Accurate measurement and physical insight: The X-ray extended range technique for fundamental atomic physics, condensed matter research and biological sciences

C.T. Chantler

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

ARTICLE INFO

ABSTRACT

Research in core physics or atomic and condensed matter science is increasingly relevant for diverse fields and are finding application in chemistry, engineering and biological sciences, linking to experimental research at synchrotrons, reactors and specialised facilities. Over recent synchrotron experiments and publications we have developed methods for measuring the absorption coefficient far from the edge and in the XAFS (X-ray absorption fine structure) region in neutral atoms, simple compounds and organometallics reaching accuracies of below 0.02%. This is 50–500 times more accurate than earlier methods, and 50–250 times more accurate than claimed uncertainties in theoretical computations for these systems. The data and methodology are useful for a wide range of applications, including major synchrotron and laboratory techniques relating to fine structure, near-edge analysis and standard crystallography. Experiments are sensitive to theoretical and computational issues, including correlation between convergence of electronic and atomic orbitals and wavefunctions. Hence, particularly in relation to the popular techniques of XAFS and XANES (X-ray absorption near-edge structure), this development calls for strong theoretical involvement but has great applications in solid state structural determination, catalysis and enzyme environments, active centres of biomolecules and organometallics, phase changes and fluorescence investigations and others. We discuss key features of the X-ray extended range technique (XERT) and illustrate applications.

© 2009 Elsevier Ltd. All rights reserved.

1. An overview: a broader picture

Research in fundamental atomic and condensed matter physics is entering a new phase. In past decades there have been two mutually exclusive groups, one looking at fundamental experiments of different types and one pursuing applications for particular tools, further divided into engineering, chemical and biomedical areas. The second type has often been semi-empirical in nature, and sometimes based on different disciplines (chemistry, engineering, biological sciences or medicine). Narrow focus has led to outstanding impacts in a publication or niche field. But it is necessary to have a big picture to achieve seemingly uncorrelated major advances across several disciplines. This vision is an important basis for the future and is a motivator of this special issue.

Major issues in modern physics relate to possible tests of quantum electro-dynamics (QED). QED is one of the two best-tested theories in physics and science. It is the primary explanation of the interaction of light and charge and is fundamental to much of the physics which we assume and rely on in the world today. Experimental and theoretical developments in 1998–2008 are questioning current theoretical approaches. QED is the most trusted example of a quantum field theory. Yet certain problems in its formulation lead people like Roger Penrose to assume fundamental flaws in the theory (Penrose, 1989). Major recent developments include Niering et al. (2000) (nobel laureate on tests of hydrogen, which arose from his development of the frequency comb); Stolker et al. (1999) (tests of high-*Z* and uranium, based at accelerator developments); Murphy et al. (2003, 2008) (tests of the constancy of the fine structure constant on astrophysical timescales, based on atomic physics modelling); Jentschura (2000) (new theoretical developments of QED higher order contributions) and many others. Our experiments (e.g. Chantler et al., 2000a, 2007a) are the most accurate in the medium-*Z* regime, and begin to probe higher order and excited-state QED. Further experiments will distinguish between theoretical implementations and may reveal theoretical inadequacy, by being more sensitive to important terms and interactions (Chantler, 2004).

Fundamental experimental atomic physics has had numerous recent milestones. The first absolute polarisation studies

performed on an EBIT (Takacs et al., 1996), early investigations of radiative electron capture to test QED (Beyer et al., 1993), and work on (difficult) laser resonance spectroscopic tests of QED (Lea et al., 1994). Electron beam ion traps (EBITs) are devices of importance for fundamental tests of QED, for high-precision spectroscopy of highly ionised atoms, for studies of plasma recombination rates, for X-ray polarisation studies, for micro-lithography and for high-frequency laser development. EBIT technology evades the Doppler-broadening limitation of conventional devices. Early EBIT work was reported in the nobel symposium for 1991 (Gillaspy et al., 1995). 1s–2p Lyman α and $n = 2-4$ Balmer β X-ray transitions in hydrogenic ions from chlorine to uranium are of importance in testing QED. Measurements allow comparison between theory and experiment for the Lamb shift in medium-to-high-Z hydrogenic ions, which is the most sensitive way to test QED at high effective coupling strength $Z\alpha$.

Our measurements of resonance lines of helium-like ions in the $Z = 19-31$ range (Chantler et al., 2000a) are sensitive to one-electron QED effects and on the verge of being sensitive to two-electron QED effects (0.14 eV accuracy for a 0.16 eV effect). This investigation has developed new types of tests of QED in the medium-Z regime. The impact of such fundamental studies is long term, but includes development of state-of-the-art detectors and spectrometers. Systematics in EBIT measurements of QED and the statistical quality of experiments have been significantly developed by these techniques and investigations.

Theoretical tools for understanding fundamental atomic physics, with a one- or two-electron system in a specialised experiment (i.e. QED), can instead be used to investigate neutral atomic physics. Atomic processes are in principle well understood: absorption, elastic and inelastic scattering cover the key processes at the undergraduate level. However, measurement of these probes our quantum mechanical understanding of atomic wavefunctions and transition probabilities. Elastic scattering can show great complexity as Rayleigh, Bragg–Laue or thermal diffuse scattering, for example, and experimentally these processes are poorly defined. Leaders in this area include Suric et al. (2003) and Carney et al. (2000) (S-matrix methods on X-ray interactions and scattering) and Bartschat et al. (2007), Bray et al. (2002) (accurate scattering of electrons from low-Z systems).

