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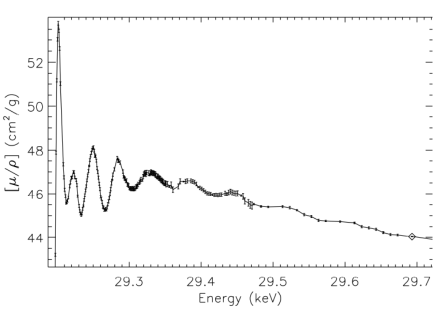
X-ray Synchrotron & atomic physics, Quantum Electrodynamics & X-ray Laboratories
Topics for Masters & Higher Degree Students

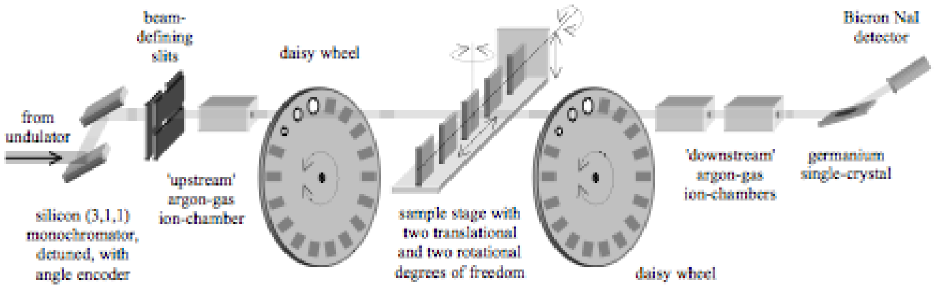


Detail of XAFS for Tin, with error bars giving the absolute accuracy

1. **Can we test QED? Is it true?** We are the only group to test QED in Australia, with highly cited breakthroughs reported in Physics Today and New Journal of Physics. These are international team efforts and doctoral thesis work, but also with contributions from Honours and Masters students.
2. **How can we get structural information from an isolated quantum system – molecule, gas or non-crystalline solid?** We have been the world leaders in extracting structural and quantum information from atomic, molecular and organometallic (i.e. biophysical) systems with advanced experiments and analysis, advancing the techniques used by more than 30% of all synchrotron researchers across the world. Accordingly, the Lawrence Bragg Medal was awarded to Prof Chantler for 2021 for recognition of the impact of our work in X-ray and Synchrotron Science and for nanostructure.
3. **Can we understand the structure of a transition metal and atom?** Copper metal is the most-tested X-ray material and source in the world, with the best experimental data and the best theory. Our group has been the world leaders in understanding copper for some 20 years. Yet despite this, there are unanswered questions for every member of the first row transition metals, including copper. This requires advanced relativistic quantum mechanics, including QED corrections, and including multi-configuration Dirac-Fock theory and analysis. As well as explaining copper for the first time, we are particularly keen to explain **Rare Earths and Critical Minerals** which provide great opportunities for applications to mining Discovery and sensitivity for exploration and processing.
4. **Why do all of the current theories of fluorescence and scattering fail when investigated by new high-accuracy experiments?** For materials, these are dominated by a vast array of Density Functional Theories. Our new XR-HERFD (eXtended Range-High Energy Resolution Fluorescence Detection) experiments, particularly at Diamond Light Source, UK, have discovered new physical processes in elements and materials, which are proving extremely difficult to understand quantitatively. We are the world leaders in both the experiment and theoretical development, particularly with collaborations with Yves Joly in France.
5. **Can I develop or invent a new field of physics?** Yes! Doctoral and Masters students have developed new fields of high-accuracy X-ray Absorption Spectroscopy [XERT; Hybrid]; high-accuracy X-ray Emission Spectroscopy [SeaFFluX] and propagation of uncertainty in XANES / XAFS analysis [mu2chi]; electron inelastic scattering (mean free path) experiment and theory; coupled plasmon theory; non-destructive nanoroughness measurement; and made major developments in dominant fields of X-ray science and relativistic Quantum Mechanics; and major contributions to Alzheiemers' disease and dementia and mammography.

- Facilities: X-ray labs; Synchrotrons around the world & Melbourne; EBIT labs around the world.

Our local laboratories develop new technology in-house, & ask fundamental questions about the universe & matter.



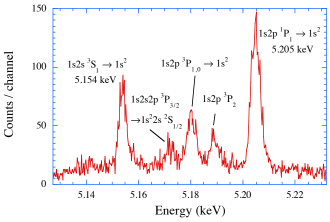
Typical experimental set-up at synchrotron in Chicago

- Two honours students (2005) produced 3 major papers from honours (one high profile Phys. Lett.). Three honours students (2006) got the best experimental thesis in the School (Ramm Prize), and one of the top 3 theory theses.

