lifetime broadening
The energy of a free-moving photoelectron excited by the absorption of an X-ray is necessarily uncertain to within a range determined by the coherent lifetime of the excitation. This is quite independent of any uncertainty in the energy of the incident X-ray photon itself, and is a natural consequence of the Heisenberg uncertainty principle. The excited state created by the absorption event consists of both the excited photoelectron that may lose coherence via subsequent inelastic scattering, and a hole (typically, for XAFS, a core hole) that may lose coherence when filled by a secondary electron relaxation. In both cases the applicable energy spectrum of the excitation is given by a Lorentzian profile with width \( \Gamma \) determined by the lifetime of the coherence \( \tau = 1/\Gamma \).

As Lorentzian profiles convolve additively, we can express the total resultant broadening of the energy-dependent XAFS spectrum in terms of broadening from both the photoelectron and core hole:

\[
\Gamma(E) = \Gamma_{\text{PE}} + \Gamma_{\text{hole}}.
\]

Since our focus here is on the broadening applied by inelastic electron scattering, we express \( \Gamma_{\text{PE}} \) in terms of the electron IMFP, \( \lambda \), following Bourke et al. (2007),

\[
\Gamma(E) = \frac{\hbar}{\lambda(E)} \left( \frac{2E}{m_e} \right)^{1/2} + \Gamma_{\text{hole}},
\]

where \( \Gamma \) is the total lifetime broadening of the excited state, \( E \) is the energy of the excited photoelectron and \( m_e \) is the electron mass. We take the core-hole width, \( \Gamma_{\text{hole}} \), as energy-independent for the range of interest to XAFS, thus assuming that all significant energy dependence of the Lorentzian type broadening comes from variations in the electron IMFP.

Deviations from this approximation, including via the low-energy breakdown of the sudden approximation, are beyond the scope of the current analysis but have been discussed in some detail by Guzzo et al. (2012).

3. IMFP measurements from XAFS
The process for quantifying the low-energy inelastic electron scattering via the electron IMFP from XAFS is therefore a matter of determination of the energy-dependent Lorentzian broadening function present within an XAFS measurement. There are two important measurement criteria for a meaningful evaluation of the IMFP.

The first criterion is high absolute accuracy of the XAFS measurement, ideally with robustly determined uncertainties. Scaling errors in the size of the XAFS oscillations can lead to unquantifiable errors in the IMFP, and therefore the photoabsorption spectrum must be calibrated to an appropriate reference material. This process is well established for solid elemental samples (de Jonge et al., 2004), but has also recently been demonstrated for compounds, mixtures and dilute materials (Islam et al., 2016). Uncertainties, evaluated by the analysis of experimental systematics, are not strictly required but are highly recommended to evaluate the validity of the result. Even small measurement uncertainties in XAFS can lead to relatively large errors in the extracted IMFP.

The second criterion is a high density of data collection with respect to the energy. This is especially true in the very near-edge region where the electron IMFP tends to infinity, leading to a small broadening width and narrow absorption peaks. It is recommended that in order to avoid aliasing and to robustly determine \( \Gamma_{\text{PE}} \), the measured energy spacing should be less than half the expected core-hole broadening of the absorbing element.

With the measurement requirements fulfilled, the IMFP is extractable from XAFS via analysis using a full-potential modelling package. Approximations in the electronic potential of the absorbing material have a significant impact on the calculated XANES spectrum (Glover et al., 2007), and so it is recommended to use a package that is free of such limitations. So far, IMFP measurements have been deduced using the FDMX package coupled with a custom fitting routine (Bourke, Chantler et al., 2016; Bourke, 2021).