2. Theoretical and experimental databases for X-ray interactions

There are numerous databases for the X-ray interaction with matter composed of experimental measurements of condensed matter systems, preferably ideal elemental systems. These may be critically compiled into bibliographic summaries (Hubbell, 1994; Hubbell et al., 2003) or experimental–theoretical empirical syntheses (Henke et al., 1993; Cullen et al., 1997). These are then used in plasma diagnosis, X-ray and radiographic filters, anode tube design, medical imaging, weapons research and fundamental investigations.

Increasingly, computational analysis has preferred a theoretical tabulation of baseline, of which there are also many examples (Berger et al., 1999; Berger and Hubbell, 2004; Saloman et al., 1988; Scofield, 1973; Creagh and McAuley, 1995). This then allows a critical comparison of experiment with theory. However, there are some limitations to the effectiveness of this. One has been that the theoretical data are generally based on an isolated atom assumption (i.e. an atomic calculation). In general this can

be used positively to investigate the condensed matter interaction, and one observation is that the atomic structure dominates far above the absorption edge, so the comparison can be quite insightful in particular regions.

Our theoretical computations (Chantler, 1995a, 2000) and FFAST (Chantler, 1995b) databases (Chantler et al., 2003) are key theoretical references for X-ray properties (atomic form factors, absorption and attenuation). They have overcome several flaws of earlier computations (Chantler, 1993, 1994).

This was successful both for the investigations of Cherenkov radiation and for the resolution of several earlier discrepancies between experiment and theory (Chantler, 1999; Chantler and Barnea, 1999).

The computed results are confirmed by several of the best datasets, compared to other models, especially on the K-edge and above, and have sparked further theoretical developments pursued by several international groups. The databases impact upon X-ray optics, DAFS (diffraction anomalous fine structure), EXAFS (extended X-ray absorption fine structure), crystallography and Cherenkov radiation studies. The X-ray data are relevant for fundamental theory, materials analysis, X-ray and synchrotron biological efforts and lithography. They also pertain to medical diagnosis and industrial shielding. Numerous reviews have been made discussing the latest developments of the database and theory. The web database has been receiving 10,000–20,000 hits per month since its electronic installation as one of the three major references for atomic form factors and attenuation coefficients.

This level of interest is very widespread—categories of academia, government, defense, industry and commercial are all well represented. It has been quoted to be the self-consistent model (i.e. atomic baseline) for interpreting XAFS and DAFS structure (Bouldin, 1994; Sorensen et al., 1994). The theory is crucial for future developments of XAFS, X-ray diffraction and powder diffraction analysis and interpretation in synchrotron research.

However, in many cases the experimental data have been inconsistent between or within datasets, with apparent precisions of order 1–20%, which therefore has prevented detailed investigation of the experimental or theoretical discrepancies (Chantler et al., 2001c; Tran et al., 2005). It was claimed that accuracies below 1%, even for metals or single crystalline elements, were not possible (due to the difficulties of addressing experimental systematics). Also, while theoretical uncertainties are difficult to estimate and are generally not reliable below 1%, different theoretical predictions can differ by up to 50%, especially for near-edge or soft X-ray energies.

3. XERT

This has sparked our series of experimental investigations, together with those of many other research groups. Careful studies from 1987 and 1990 by the International Union of Crystallography established principles for the careful measurement of attenuation coefficients and photoabsorption coefficients (Creagh and Hubbell, 1987, 1990).

We developed the X-ray extended range technique (XERT) over several years (Chantler et al., 1999, 2000b) and implemented them and others at synchrotrons to achieve accuracies of 0.2% (Chantler et al., 2001a; Tran et al., 2003a, 2003b) and 0.02% (de Jonge et al., 2005, 2007) (Fig. 1).

While the details are given in several publications, a brief outline of the approach is given here. This is adapted to the material under investigation, the beam-line, the energy range and
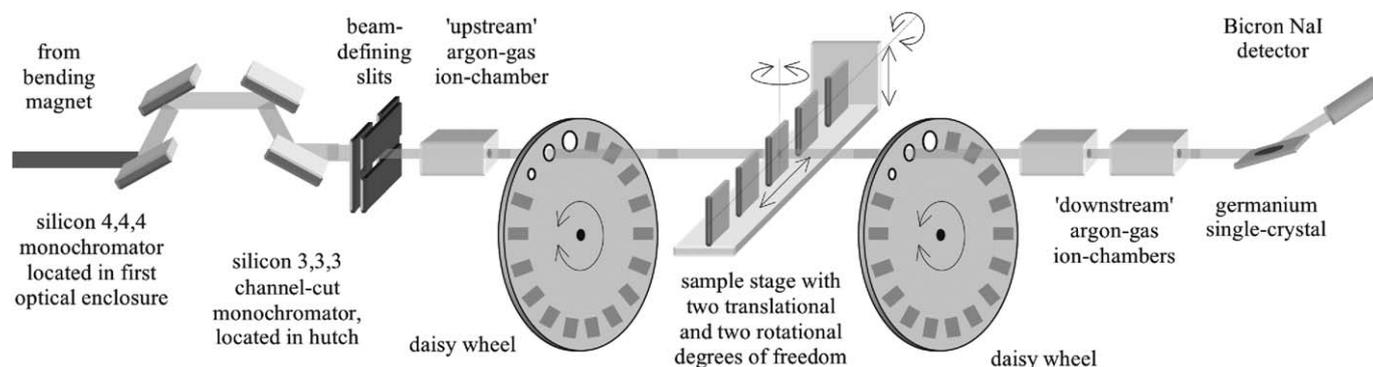
Fig. 1. Typical layout of an XERT experiment at the APS.

beam-time available, but provides a general set of principles for the accurate determination of attenuation or absorption.