Both students in 2008 got top marks in theory and experiment. These great results reflect on them, the potential of the field & our group. Martin de Jonge was awarded the Chancellor's Prize (best Doctoral Thesis at Melbourne University), 'Best Synchrotron Thesis in Australia', flew off to an exciting career at the Advanced Photon Source (Chicago) & has now returned to get first light on the Australian Synchrotron on a key beamline. We receive national & international awards for group achievements.

Our **experiments** are two orders of magnitude more accurate than all earlier publications in the field.[1] This has opened up exciting new opportunities & opened our eyes to new phenomena and new ways of testing earlier assumptions. Our experiments have been the *first* to measure scattering[2] & synchrotron bandwidth in photoabsorption experiments, have redefined international standards for (powder) diffraction[3], and have placed the field of X-ray Absorption Fine Structure (XAFS) on an absolute footing. Our *relativistic atomic **theory*** and tabulation[4] is the most successful currently available in terms of agreement with experiment. Theory must be based on *condensed matter physics* near absorption edges to explain detailed oscillations, which in turn raises new questions. Honours students have developed *new theory* & computational tools for condensed matter science, including the first extended XAFS solution avoiding 'muffin-tin' approximations[5] & the largest (organometallic) XAFS modelled without this assumption,[6] with major implications for biological science. Masters students have been developing new fields in non-destructive nano-roughness measurement applicable to nano-circuits and next-generation computation; and developed the new field of absolute fluorescence XERT, which will lead to *ab initio* XAFS determination of nano-structure.

Quantum Electrodynamics is one of the two best-tested theories in physics and science. It is the most trusted example of a Quantum Field Theory in practice. Yet certain problems in its formulation lead people like Roger Penrose to assume that there are fundamental flaws in the theory. Our experiments at the cutting edge[7] may reveal such an inadequacy, by being more sensitive to important terms and interactions than other available tests. Coming experiments can test alternate competing theories. QED 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 – 2021 are questioning the current theoretical approaches. Can hints of string theory, extra dimensions, or other formulations be found in atoms?



Recent data testing QED from NIST

Biological systems are linked to our investigations via Crystallography, Powder Diffraction, and XAFS; via development & testing of theory used to interpret these; via developments for mammography; and via lab and synchrotron experiments.
Available projects include pure theoretical topics, pure experimental topics, and mixed theory, computation & experimental projects. In our group, a normal experimental or theoretical thesis will naturally learn about the other. Doctorates link theory and experiment together in a coherent whole.
https://www.ph.unimelb.edu.au/~chantler/opticshome/home.html
& https://www.ph.unimelb.edu.au/~chantler/opticshome/xrayopt/index.html Recent developments & papers can be collected from Chris Chantler. Masters projects should lead to major international publications *within the course*. ***Current topics for Masters and higher degrees:***

1 Atomic & Condensed Physics *Theory*: New computation & theory of atomic radiation, photoionization, scattering with X-rays, IR, Vis, including laboratory astrophysics and the fine structure constant, satellites and Auger processes and spectra. Applications include precision measurements, crystallography, medical physics, tomography, fundamental X-ray experiments & new types of test of Quantum Electro-Dynamics. Atomic theory particularly represented by our developments and application of GRASP; condensed matter theory particularly represented by our FDMX, IMFP, FFAST and SeaFFlux software packages. Recent major publications in Phys Rev etc. and for Transition Metals including Cu and Sc.

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[1] de Jonge *et al.*, *Phys. Rev.* A **71**, 032702 (2005); C Q Tran *et al.*, *Phys. Rev. Letts 90 (2003) 257401*

[2] C Q Tran *et al.*, *J. Phys. B37 (2004) 3163-3176;* de Jonge *et al.*, *Phys. Rev. A 69 (2004) 022717*

[3] C. T. Chantler et al., *Phys. Rev. A69* (2004) 042101

[4] C.T. Chantler, *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 (1995)**;** C.T. Chantler, J. Phys. Chem. Ref. Data. 29 (2000)

[5] J. D. Bourke et al., *Phys. Lett. A360 (2007);* also *Cosgriff et al., Phys. Lett. A343 (2005) 174*

[6] J. L. Glover et al., 625-627 *CP882, "X-ray Absorption Fine Structure – XAFS13", B. Hedman, P. Pianetta, eds (2007,AIP)*