The fitting routine runs successive iterations of energy-dependent Lorentzian broadening applied to highly precise calculations from FDMX using an extremely dense representation of the electronic potential in the absorbing material. Finite-element solutions to the Schrödinger equation are evaluated over a three-dimensional real-space grid with spacing ranging from 0.2 Å to as little as 0.05 Å as the energy is increased. Values for the energy-independent core-hole broadening are taken from the tabulations of Scofield and of Kostooun and coworkers for \( Z = 21–50 \) (Scofield, 1969; Kostooun et al., 1971), and from Bambaneyk and coworkers for \( Z = 51–100 \) (Bambaneyk et al., 1972). The energy dependence of the broadening, \( \Gamma_{\text{PE}} \), is then represented by a modified power series, given in terms of adjustable parameters \( x_n \) by

\[
\Gamma(E) = \sum_{n=1}^{N} \frac{x_n}{E^{n/2}}.
\]

An equivalent description of the energy broadening can also readily be obtained by considering the exponential decay of the photoelectron wave-function, coupled with the Fourier relationship between this wavefunction and the XAFS spectrum (Bourke et al., 2007).
\[ \Gamma_{PE}(E) = \frac{\sum_{i=1}^{n} E^{x_i}}{\sum_{i=1}^{n} E^{x_i}}, \]  

(3)

This empirical formula is of limited direct physical significance, and so is certainly not the only option for a fitting algorithm. Natural alternatives include broadening based on the TPP-2M formula for IMFPs (Tanuma et al., 2011), the Gries formula (Gries, 1996) or even an arctangent form (Joly, 2001). Analysis of materials with relatively simple loss spectra, such as aluminium, which is strongly dominated by a single plasmon pole, may even facilitate alternate forms with parameters related more directly to physical attributes such as the peak resonant energy or net oscillator strength. However, the relatively flexible power series of equation (3) has been found to produce good results so far for measurements of elemental copper and molybdenum, which possess broad loss spectra with myriad collective and single-electron contributions (Bourke & Chantler, 2010; Chantler & Bourke, 2010).

The fitting form is designed to mimic the normal behaviour of an IMFP broadening curve based on standard theoretical IMFP tabulations up to 150–200 eV. The function begins at the origin with an initial gradient given by \( x_1 \), and increases smoothly and monotonically up to a maximum value of the highest-order fitting parameter \( x_n \) \( (x_4 \) is found to be sufficient up to 120 eV). The other parameters control the rate of increase in broadening across the energy spectrum.

The results so far have been highly inconsistent with both existing experimental and theoretical tabulations. In particular, the IMFPs measured by XAFS have been significantly lower than those from other methods, especially for energies below 50 eV. Comparisons with freely available theoretical tabulations are shown in Fig. 1.

These results, however, are not entirely inconsistent with expectation, owing to a range of known shortcomings in alternative approaches for determining low-energy electron IMFPs. Rather, they represent an opportunity to critically evaluate the efficacy of a range of experimental techniques and to test the validity of the prevailing assumptions and approximations in current theoretical modelling of low-energy electron transport.

4. Alternative experimental approaches

Traditionally, the most common experimental techniques for measuring electron IMFPs have been the overlayer technique (Seah & Dench, 1979) and, more recently, elastic peak electron spectroscopy (EPES; Tanuma et al., 2005). An excellent and extensive review of these approaches has been given by Powell & Jablonski (1999). However, it is worth summarizing here some relevant properties of these approaches and how they compare with the physical processes involved in an XAFS measurement.

In the case of an overlayer experiment, the IMFP is inferred from repeated measurements of Auger or photoelectron emission from a thin film of material as it is deposited in layers upon a flat substrate while subjected to optical excitation. As the film increases in thickness (or, alternatively, the angle of emission is varied), fewer electrons escape to a detector owing to inelastic scattering within the film. These measurements allow determination of the ratio of the electronic signal from a film of known thickness to that of an identical bulk material, which in turn may be used to deduce an electron IMFP.

This approach is relatively straightforward to carry out, but is susceptible to a number of systematic errors. One of the most pressing of these is the difficulty in achieving, and demonstrating, uniformity of the film deposition, the width of which is a direct determinant of the measured IMFP. Surface excitations within the film can also be significant owing to the need for very thin films, particularly in the measurement of low-energy IMFPs, which are commonly less than 10 Å.