1. We do not assume the monochromator axis is highly calibrated under arbitrary or adaptive step-sizes (or continuous scans) of energy, nor do we use a single relatively beam-dependent calibration foil edge to determine the energy based upon a tabulation of reference energies. We have shown that these assumptions may have an energy-dependent error across an extended absorption edge of several eV or up to 100 eV (Chantler et al., 2004; de Jonge et al., 2007). Instead, we independently calibrate the monochromated, delivered energy using either powder diffraction standards (silicon or LaB_6) or single crystal standards (silicon or germanium), depending upon beam-line, which maps out the energy axis for the measurements involved and removes slope error and higher order hysteresis. Some 10–12 points of energy are usually used to calibrate the energy and the encoder offsets, but even two to three points measured in this manner can avoid several systematics. An edge energy or E_0 error of only 6 eV in measurement or refinement analysis (e.g. using XAFS code) can yield a 3.2% error in lattice spacing, radial bond distances and overall scale (Glover and Chantler, 2007).

2. Step size in energy is commensurate with structure. A finer grid is used near edges. This part of our technique has developed over several experiments since the earlier experiments focussed on accurate individual attenuation or absorption measurements rather than near-edge structure.

3. For each energy, we measure multiple foils with a range of thicknesses and attenuation ratios. We use multiple foils, unlike nearly all previous work, addressing alignment uncertainty and impurity contamination by testing sample dependence of attenuation and random error. Seven to fifteen samples of varying thickness cover the range. For each energy, a minimum of three sample thicknesses quantify scattering, detector and sample systematics (thickness, linearity and alignment errors). These sample thicknesses are generally chosen to investigate a wide range of attenuation space to quantify these systematics. Our multiple foil technique calibrates detector response non-linearities.

4. For each foil, we measure several different apertures to the upstream and downstream detectors. This serves to remove any backscattering or forward scattering components from the beam and to therefore get an accurate total attenuation measurement. By characterising the scattering and fluorescence contributions, we can also help to determine the separated photoabsorption coefficient from the final analysis.

5. For each foil-aperture combination, we measure the dark current (the noise level of the detector chain), the blank (air measurement without the sample) and the sample. This normalises the signal to a baseline and calibrates for air or path attenuation and scattering.

6. For each combination, we repeat the measurement typically 10 times to provide a robust estimate of random or correlated noise and hence precision or time-dependent drifts. Raw repeatability of a measurement is usually limited by synchrotron beam fluctuations, but the precision of the normalised signal is often below 0.01%.

7. Periodic tests are made for harmonic contamination of the beam using a series of daisy wheels mounted on either side of the samples. Our daisy wheel and wedge devices measure harmonic contributions and enable high-accuracy calibrations of detector performance. At extreme energies or on insertion devices, large harmonic contamination is difficult to isolate. An undiagnosed 0.1% contamination by a higher harmonic can invalidate an experiment.

8. Detailed materials characterisation is performed to map the measured values to a calibrated absolute coefficient. This includes measurement of thickness profiles and impurity tests, and the mapping of the average mass per unit area of the samples.

Our analysis typically follows this same logic:

1. Calibrating the measured energy points and establishing the functional offset and curvature of the hysteresis of monochromator readings. Search for any energy drifts or motor/crystal relaxation effects during the measurements.

2. Normalise the count rates for air absorption and scatter, and for detector base noise. Optimise the detectors, apertures and geometry for high correlation between upstream (normalising monitor) and downstream (detector) ion chambers. Hence determine point precision and consistency.

3. Use the material or standard characterisation to determine the absolute thickness of the sample region in the X-ray illumination. Transfer that thickness calibration to all other foils to give absolute accuracies (with error bars).

4. Use daisy wheels to independently check for harmonic contamination and correct where necessary. Confirm with the comparison of foil or material absorption.

5. Compare the different apertures and search for the effects of scattering. Correct the raw total attenuation coefficient for any scattering effects observed.

6. Compare the different thicknesses and search for the effects of bandwidth, roughness. Search for any remaining unexplained systematic signature.

7. Propagate errors and summarise results.

Accuracy is limited by several factors including thickness calibration or the absolute calibration and thickness transfer steps; but we attain 0.02% accuracy for Mo. Compared to earlier best quoted uncertainties of 1% for attenuation, and typical divergences of 10–20% between measurements claiming similar accuracy, this is a substantial development which enables new processes to be observed and new approaches to be made to old problems.

4. Outcomes of XERT for powder diffraction standards

Powder diffraction is responsible for 20% or so of all synchrotron research and primarily solves structures of micro- or nano-crystallites which do not produce large crystals: these techniques have been very useful in a range of biological and biomedical applications. Problems can arise in conventional Rietveld methods because of potential unphysical parameterisation and parameter correlation, especially for thermal, mosaic and roughness parameters. These can be addressed by model systems, careful calibration and calibrated standards.

At the Australian National Beam-line Facility in Tsukuba, Japan, energy calibration is carried out using a powder diffractometer BigDiff, using the National Institute for Standards and Technology standard reference powders of silicon and lanthanum hexaboride. The accuracy of our energy determinations over a large range of X-ray energies revealed a discrepancy between the reported lattice spacings of the standards, and implied that such standards could be calibrated at a synchrotron (Chantler et al., 2004). Sequel experiments have supported these conclusions (Rae et al., 2006; Chantler et al., 2007b), but more work is underway, especially with respect to the high accuracies of recent standards.

5. Outcomes of XERT for scattering studies

Measured absolute scattering amplitudes for X-rays enable key tests of theory but are extremely difficult. Possibilities like this open up major new fields and avenues. Our absorption experiments may enable new approaches for testing theoretical models because of their high accuracy. This has opened up exciting opportunities for new phenomena and ways of testing earlier assumptions.

We were able to directly observe the contribution of scattering processes in X-ray attenuation measurements, and to show evidence for Rayleigh scattering from copper samples (Chantler et al., 2001b). In absorption experiments, scattering is typically 0.1% of the total attenuation, so high accuracy is needed just to observe the contribution in the data. Our experiments are the first to measure scattering (Tran et al., 2004a) in photoabsorption experiments. The calibration of the absolute scattering amplitude is a difficult problem and work continues in this area.