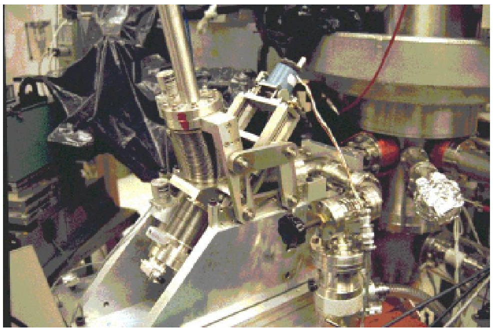
[7] C.T. Chantler *et al., Phys. Rev. A62 (2000) 042501*; C. T. Chantler *et al., Phys. Rev. A71 (2005) 032702*

1.1 XAFS and near-edge structure (scattering, atomic structure & crystals). X-ray Absorption Fine Structure is due to a coherent interaction of an emitted photoelectron wave with its elastically scattered wave, yielding rich structure near absorption edges, which is poorly understood. This is one of the three *most popular experimental X-ray techniques* used [2500 papers pa]. Our aim is to revolutionise the field and create new techniques & understanding for use by all researchers. **[Project*]** Students can analyze and *develop* models, experiment, analytic tools & theory, leading to higher degree projects & new self-consistent theory. Post-doctoral, Masters & honours students have worked on this 2003-24. Major limitations of current theory *can be addressed within a Masters project*. We have just published the first encyclopaedia on XAFS and related techniques, with Nature papers following.

1.2 Relativistic Quantum Mechanics theory (X-rays/diffraction/atomic structure). **[Project*]** Our web-site receives 1200 hits per month. But (our) earlier formulations have limitations. Interesting questions relate to high-energy limits, analytic formulations, S-matrix field theory and correlated perturbation theory. An honours student worked on new analytic calculations of relativistic atomic form factors and was awarded school physics prizes for honours. We have several high-profile Phys. Rev. papers on our new developments. Interestingly, 1.1 and 1.2 both (and other topics) have significant industrial applications.

1.3 Dynamical diffraction from curved crystals (diffraction / mosaicity). Development of theory of mosaic diffraction of X-rays is necessary in high-efficiency diffraction experiments in the X-ray regime. We have published the first dynamical theory of X-ray diffraction for non-ideally imperfect curved crystals. This theory can be used to test QED and to understand bonding, both of which are major questions in current world research. Mosaic crystals have the lattice plane orientation (or phase relationship) varying with position or depth. This is a promising area for further research. Recently we have investigated use of neutron diffraction to investigate crystalline nanostructure.

2 Experiments on X-ray Processes and QED: Investigations using XAFS by our group has yielded accurate measurements probing atomic physics, scattering theory, electron wavefunctions & condensed structure. This has revealed problems about relativistic, QED & other theoretical contributions to observed interactions. [**New Projects***] Masters projects can develop new state-of-the-art detection systems, analyse data to yield new critical tests of QED or complete high-accuracy experiments in labs or at synchrotrons, including the Australian Synchrotron. **Synchrotron techniques:** New understanding in atomic, molecular, condensed matter and biophysical systems. Especially XAS, XRD, PD, IR, ND.


Melbourne detector and spectrometer at NIST, USA

X-ray Free Electron Lasers: XFEL investigations require advanced theory and innovation in experiment. We are involved in activities at Stanford [SLAC].

Biophysics: X-ray irradiation, biological structures and catalysts. Some of our focus relates to ferrocene, active centres, infrared and X-ray response modeling, di-iron and nickel catalysts. Past students have been involved in separate humanitarian activities where physics crosses boundaries into real-world problems, including Alzheimers' and dementia [the physics and measurement of].

2.1 Effect of excitation energy on characteristic radiation: a new ruler in atomic and condensed matter science. Invitations from the major world international labs have asked us to be involved in determining new standards of energy determination and accuracy. This involves preparation of new experiments with Kα sources, and better tests of QED, antihydrogen, better detector technology, and applications to more incisive synchrotron research. Key is a new combined approach to theory and experiment. **[Project*]** New technology of **high-resolution microcalorimetry** and **Electron-Beam Ion Traps** are showing great promise internationally.

2.2 High-accuracy measurement of photoabsorption. Our synchrotron techniques have surpassed the world's best results by two orders of magnitude in accuracy & have been announced as amongst the top five experiments on two separate beam-lines at one of the world's largest synchrotrons. **[Project*]** We can test critical differences between implementations of relativistic quantum theory.