The overlayer technique is also particularly fraught in that its direct measurement is in fact not of the electron IMFP but rather of a separate quantity known as the electron effective attenuation length (EAL; Powell & Jablonski, 2009). This quantity differs from the IMFP in that it is the mean displacement between successive inelastic scattering events, rather than the distance travelled by the electron. In the absence of elastic scattering events these quantities are equal, but when elastic scattering is present the EAL can be significantly smaller. Therefore, to convert the quantity measured by an overlayer experiment into a true electron IMFP, a Monte Carlo routine is required to simulate the path of the excited electron, the uncertainty of which can often be greater than the measurement itself (Powell, 1988).

These difficulties have led to the recognition of EPES as a more reliable method for measuring IMFPs. EPES involves the bombardment of a sample with electrons of a given energy and measurement of the elastically backscattered signal. This method alleviates some of the experimental systematics of the overlayer technique, and the spectroscopic measurements are generally robust provided that the surface of the material
being studied is sufficiently disordered to avoid coherent diffraction. The ratio of the backscattered signal to the incident intensity is then directly and proportionately related to the electron IMFP.

Unfortunately, however, this proportionality varies by material and is still subject to a Monte Carlo algorithm in order to quantify the electron-transport properties within the sample. Further, measurements of a reference material of known IMFP are usually required (Tanuma et al., 2005), producing additional experimental uncertainty and potential errors if the reference IMFP is incorrect. This is particularly problematic for low-energy measurements owing to known weaknesses in established theoretical tables, as discussed in the next section.

It is also possible to utilize a more general experimental technique than EPES, whereby an extended spectrum of inelastic scattering losses is also measured. This is then referred to simply as electron energy-loss spectroscopy, and can be performed via transmission measurements (EELS; Egerton, 2009) or reflection measurements (REELS; Werner et al., 2009), with REELS typically being favoured for low-energy studies. In this way a determination of the imaginary component of the dielectric function can be obtained, again with the use of theoretical models including Monte Carlo tracking of electron-scattering paths and a robust account of surface-excitation phenomena (Vos, 2013). The dielectric function can then be transformed into an estimate of the IMFP from REELS using one of a number of available optical data models (Vos & Grande, 2017). Again, however, this is contingent upon the validity of such models, which are shown in the next section to be incomplete for low electron energies.

Thus, while we have some alternative experimental techniques that are relatively reliable for high-energy electrons, and even down to a few hundred eV, in the region of interest to XAFS there are several compelling reasons to be wary of existing measurements. Fortunately, the nature of the XAFS process removes a large number of the constraints that exist in these other techniques.

Firstly, the relative quantification of elastic and inelastic scattering cross sections, and the explicit tracking of electron trajectories, is not required in an XAFS analysis. This is because the elastic and inelastic scattering processes present orthogonally in an XAFS signal: (coherent) elastic scattering creates the signal, while inelastic scattering destroys it. Secondly, XAFS measurements are significantly more sensitive to the IMFP in the low-energy regime, making XAFS unique among experimental approaches.

Thirdly, XAFS is substantially less limited by the physical properties of the sample under investigation. Since the photoexcitation process takes place primarily in the bulk of the material, surface effects are typically of minimal consequence to an XAFS measurement of IMFPs. The same is also true of highly ordered materials, where even single-crystal samples are potentially usable. In general, XAFS measurements may be quantified with uncertainties of well below 0.01% with a robust account of all major experimental systematics (Chantler, 2009).

The primary point of weakness with the XAFS technique lies in the use of theoretical analysis software, which may be seen as analogous to the implementation of Monte Carlo algorithms in alternative techniques. Although it is currently believed that less error is introduced into the approach by the XAFS software, most particularly in the low-energy regime, the existence of continued disagreement between experimental and theoretical IMFP values demonstrates that there remains potential for error in this respect.