One of the areas which is not widely appreciated is that the range of systematics varies significantly with atomic number, absorption and the range of energies. Whereas early experiments were with light elements (silicon and copper), later experiments investigated the rise of the significance of scattering at higher energies such as for tin and silver (Tran et al., 2005).

6. Outcomes of XERT for beam diagnostics

We developed techniques for diagnosing more detailed systematics (Chantler et al., 2001c) including the quantitative determination of harmonic content in synchrotron beams (Tran et al., 2003c) and the measurement of X-ray bandwidth from the effect on on-edge absorption coefficients (de Jonge et al., 2004a).

Our efforts developed tools for the accurate determination of the thickness of thin foils and single-crystal wafers (Tran et al., 2004b) and the full-foil mapping of integrated column density (de Jonge et al., 2004b).

7. Nano- and condensed matter investigations

Fundamental tools for neutral atomic physics, from theory and experiment, can be used to probe important processes in molecules, clusters and solids. Moreover, these tools can be used to investigate crystals, nano-crystals, single molecules, glasses and solutions, in ways impossible a few years ago (Glover et al., 2009). The structure of molecules is probed by the wavelength corresponding to the structure separation. For photons, this is given by X-rays, which therefore serve as the primary tool for electronic structure. Other major technologies include electron microscopy, NMR, IR and neutron diffraction.

Our experimental benchmarks for the measurements of absorption and XAFS at synchrotrons now allow key insight and development of theoretical issues. In particular, they can probe the inelastic mean free path of the photoelectron. The X-ray extended range technique (XERT) calibrates energy and absolute absorption and can achieve accuracies of 0.02%, revealing new understanding and new fields with this new ruler. The new accuracies investigate the solid state interaction for local structure and develop key techniques for condensed matter characterisation (Bourke et al., 2007; Smale et al., 2006).

8. XERT and XAFS and XANES

X-ray absorption fine structure (XAFS) and X-ray absorption near-edge structure (XANES) have been major techniques for local structural investigation for many years. The anomalous scattering contributions have been recognised as significant and useful since the development of the dynamical diffraction theory (Zachariasen, 1945) for crystallography and the developments of the Bijvoet ratio (Bijvoet, 1949) for absolute configurations and the phase problem. Meanwhile, early theory of the XAFS region (de Kronig, 1932) was not useful for interpreting experiment, which awaited the Fourier transform approach to prove that short range order of the photoelectron was responsible (Sayers et al., 1971). A major development arose from the consideration of spherical wave propagation rather than plane wave propagation (Rehr and Albers, 2000). World-wide, muffin-tin approaches for the (solid state) potential have dominated analysis and theoretical interpretation over the last 20 years.

XAFS and XANES with the related technique of microspectroscopy are now powerful techniques for the characterisation of nano- and macro-materials for non-crystalline materials or solutions, and for solids. Some 30% of all synchrotron activity uses these techniques. Further, these techniques in general require the availability of a synchrotron. Powder diffraction, single-crystal crystallography and e.g. electron or neutron diffraction are primary vehicles for determining the structure of crystalline forms, but for non-crystalline systems the bond lengths and orientations around an active site can be determined most effectively by investigating the interference of the outgoing photoelectron wave with that reflected (scattered) back from any electron (charge) density. Many synchrotron beam-lines specialise in XAFS or XANES techniques and hundreds of papers investigate coordination and bonding effects using XAFS or XANES annually.

In chemistry, they are used to confirm structures, active centres, coordination shells, correlated bond lengths and motions and other key aspects of bonding and valence. They are also used in reaction kinetics to identify and solve the structures of reactive or transition intermediates. In biology and biomedicine, they are particularly useful for understanding binding sites near active centres independently of the complexity of conformation and tertiary folding (enzymes, catalysts, etc.). In Earth sciences and mineralogy/engineering, they are particularly useful at investigating complex phase systems, phase changes and mixtures as functions of temperature and pressure, whether for mining, geology or mineral processing. In physics, they are used to investigate the wavefunctions and electron density in the condensed matter system, for accurate or detailed investigations of absorption and scattering processes including the inelastic mean free path of the photoelectron and the nature of near-edge processes.

Our XERT accuracy opens up new possibilities for critical insight in these areas, and existing and potential linkages across multi-disciplinary fields are exciting. However, there are a series of key challenges:

1. Often XAFS and XANES are investigated using fluorescence or solid state (energy dispersive) scattering detectors. The XAFS shape, structure, statistics and hence accuracy are heavily affected by several systematics including self-absorption and orientation. Since many users require fluorescence detection, it is important to discover how to collect such data with minimal loss of accuracy to enhance the information extractable from these systems and these experiments. This calls for experimental collaborations with interested groups.
2. Long-range disorder and dilute systems are key challenges for the information content of XAFS and XANES spectra. Hence plastics, polymers, glasses and dilute solutions all have higher noise levels on a smaller signal base. How much can be achieved with such systems and how critical a diagnostic on in situ local order can we achieve? This can call for collaborations with different groups especially including solution chemistry. Similarly, some have cited that for photoreactive systems high accuracy is impossible as the disorder of the target precludes long counting times—what can be done here, and is it possible to increase the accuracies or structure of the data in these studies using XERT?
3. XERT is a complex and time-consuming technique for experts (at present). A major challenge is to develop the ideas into routine tools for normal and interested users. Experimentally this requires routine station set-ups rather than extreme custom arrangements. But it also requires standard experimental driver codes and macros.
4. Most XAFS and XANES data collected routinely at present are not calibrated on the energy or attenuation axes. This limits an accurate quantification of goodness-of-fit such as χ_r^2 for hypothesis testing. Some XAFS and XANES are partially calibrated with a single nearby absorption edge, of a foil (metal) or reference standard. One difficulty is that accuracies and error propagation are often not propagated correctly in reference codes for analysis. We have begun investigations into the robust determination of structure from XAFS (Smale et al., 2006; Glover and Chantler, 2007), but new analytical tools are needed. XAFS and XANES analyses are extremely effective and widely used techniques and can be used to obtain a multitude of parameters related to molecular and atomic structure and bonding. By investigating a number of analysis techniques in both the near-edge and extended energy regions, using experimental data of high accuracy and accurate theoretical