International experiments are often part of a Masters or higher degree. Several doctoral students have worked in this area. We are often ranked top proposal for international experiments. New technology of **eXtended Range-High Energy Resolution Fluorescence Detection (XR-HERFD)** are showing great promise internationally and hopefully will be brought back to Australia over the next five years following our successful international experiments.

2.3 **Absolute measurement of absorption coefficients of metals and molecules using local and international sources.** We have the best data in the world to investigate new physics in XAFS (near edge atomic and solid state structure) and measure nanoroughness and electron inelastic scattering. We have made the first XERT-like and Hybrid-like experiments at the Australian Synchrotron.

2.4 **Investigation of X-ray scattering and fluorescence distributions.** These investigate the radial electron density in atomic systems. **[Project*]** A Masters project would use existing facilities to investigate the shape of inelastic scattering.

2.5 **Biophysics** links with labs & analysis to probe X-ray irradiation, biological structures and catalysis including of Alzheimer's disease and Amyloid-β.

2.6 **Dynamic processes in catalysis and reaction coordinate systems using FTIR and XAS.** FTIR is considered an old and turn-key technology, 'just' a core component of undergraduate and graduate chemistry. We have begun to transform this to a key signature for conformational diagnosis (e.g. between toxic and safe conformers) with possible machine learning apparatus, especially with the high-resolution FTIR at the Australian Synchrotron and our ability to define information content and uncertainty in FTIR spectra.

2.7 **Quantum Electro-Dynamics: X-ray spectrometers for high-precision measurement in X-ray physics and QED. [Project*]** Current students have made exciting progress, directly related to new tests of QED. We made the highest precision tests of QED for Vanadium atoms (Z=23) using an Electron Beam Ion Trap, with a new measurement, new detector and new spectrometer.[8] We can investigate discrepancies in QED at the level of 2×10^{-5} (or 20 parts per million) in medium-Z ions, and are developing state-of-the-art detector and spectrometer equipment to ask whether current discrepancies from theory yield fundamental insights into laws of physics. Recently we have measured spectra and transitions with absolute accuracy down to 2×10^{-6} (or 2 parts per million).

All topics lead to higher degrees, & research papers within a Masters project; most can lead to

- precision tests of QED (in systems such as He-like Vanadium & H-like Nickel) or
- new understanding of atomic & condensed matter physics & fundamental X-ray spectroscopy (How accurate is atomic physics for a real atom or a real element?) and X-ray Optics and Synchrotron Science (how does light interact with matter; or how does the photoelectron in a material interact with matter?).

Each experimental topic is a fundamental research area. Work is in-house and in collaboration with NIST (Washington DC; Boulder, Colorado); CSIRO; ANU; ANSTO; the University of Oxford; & Synchrotrons (Japan, Chicago, Australian Synchrotron, Diamond UK). Selected research on X-ray experimental measurement[9] has links with industry. Projects linked with medicine & mammography have yielded publications & patents. Our group has links with biological & biochemical groups & investigations in Australia & around the world.

Selected MSc topics:

Extension and development of new cluster theory - XAFS FDMX technique [inelastic mean free paths] [JDBourke]. Application to new field of inelastic mean free paths; band theory; XANES; EXAFS

Development of new theory of atomic spectra and continuum regions [Truong Nyugen, Jonathan Dean]. Applications to laboratory astrophysics; the fine structure constant; international tables; theory of resonant transitions in relativistic QM; QED; satellite and Auger spectroscopy. A search for Axions [ANU, CSIRO, NIST].

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[8] J.D. Gillaspy, Y. Aglitskiy, E.W. Bell, C.M. Brown, C.T. Chantler, et al., *Overview of the EBIT Program at NIST*, Physica Scripta, **T59**, 392-395, 1995; C.T. Chantler, et al., *Absolute measurement of the resonance lines in heliumlike vanadium on an electon-beam ion trap*, Phys. Rev. A 29 (2000).