5. Theoretical insights from XAFS measurements

The significant variation between experimental IMFP results from XAFS and existing tabulations has prompted a significant rethink and advancement in the theoretical modelling of low-energy electron scattering. Most commonly, IMFPs are calculated according to a variation of the optical data model developed by Tung et al. (1979) and Penn (1987). This model facilitates a representation of the electron energy-loss function (ELF), a simple transform of the dielectric function, \( \varepsilon(q, \omega) \), given by \( \text{Im}[-1/\varepsilon(q, \omega)] \). The physical significance of the ELF is that it is proportional to the probability of an electron-scattering event depositing energy \( \hbar \omega \) and momentum \( \hbar \mathbf{q} \) into the scattering material (Nikjoo et al., 2012), meaning that the total scattering cross section may be readily calculated by an appropriate integral over the ELF (Tanuma et al., 1991). This idea is also central to the solid-state self-energy approach favoured in some popular \textit{ab initio} XAFS theories (Rehr et al., 2009).

Therefore, the question has arisen as to how common implementations of the optical data model may be deficient in their representation of the ELF, such that the IMFP may be overestimated (Chantler & Bourke, 2014). Until recently, the most sophisticated and uniquely robust implementation has been the Penn equation (Penn, 1987), which may be expressed as

\[
\lambda(E)^{-1} = \frac{\hbar}{a_0 \pi E} \int_0^{q_{\text{max}}} \int_{-q_{\text{max}}}^{q_{\text{max}}} 2 \text{Im} \left[ \frac{-1}{\varepsilon_{\text{data}}(0, \omega')} \right] \times \text{Im} \left[ \frac{-1}{\varepsilon_{l}(q, \omega'; \omega_l = \omega')} \right] d\omega' dq d\omega,
\]

where the \( q \pm \) limits are generally given by

\[
q_\pm = \left( \frac{q^2 E}{\hbar \omega} \right)^{1/2} \pm \left[ \frac{E}{\hbar \omega} (E - \hbar \omega) \right]^{1/2}.
\]

In this equation an input optical dielectric function, \( \varepsilon_{\text{data}}(0, \omega') \), is taken from optical measurements (Palik, 1998), a density-functional theory (DFT) implementation such as WIEN2k (Blaha et al., 2020; Ambrosch-Draxl & Sofo, 2006) or otherwise (Werner et al., 2009), and is extrapolated into a momentum-dependent ELF by assigning each permissible optical excitation to a corresponding Lindhard-type electronic excitation (Lindhard, 1954). The functional form for a Lindhard excitation of resonant energy in the optical limit of \( \omega_l \) is
denoted in equation (4) by $\epsilon_1(q, \omega, \omega_p = \omega_0)$, where $\omega_p$ is the plasma energy.

This model is responsible for many standard tabulations of IMFP data ranging from 50 eV to tens of keV for a wide array of materials (Tanuma et al., 2011). Its most pressing weakness, however, and one that prevents robust calculation below the 50 eV limit, is the use of the Lindhard representation itself, which is explicitly a lossless model of electronic excitation. In a physical sense, this means that states excited by inelastic electron scattering are considered, within this model, to be of infinite lifetime and hence possess no natural energy broadening. The consequences of such an approximation include that it does not, for example, enable excitations below the plasma frequency for electrons of high momentum (Chantler & Bourke, 2014). This means that the propensity for energy loss via inelastic scattering is artificially reduced at low energies$^2$, and thus the IMFP is potentially overestimated.

The solution to the problem of lossless excitations (sometimes denoted lossless oscillators) was proposed as early as 1970 by Mermin as an extension to the Lindhard dielectric function (Mermin, 1970). This Mermin function, labelled $\varepsilon_M$, has only gained traction for IMFP evaluation in recent years, partly owing to computational complexity (Denton et al., 2008) and partly owing to a lack of constraint on the broadening to be applied to each excitation. On the other hand, the evidence from IMFP measurements using XAFS spectra has demonstrated that an account of broadening within the electron ELF is critical to finding agreement between experimental and theoretical IMFP data at energies below 100 eV.