tabulations of mass-attenuation coefficients, various experimental and analysis errors can be simulated including harmonics, bandwidth, detector response and energy determination errors. These systematics can affect the conclusions and derived parameters, particularly relating to determinations of photon energy.
5. A key theoretical problem is the prediction of the XANES and XAFS structure with condensed matter theory. Currently XAFS is analysed by one type of program and theory, and XANES is analysed either without reference to a model (just an empirical or ad hoc relation using a series of standards) or with a very different type of model. Developments envisaged here would enable simultaneous analysis of the XANES and XAFS structure. But for this, new theory and theoretical tools are required. This can call upon collaborations with advanced theoretical atomic and condensed matter groups.

We have begun the investigation of the underlying condensed matter theory with promising results so far (Bourke et al., 2007; Witte et al., 2006; Cosgriff et al., 2005). Extensions of the finite difference method for near-edge structure (FDMNES) have been employed to calculate X-ray absorption fine structure (XAFS) for solid state copper. These include the incorporation of a Monte Carlo frozen phonon technique to simulate the effect of thermal vibrations under a correlated Debye–Waller model, as well as a consideration of the XAFS broadening induced by the finite photoelectron inelastic mean free path. Spectra are computed over an energy range in excess of 300 eV above the K absorption edge, which is more than twice the greatest energy range previously reported for a solid state calculation using this method. The dominant theoretical techniques currently used in the literature to model these systems in the XAFS region are the muffin-tin approach (Rehr and Albers, 2000), the discrete variational method and the full linear augmented plane–wave approach. All these techniques have value, have limitations, and are under development. FDMNES can be extended successfully from the near-edge region to the dominant XAFS regime. These calculations reveal considerable agreement but also particular areas of discrepancy. Results agree with current experimental data to within 3%, a significant improvement over previous non-muffin-tin calculations.

Our theoretical development of the technique involves a development of Chantler DHF theory for atomic systems, together with direct development of the finite difference method for near-edge structure (FDMNES) to address several key topical problems. The FDMNES approach had previously been successful for XANES but not for XAFS. Our work proves that much more is possible, and that we can compute XAFS in a self-consistent manner using this approach. We are the first group in the world to achieve this. Our work also proves that this method can be applied successfully to complex organometallic clusters (Glover et al., 2007).

XANES is one of the most powerful techniques for investigating the active centres of non-crystalline systems such as synthetic catalysts and enzymes. We have investigated XANES for an active species in the Ni-catalysed polymerisation of isocyanides, the activated Ni (*t*-amylisocyanide) complex, using two of the most popular theoretical approaches. This is a very large cluster for which it is extremely difficult to derive a converged solution using the finite difference method. The cluster has been linked to important chemical developments for catalysts for isocyanide polymerisation. Predicted XANES for the nano-cluster are compared with experimental data, providing an important test for different theoretical approaches. Developments of a finite element method gave excellent agreement with the experimental data, while simpler models were relatively unsuccessful.

Standard muffin-tin approaches (such as FEFF used most commonly by Australian researchers) are formally invalid for non-infinite or non-spherical solids. Our FDM approach can yield credible results in comparing theory to experiment for dilute samples or non-infinite solids. The FDM approach in turn suffers from key limitations, including the absence of absolute determination of energies or energy scales, the inadequate treatment of scattering and near-resonance processes such as shake-up and shake-off which make major contributions to XAFS and to hole-widths, a strong feature of observed structure. The correct treatment of relativistic corrections and of boundary regions (while much better than muffin-tin approaches) requires investigation, and we have the experience to address this. The issue of excited state and photoelectron lifetimes has been seen as crucial to further developments, and we have made progress on this front.

In principle these techniques can be applied generally to elemental and complex organometallic systems, and we look forward to opportunities for future developments. Developments have been pursued with Rehr (2005) Other groups such as Kodre (Mihelic et al., 2004) have been attempting to measure the X-ray absorption of monatomic (gaseous and non-diatomic) iodine and other atomic vapours directly. In a careful and meticulous experiment from 300 to 1000 °C, the dissociation of the molecular binding was shown to progressively shift the photoexcitation spectrum in the X-ray absorption near-edge structure (XANES). Hence the limit of fully dissociated iodine is then an indication of the atomic, isolated atom spectrum. However, there is conflicting evidence on these extremely interesting studies in the literature.

9. Other cross-disciplinary studies

Biomedical research and background: Work in medical radiography (Chantler et al., 1996; Hudson et al., 1996) has led to a patent and subsequent commercialisation of the kV voltage calibration to much higher diagnostic accuracy than previously attained. This has high impact upon the safety of mammography in terms of exposure and sensitivity. Currently we have a collaboration with genetics to address the question of beneficial mutation frequency. This ambitious project may lead to high-profile outcomes.

New technology has been developed as needed tools in these fields, including state-of-the-art backgammon detector technology and spectrometry in the X-ray regime, particularly for high-accuracy applications (Paterson et al., 1997; Kinnane et al., 2005; Kimpton et al., 2007). The pursuit of high accuracy has led to the characterisation of K α spectral profiles to the highest level, for use by many experimentalists (Chantler et al., 2006). Other issues have investigated coherent fields and quantification of the coherence of a synchrotron (Chantler et al., 2000c; Paterson et al., 2001; Lin et al., 2003).