New experimental tools for QED. Measurements of relativistic quantum mechanics, X-ray optics, synchrotron science. Our lab has produced several great data sets and begun to develop Super-Resolution for Advanced Detectors

X-ray Free Electron Lasers. Kα doublet scaling for hole satellite spectra for copper and Mn… as a function of incident electron or photon energy. Atomic photoionisation cross-sections pre- & post- edge [Truong Nyugen, Jonathan Dean]

XR-HERFD experiments and theory [Chanh Tran, La Trobe; Diamond, UK; Yves Joly, France; JD Bourke; Nich Tran, Daniel Sier]

Neutron Diffraction of phases of crystalline Ferrocene and thermal disorder [ANSTO]

Development of XERT and Hybrid technology at the Australian Synchrotron [ANSTO, La Trobe, AS]

Ideal experimental biological & organometallic systems [Prof Feng Wang (Swinburne); Bio21; Diamond, UK]

Application of molecular codes within the cluster framework [Prof Wang, Swinburne]

XERT data for fluorescence and solutions [Nich Tran, Daniel Sier]

Complex organometallic clusters by (non-muffin-tin) FDMX [Nich Tran, Daniel Sier, JD Bourke]

New software and analysis of exemplary systems [Mn, Zn, Se, ZnSe, Sc]

FDM Theory and implementation for a least-squares fitting technique to experimental data; AXAFS & unresolved transitional arrays [Y Joly, JD Bourke, Daniel Sier]

Detector Gas Resolution Study; Crystal Redesign & control; Horizontal Spectrometer; digitization design / study

Lab. Scattering; Absolute Absorption Coefficient; analysis

Lab. Detector Calibration and Diagnosis for QED, RQM, XERT

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[9] C.T.Chantler, *Photographic response to X-ray irradiation I: Estimation of the photographic error statistic, and development of analytic density-intensity relations*, Applied Optics **32** 2371-2397, 1993.

Highlights: Encyclopaedia on XAFS 2024. Nature paper on XAFS 2024. Recent papers on discoveries with XR-HERFD 2020-2024, theory of transition metals and rare earths 2020-2024, new experiments on the Complex Atomic Fine Structure for materials with La Trobe 2020-2024.

2016: Invited to be front cover of one of top chemistry journals, on Development of Quantum Mechanical Insight to solve chemical structures unexplained for 50 years [Chemistry - a European Journal]

2015-2016: Sets of new software for cutting edge atomic, plasma and condensed matter theory. First experimental results on the new field of low energy measurement of Inelastic Mean Free Path of the electron in Matter. [Physical Review Letters, J Physical Chemistry Letters, J Synchrotron Radiation]

May 2013: Addressing anomalies back to 1934 in astrophysics, on the aurora, terrestrial and other, using advanced atomic physics theory of forbidden spectra. [The Astrophysical Journal]

December 2012 [Physics Today]:

Highly charged ions challenge QED

Energy transitions in the three-body systems are intriguingly different from what theory calculates.

Quantum electrodynamics (QED), the relativistic field theory describing interactions of light and charge, is justly celebrated for the astonishing accuracy with which it predicts, for example, the anomalous magnetic moment of the lone electron. But the reach of QED extends to substantially more complex systems. One class of objects amenable to experimental study and QED calculation includes helium-like ions with atomic number Z of about 25 and two orbiting electrons. In those three-body entities, the significant nuclear charge enhances the QED interactions.

A recent experiment by an international team led by Christopher Chantler (University of Melbourne, Australia) has made the most precise measurement to date for the energy of a specific atomic transition, called the w transition, in helium-like titanium $^{22}\mathrm{Ti}^{20+}$ at the NIST EBIT and has obtained a value that disagrees with QED by three standard deviations. But the bigger surprise came when the group reviewed the published literature for w transitions in helium-like ions with Z between 16 and 36.

Taken as a whole, the experimental data differed from theory by five standard deviations, and, as the figure shows, a least-squares fit through the data indicates that the discrepancies scale as Z^3. (The green swath displays the 68% confidence interval for the fit.) Chantler and company note that the mismatches between experiment and theory potentially involve a variety of QED effects with various Z dependencies. Future experiments in the unexplored $Z = 27–31$ range, they say, could further systematize the discrepancies and guide theoretical work. (C. T. Chantler et al., *Phys. Rev. Lett.***109**, 153001, 2012.)—Steven K. Blau

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An absolute energy characterisation of scandium Kβ to 2 parts per million

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Abstract

We present an absolute energy measurement of the K$\beta_{1,3}$ (KM$_{2,3}$) emission spectrum of scandium ($Z = 21$) accurate to 2.1 parts per million (ppm). The previous experimental uncertainty was estimated as 105 ppm, or 0.47 eV, therefore we improve the accuracy of this measurement by a factor of 50 for use in any x-ray standards. There is a long-standing discrepancy between the most recent experimental and theoretical values. This work reports a Sc Kβ peak energy of 4460.845 eV with estimated standard error uncertainty of 0.0092 eV. The satellite component centroids, line-widths, and relative intensities are determined as a sum of five Voigt functions. The same analysis and experimental method shown here can be applied to advanced experiments in quantum electrodynamics, astrophysics and particle physics on soft x-ray spectra. This value has reconciled some of the previous discrepancy. However, the theoretical value is still discrepant from the new experimental measurement by 1.745 eV with a much tighter constraint on the experimental uncertainty. This strongly strengthens the need for new theoretical calculations and experimental measurements.