This has led to a recent breakthrough in the representation of the electron ELF, and thus IMFP, as a recursive integral over Mermin oscillators, utilizing a self-consistent algorithm for the determination of excitation broadening based on the oscillator strength of the material itself. This model is described in detail in Bourke & Chantler (2015), and can be expressed as

$$\lambda(E)^{-1}_N = \frac{\hbar}{a_p \pi E} \sum_{q \neq 0} \int \frac{2 \pi \omega' \omega}{\pi \omega' \omega} \times \text{Im} \left[ \left. \frac{-1}{\varepsilon_{\text{data}}(0, \omega')} \right|_{\omega = \omega_0} \right] \frac{\text{d} \omega'}{\text{d} q} \frac{\text{d} q}{\text{d} \omega},$$

where $\gamma(q)$ is an energy- and momentum-dependent broadening parameter, $\theta$ is the Heaviside step function and $q_{\pm}$ are the generalized limits given in equation (5). Use of this model, called the coupled-plasmon model, generates significant extra losses at low energies without affecting high-energy IMFPs and thus improves the agreement with experiment dramatically. An example of how excitation broadening can affect the IMFP is given for elemental copper in Fig. 2.

In this case the reduction is generated by a fit of Mermin parameters to a DFT-calculated optical ELF (Bourke & Chantler, 2012). This result was the first to demonstrate agreement between theoretical and experimental IMFP values for energies below 100 eV. Although significant discrepancies persist below 50 eV, it is clear that our theoretical understanding continues to be ripe for development, along with the sophistication of our experimental methods.

### 6. Limitations and conclusions

The extraction of IMFPs from XAFS has proven to be robust and effective in its limited use so far for energies between 50 and 120 eV, showing reasonable agreement with theory once compensation has been made for the effects of broadening in the electron ELF. The remaining discrepancies in the very low-energy region, however, are a topic of continued interest and development in the field.

From the experimental side, particular points of interest include the impact of beam broadening and its quantification via measurements of the shape of the absorption edge. This problem is particularly difficult owing to its entanglement with the natural broadening of the spectrum owing to the core hole, $\Gamma_{\text{hole}}$. Additionally, technical matters in classifying XAFS spectra persist, such as the correct method for isolating the XAFS oscillations themselves from the background absorption via the use of splines (Ravel & Newville, 2005) or scaled ab initio calculations (Bourke, Chantler et al., 2016).

The computational analysis tools for XAFS have potential shortcomings in the near-edge region owing to the strong sensitivity of this region to details such as the joint density of states and the exchange–correlation potential, which are not always well approximated (Bourke, Islam et al., 2016). Further, it is likely that in some cases the high energy sensitivity of the effective thermal correction necessary for XAFS spectra may cause an underestimate of the electron IMFP for energies

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$^2$ Although this is necessarily true for low energies, typically below 100 eV, where plasmon excitations are dominant, it is not true for higher energies as the integral of inelastic losses is constrained by dielectric sum rules (Smith & Shiles, 1978). This is the reason why, despite the use of Lindhard excitations, the Penn model is nevertheless highly accurate at keV energies.

**Figure 2**

IMFP data for elemental copper measured by XAFS are compared with theoretical predictions using lossless modelling and a model inclusive of a broadening effect (Bourke & Chantler, 2012).
within a few tens of eV of the absorption edge (Tantau et al., 2015).

In terms of our theoretical understanding, some approximations still exist even within the coupled plasmon model. These include the differential treatment of bulk-electron and single-electron excitations, which have recently been suggested by first-principles calculations to diverge significantly (Alkauskas et al., 2013), in contrast to existing optical data modelling. Further, the precise impacts of exchange, correlation and excitonic effects are not wholly understood with respect to the Mermin dielectric formalism, nor are their impacts on density-functional theory for valence, conduction and continuum states.

Given these known issues, it is at once a pleasant surprise that we can already achieve such convergence for experimental and theoretical IMFP values for energies down to 50 eV, but also a difficult and interesting challenge to develop our techniques further to create greater agreement down to energies of only a few eV. With our improving technologies in first-principles DFT investigations, breakthroughs in full-potential XAFS modelling and constant development of high-accuracy measurement techniques for XAFS spectra, there exists much promise within this field for further insights into our fundamental understanding of critical electron-transport properties in energy regimes that until recently have been near-impossible to explore.

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References