These developments can be applied to commercial, industrial and biophysical systems, including metals and aircraft defects, catalysts and enzymes and geophysical phases of minerals for discovery or extraction.

10. More key questions for future research

A short list of other important questions includes

(1) Applications (theory): How can we find a theoretical model which is useful for non-crystalline samples and solutions, for problems in geophysics and biomedical science? In particular, what do the in vivo (or in vitro) active centres of enzymes and catalysts look like for chemical processing in diseased or healthy tissue functions?

(2) Applications (experiment): How can the success of XERT be applied to dilute systems (polymers, glasses, solutions or gases)? This would allow the application of a new regime of accuracy and experimental understanding for mineralogy and the crystallisation of phases from a melt; for proteins and enzymes which do not crystallise; and other applications. Just as the first point gives theoretical understanding of a wide range of problems, so answering this question will provide critical data to get real experimental answers to these problems.

(3) QED: Is the current implementation of QED (and electro-weak theory) a sufficient theory for neutral atoms, or isolated molecules? How can we develop tests of the second order correction terms in QED for elements with more than two electrons i.e. for most normal matter? How do we test excited state quantum mechanics and QED in a way that has been fruitful for the ground state? QED underlies all of the rest of atomic theory, so that from a 'big picture' perspective, this question lies at the heart of our understanding for other key questions. Karshenboim, a leading Russian theorist, and Hansch, Nobel Laureate, have highlighted parts of this question for current research in a series of recent conferences.

(4) Atomic physics: Can we find any experimental understanding of key scattering processes including especially the functional form (and theory) of thermal diffuse scattering (TDS) and elastic scattering in a non-ideally crystalline solid or in a solution? Rephrased, what is TDS? Can an experiment be devised which can measure an absolute scattering coefficient in order to address many outstanding issues in fundamental atomic physics (of neutral systems)? Answers to this question impact directly upon condensed matter physics, applied crystallography and traditional synchrotron approaches to structure determination.

(5) Synchrotron development of breakthroughs by new insight: How can we combine novel experimental approaches with new theoretical understanding to produce new (routine?) tools for general researchers, whether in single crystal diffraction, powder diffraction, XAFS, developing areas or boutique experiments? What will the Australian synchrotron achieve and where will the cutting edge (as opposed to routine) science come from? What will the next breakthrough in crystallography be and how will we recognise it? Some have discussed ultra-fast dynamics, ultra-short pulses, and high coherence these are all partial answers in specific fields, but sometimes focus too much on a key specialised technology rather than a broader issue.

(6) How does this developing knowledge impact upon possible improved understanding of genetics, mammography, radiation safety and other diverse fields? The impact upon structural determination, active centre dynamics and catalysts seems obvious. However, other diverse fields can be developed by the insight obtained from less applied studies. For example, the insight into dose rate and accurate calibration may have major impact upon key genetics questions; the impact of advanced diffraction theory has had major impact upon the safety and diagnosis of mammography and chest X-rays in the US; and the basic insight of X-ray propagation has led to safer radiation enclosures.

11. Summary

This highlights the issues of the interrelation between atomic physics theory and computations, cluster theory and computations,

and band or condensed matter theory and computations. Key dilemmas with high temperatures or disordered systems are the softening of any structure due to thermal broadening of the photoelectron interference wave; and the problem of density calibration. We have begun experiments to investigate disordered solutions and the quality and accuracy of XANES and XAFS which can lead to investigations of theory or of materials, and hence perhaps to an accurate elucidation of atomic or biomedical structure.

Separately, this would quantify the true baseline for condensed interference effects from XAFS as opposed to Fermi level shifts, shake processes and related XANES or discrete processes. Another burgeoning area is the possible investigation of complex systems (dilute or organometallic) and the theoretical and computational information which may be extracted (Glover et al., 2007). Work is in progress on these fronts but opportunities invite larger collaborations and links across diverse fields.