Keywords: scandium, characteristic radiation, K beta, x-ray spectroscopy, absolute energy measurement, parts per million

(Some figures may appear in colour only in the online journal)

1. Introduction

Spectral lines resulting from atomic transitions gave the empirical evidence needed to kick-start the quantum revolution of the early 1900s, suggesting that electronic energy states are quantised, rather than continuous. After more than a 100 years, spectral lines of electronic and exotic atoms and ions remain the primary tool to experimentally investigate theories of quantum electrodynamics (QED) [1–5] and the standard model. With new techniques, researchers have been able to probe these spectra at ever-increasing resolution and precision, showing that our current best theories still do not fully account for the observed results [6].

As well as the motivation for probing theoretical calculations of advanced quantum mechanics, there is a significant industrial motivation for tight constraints to $3d$ K-series energies. Lanthanides, the rare earth elements, are becoming increasingly desirable to manufacturers of electronics, lighting, and permanent magnets. Therefore there is great interest in analysing lanthanide-bearing ores by x-ray fluorescence. Since the L-series of the lanthanides is in the same energy regime as the K-series of $3d$ metals, tying down the uncertainties on these elements will aid in analysing materials for possible lanthanide deposits [7].

This investigation reports on the K$\beta_{1,3}$ (KM$_{2,3}$) transition in scandium ($Z = 21$) yielding a new measurement of profile and energy with standard uncertainty reduced by approximately a factor of 50. This fills a gap in the current literature. All other $3d$ transition metals have experimental uncertainties for the energy of Kα and Kβ less than 0.1 eV, showing that the 0.47 eV uncertainty for Sc Kβ is outdated and in need of improvement.

The K$\beta_{1,3}$ transition occurs when a core ($1s$) electron is ejected, and a $3p$ electron fills the hole. The p orbital is an energy doublet of $j = \{\frac{3}{2}, \frac{1}{2}\}$ resulting in two spectral (diagram) lines; Kβ_1 from $3p_{3/2} \rightarrow 1s$ and Kβ_3 from $3p_{1/2} \rightarrow 1s$. However, these two spectral lines are only well-resolved in

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High accuracy determination of photoelectric cross sections, X-ray absorption fine structure and nanostructure analysis of zinc selenide using the X-ray extended range technique

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Keywords: ZnSe; XAFS; XERT; *K*-edges; 0.1% accuracy.

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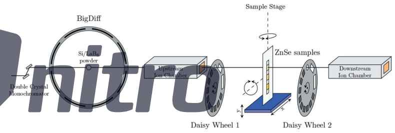
Measurements of mass attenuation coefficients and X-ray absorption fine structure (XAFS) of zinc selenide (ZnSe) are reported to accuracies typically better than 0.13%. The high accuracy of the results presented here is due to our successful implementation of the X-ray extended range technique, a relatively new methodology, which can be set up on most synchrotron X-ray beamlines. 561 attenuation coefficients were recorded in the energy range 6.8–15 keV with measurements concentrated at the zinc and selenium pre-edge, near-edge and fine-structure absorption edge regions. This accuracy yielded detailed nanostructural analysis of room-temperature ZnSe with full uncertainty propagation. Bond lengths, accurate to 0.003 Å to 0.009 Å, or 0.1% to 0.3%, are plausible and physical. Small variation from a crystalline structure suggests local dynamic motion beyond that of a standard crystal lattice, noting that XAFS is sensitive to dynamic correlated motion. The results obtained in this work are the most accurate to date with comparisons with theoretically determined values of the attenuation showing discrepancies from literature theory of up to 4%, motivating further investigation into the origin of such discrepancies.

1. Introduction

X-rays can act as direct probes into many systems, due to their strong depth penetration, energy-dependence and their non-destructive nature. Absorption and scattering interactions of X-rays are quantifiable, with the accuracy of measurements being dominated by the availability of accurate values for X-ray mass attenuation coefficients. In situations where attenuation coefficients are available and accurate, the absorption and scattering interactions of X-rays with matter can be used to create a more precise probe. X-ray absorption fine structure (XAFS) can measure dilute or disordered systems (Chantler *et al.*, 2015) which cannot be probed by other methods such as X-ray diffraction (XRD) or electron microscopy. This has led to new and important discoveries in a variety of disciplines from chemistry to biomedicine to agriculture (Waychunas *et al.*, 1993; Neidig *et al.*, 2011; Chevallier *et al.*, 2014).