References

Bartschat, K., Bray, I., Fursa, D.V., Stelbovics, A.T., 2007. Phys. Rev. A 76, 024703.
Berger, M.J., Hubbell, J.H., Seltzer, S.M., Coursey, J.S., Zucker, D.S., 1999. XCOM: photon cross section database (version 1.2) (online). Available from: http://physics.nist.gov/xcom⟩, National Institute of Standards and Technology, Gaithersburg, MD.
Berger, M.J., Hubbell, J.H., 2004. Photon cross sections on a personal computer. NIST Standard Reference Database 8, vol. 87, p. 3597.
Beyer, H.F., Finlayson, K.D., Liesen, D., Indelicato, P., Chantler, C.T., Deslattes, R.D., Schweppe, J., Bosch, F., Jung, M., Klepper, O., Konig, W., Moshammer, R., Beckert, K., Eickhoff, H., Franzke, B., Gruber, A., Nolden, F., Spadtke, P., Steck, M., 1993. J. Phys. B 26, 1557–1567.
Bijvoet, J.M., 1949. Proc. K. Ned. Akad. Wet. B 52, 313.
Bouldin, C.E., 1994. Private communication.
Bourke, J.D., Chantler, C.T., Witte, C., 2007. Phys. Lett. A 360, 702–706.
Bray, I., Fursa, D.V., Kheifets, A.S., Stelbovics, A.T., 2002. J. Phys. B 35, R117–R146.
Carney, J.P.J., Pratt, R.H., Kissel, L., Roy, S.C., Sen Gupta, S.K., 2000. Phys. Rev. A 61, 052714.
Chantler, C.T., 1993. Radiat. Phys. Chem. 41, 759–766.
Chantler, C.T., 1994. In: Materlik, G., Fischer, K., Sparks, C.J. (Eds.), Resonant Anomalous X-Ray Scattering. Theory and Applications. Elsevier, North-Holland, pp. 61–78.
Chantler, C.T., 1995a. Theoretical form factor, attenuation and scattering tabulation for $Z = 1$–92 from $E = 1$–10 eV to $E = 0.4$–1.0 MeV. J. Phys. Chem. Ref. Data 24, 71–643.
Chantler, C.T., 1995b. NIST Database 66: FFAST—form factor attenuation scattering tables (version 1.0).
Chantler, C.T., Deslattes, R.D., Henins, A., Hudson, L.T., 1996. Brit. J. Radiol. 69, 636–649.
Chantler, C.T., 1999. Rad. Phys. Chem. 55, 231–237.
Chantler, C.T., Barnea, Z., 1999. J. Phys. C 11, 4087–4091.
Chantler, C.T., Barnea, Z., Tran, C.Q., Tiller, J., Paterson, D., 1999. Opt. Quant. Electron. 31, 495–505.
Chantler, C.T., Paterson, D., Hudson, L.T., Serpa, F.G., Gillaspy, J.D., Takacs, E., 2000a. Phys. Rev. A 62, 042501:1–13.
Chantler, C.T., 2000. J. Phys. Chem. Ref. Data 29 (4), 597–1056.
Chantler, C.T., Tran, C.Q., Paterson, D., Cookson, D.J., Barnea, Z., 2000b. X-Ray Spectrom. 29, 459–466.
Chantler, C.T., Tran, C.Q., Paterson, D., Barnea, Z., Cookson, D.J., 2000c. X-Ray Spectrom. 29, 449–458.
Chantler, C.T., Tran, C.Q., Paterson, D., Cookson, D., Barnea, Z., 2001a. Phys. Lett. A 286, 338–346.
Chantler, C.T., Tran, C.Q., Paterson, D., Barnea, Z., Cookson, D.J., 2001b. Rad. Phys. Chem. 61, 347–350.
Chantler, C.T., Tran, C.Q., Barnea, Z., Paterson, D., Cookson, D., Balaic, D.X., 2001c. Phys. Rev. A 64, 062506-1–15.
Chantler, C.T., Olsen, K., Dragoset, R.A., Kishore, A.R., Kotochigova, S.A., Zucker, D.S., 2003. NIST database: FFAST II—form factor attenuation scattering tables (version 2.0), X-ray form factor, attenuation and scattering tables (version 2.0) (online). Available from: http://Physics.Nist.Gov/Ffast⟩, National Institute of Standards and Technology, Gaithersburg, MD.
Chantler, C.T., 2004. Radiat. Phys. Chem. 71, 607–617.
Chantler, C.T., Tran, C.Q., Cookson, D.J., 2004. Phys. Rev. A 69, 042101-1–11.
Chantler, C.T., Kinnane, M.N., Su, C.-H., Kimpton, J.A., 2006. Phys. Rev. A 73, 012508.
Chantler, C.T., Laming, J.M., Dietrich, D.D., Hallett, W.A., Mcdonald, R., Silver, J.D., 2007a. Phys. Rev. A 76, 042116-1–19.
Chantler, C.T., Rae, N.A., Tran, C.Q., 2007b. J. Appl. Cryst. 40, 232–240.
Cosgriff, E., Chantler, C.T., Witte, C., Smale, L., Tran, C.Q., 2005. Phys. Lett. A 343, 174–180.
Creagh, D.C., Hubbell, J.H., 1987. Acta Crystallogr. Sect. A 43, 102–112.