XAFS consists of complex oscillations in the region above the edge of the X-ray absorption spectrum. Photoelectrons backscatter from neighbouring atoms toward the photoemitter causing quantum mechanical self-interference of the photoelectron with its own wavefunction.

Synchrotrons provide high-flux, dependable, coherent, tunable sources of X-rays. The first synchrotron revealed the potential of high-brightness X-ray sources (Johnston &



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The characteristic radiation of copper $K\beta$ including radiative Auger processes

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Abstract

Two characterisations of the Cu $K\beta_{1,3}$ spectrum are developed, which are robust and transferable to other experimental x-ray geometries. By observing and considering the significant contribution of radiative Auger emission to the $K\beta$ profile, we obtain an improved and more robust characterisation. The contribution of the $KM_{2,3}M_{4,5}$ and $KM_{2,3}N_1$ radiative Auger satellites to the $K\beta_{1,3}$ spectrum is measured to be 1.96%. The contribution of radiative Auger emission is often significant and should be included in defining characteristic x-ray spectra. This is a step in the renewed efforts to resolve inconsistencies in characteristic x-ray spectra between theory and common experimental geometries. The spectrum was measured using a rotating anode, monolithic Si channel-cut double-crystal monochromator and backgammon detector. The experimental setup provides insight into the portability of spectral characterisations of x-ray spectra.

Keywords: copper, characteristic radiation, K beta, x-ray spectroscopy, radiative Auger effect

(Some figures may appear in colour only in the online journal)

1. Introduction

Characteristic atomic spectra have been used for decades in the range of scientific applications, including plasma spectroscopy [1, 2], perturbed atomic structure physics [3], laser-produced plasmas [4], the transition from solid to plasma visualized by K-radiation excited by suprathermal electrons [5], solid state [6] and chemical physics [7]. Knowledge of the precise shape of x-ray spectra is fundamental for applications such as reference spectra in dense plasma atomic physics and in the calibration of energy scales in high accuracy x-ray experiments [8–12]. The study and characterisation of emission spectra gives insight into atomic processes through the empirical fitting of components attributed to electronic transitions. Absolute measurement is a necessary component of characterisation; here the transfer and portability of the spectrum is investigated through a relative measurement. Asymmetries in the line shape have long been explained by the presence of spectator vacancies, created when the photo-electron causes excitation of outer shell electrons, either to the continuum (shake off) or higher shell (shake up). Contributions to the spectrum created in this way are referred to as shake satellites.

The x-ray spectrum of Cu is the most studied of all the transition metals, with numerous characterisations of the Cu $K\alpha$ spectrum reported over the last century [13–22]. However, there exists very few Cu $K\beta$ characterisations in the literature. The $K\beta$ spectrum is caused by the transition $3p \rightarrow 1s$, this can be further split into the $K\beta_{1,3}$ lines attributed to the hole transitions: $[1s] \rightarrow [3p_{3/2}]$ and $[1s] \rightarrow [3p_{1/2}]$. The energy splitting of the $3p$ subshells is significantly smaller than the $2p$ subshells meaning that the $K\beta$ component lines cannot easily be resolved and so the spectrum appears as an unresolved doublet.

The best current characterisation of the Cu $K\beta$ profile uses a sum of five Lorentzians [18]. The fit shows excellent agreement between data and model. However the physical significance of each Lorentzian is undetermined. This is in contrast to earlier work on the Cu $K\alpha$ spectrum by Deutsch *et al*, where each Lorentzian is attributed to an electronic transition and therefore to specific atomic processes [17].

Alongside experimental investigations, theoretical investigations give a unique insight into the interaction between

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Solving self-absorption in fluorescence

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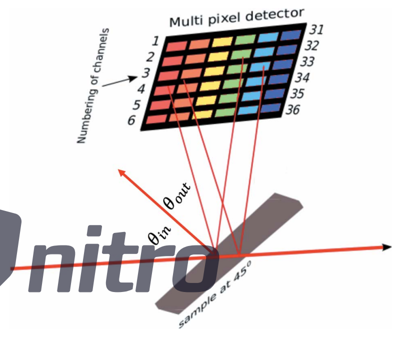
One of the most common types of experiment in X-ray absorption spectroscopy (XAS) measures the secondary inelastically scattered fluorescence photon. This widespread approach has a dominant systematic of self-absorption of the fluorescence photon. The large impact of self-absorption compromises accuracy, analysis and insight. Presented here is a detailed self-consistent method to correct for self-absorption and attenuation in fluorescence X-ray measurements. This method and the resulting software package can be applied to any fluorescence data, for XAS or any other experimental approach detecting fluorescence or inelastically scattered radiation, leading to a general solution applicable to a wide range of experimental investigations. The high intrinsic accuracy of the processed data allows these features to be well modelled and yields deeper potential insight.