Creagh, D.C., Hubbell, J.H., 1990. Acta Crystallogr. Sect. A 46, 402–408.
Creagh, D.C., McAuley, W., 1995. 4.2.6. In: Wilson, A.J.C. (Ed.), International Tables for X-ray Crystallography, C. Kluwer Academic Publishers, Dordrecht.
Cullen, D.E., Hubbell, J.H., Kissel, L., 1997. LLNL Report UCRL50400.
de Jonge, M.D., Barnea, Z., Chantler, C.T., 2004a. Phys. Rev. A 69, 022717-1–12.
de Jonge, M.D., Barnea, Z., Tran, C.Q., Chantler, C.T., 2004b. Meas. Sci. Technol. 15, 1811–1822.
de Jonge, M.D., et al., 2005. Phys. Rev. A 71, 032702.
de Jonge, M.D., et al., 2007. Phys. Rev. A 75, 032702-1–14.
de Kronig, R.L., 1932. Z. Physik 75, 191–210.
Gillaspy, J.D., Aglitskiy, Y., Bell, E.W., Brown, C.M., Chantler, C.T., Deslattes, R.D., Feldman, U., Hudson, L.T., Laming, J.M., Meyer, E.S., Morgan, C.A., Pikin, A.I., Roberts, J.R., Ratliff, L.P., Serpa, F.G., Sugar, J., Takacs, E., 1995. Phys. Scripta T 59, 392–395.
Glover, J.L., Chantler, C.T., 2007. Meas. Sci. Tech. 18, 2916–2920.
Glover, J.L., Chantler, C.T., Soldatov, A.V., Smolentsev, G., Feiters, M.C., 2007. In: Hedman, B., Pianetta, P. (Eds.), CP882, X-ray Absorption Fine Structure XAFS13 (AIP 978-0-7354-0384-0), pp. 625–627.
Glover, J.L., Chantler, C.T., de Jonge, M.D., 2009. Phys. Lett. A 373, 1177–1180.
Henke, B.L., Gullikson, E.M., Davis, J.C., 1993. At. Dat. Nucl. Dat. Tables 54, 181–342.
Hubbell, J.H., 1994. NISTIR 5437. NIST, Gaithersburg, MD.
Hubbell, J.H., Coursey, J.S., Hwang, J., Zucker, D.S., 2003. Bibliography of photon total cross section (attenuation coefficient) measurements (version 2.3) (online). Available from: http://physics.nist.gov/photoncs⟩, NIST, Gaithersburg, MD.
Hudson, L.T., Deslattes, R.D., Henins, A., Chantler, C.T., Kessler, E.G., Schweppe, J.E., 1996. Med. Phys. 23, 1659–1670.
Jentschura, U.D., 2000. Phys. Rev. D 62, 076001.
Kimpton, J.A., Kinnane, M.N., Smale, L.F., Chantler, C.T., Hudson, L.T., Henins, A., Szabo, C.I., Gillaspy, J.D., Tan, J.N., Pomeroy, J.M., Takacs, E., 2007. NIMA 580, 246–249.
Kinnane, M.N., Kimpton, J.A., De Jonge, M.D., Makonyi, K., Chantler, C.T., 2005. Meas. Sci. Technol. 16, 2280–2286.
Lea, S.N., Hallett, W.A., Varney, A.J., Chantler, C.T., Baird, P.E.G., Silver, J.D., Lee, A.R., Billowes, J., 1994. Phys. Lett. A 185, 327–332.
Lin, J., Paterson, D., Peele, A.G., Mcmahon, P.J., Chantler, C.T., Nugent, K.A., Lai, B., Moldovan, N., Cai, Z., Mancini, D.C., Mcnulty, I., 2003. Phys. Rev. Lett. 90, 074801-1.
Mihelic, A., et al., 2004. Acta Chim. Slov. 51, 33; Gomilsek, J.P., et al., 2003. Phys. Rev. A 68, 042505.
Murphy, M.T., Webb, J.K., Flambaum, V.V., 2003. Mon. Not. R. Astron. Soc. 345, 609–638.
Murphy, M.T., Webb, J.K., Flambaum, V.V., 2008. Mon. Not. R. Astron. Soc. 384, 1053–1062.
Niering, M., et al., 2000. Phys. Rev. Lett. 84, 5496.
Paterson, D., Chantler, C.T., Tran, C., Hudson, L.T., Serpa, F.G., Deslattes, R.D., 1997. Phys. Scripta T 73, 400–402.
Paterson, D., Allman, B.E., Mcmahon, P.J., Lin, J., Moldovan, N., Nugent, K.A., Mcnulty, I., Chantler, C.T., Retsch, C.C., Irving, T.H.K., Mancini, D.C., 2001. Spatial coherence measurement of X-ray undulator radiation. Opt. Commun. 195, 79–84 (P10).
Penrose, R., 1989. The Emperor's New Mind. Penguin, New York, and elsewhere.
Rae, N.A., Chantler, C.T., Tran, C.Q., Barnea, Z., 2006. Rad. Phys. Chem. 75, 2063–2066.
Rehr, J.J., 2005. Private communication.
Rehr, J.J., Albers, R.C., 2000. Theoretical approaches to X-ray absorption fine structure. Rev. Mod. Phys. 72 (3), 621–654.
Saloman, E.B., Hubbell, J.H., Scofield, J.H., 1988. At. Dat. Nucl. Dat. Tables 38, 1–197.
Sayers, D.E., Stern, E.A., Lytle, F.W., 1971. Phys. Rev. Lett. 27, 1204.
Scofield, J.H., 1973. LLNL Report UCRI-51326.
Smale, L.F., Chantler, C.T., de Jonge, M.D., Barnea, Z., Tran, C.Q., 2006. Rad. Phys. Chem. 75, 1559–1563.
Sorensen, L.B., Cross, J.O., Newville, M., Ravel, B., Rehr, J.J., Stragier, H., Bouldin, C.E., Woicik, J.C., 1994. In: Materlik, G., Sparks, C.J., Fischer, K. (Eds.), Resonant Anomalous Scattering Theory and Applications. Elsevier, New York, pp. 389–420.
Stolker, Th., et al., 1999. Phys. Rev. Lett. 82, 3232.
Suric, T., Drukarev, E.G., Pratt, R.H., 2003. Phys. Rev. A 67, 022709.
Takacs, E., Meyer, E.S., Gillaspy, J.D., Roberts, J.R., Chantler, C.T., Hudson, L.T., Deslattes, R.D., Brown, C.M., Laming, J.M., Feldman, U., Dubau, J., Inal, M.K., 1996. Phys. Rev. A 54, 1342–1350.
Tran, C.Q., Chantler, C.T., Barnea, Z., Paterson, D., Cookson, D.J., 2003a. Phys. Rev. A 67, 042716.
Tran, C.Q., Chantler, C.T., Barnea, Z., 2003b. Phys. Rev. Lett. 90, 257401-1–4.
Tran, C.Q., Barnea, Z., de Jonge, M., Dhal, B.B., Paterson, D., Cookson, D., Chantler, C.T., 2003c. X-ray Spectrum. 32, 69–74.
Tran, C.Q., De Jonge, M.D., Barnea, Z., Chantler, C.T., 2004a. J. Phys. B 37, 3163–3176.
Tran, C.Q., Chantler, C.T., Barnea, Z., de Jonge, M.D., 2004b. Rev. Sci. Inst. 75, 2943–2949.
Tran, C.Q., et al., 2005. J. Phys. B At. Mol. Opt. Phys. 38, 89–107.
Witte, C., Chantler, C.T., Cosgriff, E.C., Tran, C.Q., 2006. Radiat. Phys. Chem. 75, 1582–1585.
Zachariasen, W.H., 1945. Theory of X-ray Diffraction in Crystals. Wiley, New York, p. 135.