1. Introduction

X-ray absorption fine structure (XAFS) is the oscillatory behaviour in photoelectric X-ray absorption spectra above an ionization edge. The oscillations are caused by backscattering and self-interference of the wavefunction of an emitted photoelectron within the material near the emitting atom. From these oscillations, we can extract highly accurate information on the local atomic structure surrounding the X-ray absorbing atom. XAFS is one of the most popular techniques used in synchrotron measurements and applications have been found in many diverse fields: fundamental physics (Bertoni, 2015), pure and applied chemistry (Lamberti & Bokhoven, 2016; Islam *et al.*, 2016), biological and medical science (Fornasini, 2015), earth sciences and engineering (Boscherini, 2015; Ramaker, 2016), and art and cultural heritage (Farges & Cotte, 2016). However, the potential of this technique is often limited by poorly quantified experimental uncertainties or untreated systematic effects (Creagh & Hubbell, 1987, 1990; Krappe & Rossner, 1999). Fluorescence measurement, developed by Jaklevic *et al.* (1977), is a particularly useful technique for dilute systems (Jaklevic *et al.*, 1993; Lee *et al.*, 1981) and is very commonly used for modern experiments. For XAFS measurements conducted using fluorescence detection, there is particular difficulty in obtaining accurate statistical uncertainties compared with experiments conducted in 'transmission mode', and most publications are reported with no uncertainties.

One of the earliest attempts to explain the distortion of fluorescence X-ray absorption spectroscopy (XAS) was made by Goulon *et al.* (1982). They recognized the key limitations of fluorescence measurement from the loss of statistics in the signal-to-noise ratio, some attenuation of both the edge jump and the XAFS oscillations, the fluorescence yield, the solid angle and the core integral.

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Research paper

Resolution of ferrocene and deuterated ferrocene conformations using dynamic vibrational spectroscopy: Experiment and theory

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ABSTRACT

The signature of molecular vibrations and distortions in dynamic molecules gives a complex fingerprint which is insightful and can substantiate (or otherwise) chemical hypotheses regarding molecular and conformer stability. Using high-accuracy experimental data of ferrocene (Fc) and deuterated ferrocene (dFc, Fc $- d^{10}$) at temperatures from 7 K through to 388 K, we obtain complex spectral profiles which require an advanced reaction coordinate model to explain. We obtain compelling evidence that the single conformer model (staggered D_{5d} or eclipsed D_{5h}) used to interpret and explain many experimental results on ferrocene is invalid. However we also present compelling evidence that mixed conformer models are invalid, where ferrocene is represented by an effective dihedral angle between the cyclopentadienyl (Cp) rings; or by a mixture of Boltzmann populations of the two conformers. We find no evidence for single or mixed conformer models despite covering almost all conclusions from past literature for gas, solution or solid phase Fc. Some molecular dynamics computations have imputed free rotation at liquid helium temperatures or at room temperature – we find no evidence for either of these hypotheses.

We measure and derive point-wise experimental uncertainty of the spectra, enabling quantitative assessment of specific chemical and physical models about the origin of the spectral line-shapes. A new principle based on the reaction coordinate is introduced. Advanced spectroscopy and modelling is introduced for hypothesis testing, to articulate the nature of the potential surface, the reaction coordinate and subtle conformational changes in dilute systems. Two expected spectral peaks appear inverted in the gas phase, but are explained by our Reaction Coordinate Method (RCM) model. The non-uniform broadening of the singlet and doublet peaks with increasing temperature is explained. Our experimental analysis shows that the lowest energy conformer is D_{5h} for both Fc and dFc. We are able to represent the reduced mass ratios of the lowest vibrational modes for Fc and dFc of 1.11 for ν_1 for Fc to and of 1.10 for Fc to $Fc - d^{10}$. The measured barrier height for rotation is 7.4 kJ mol^{-1} and 6.3 kJ mol^{-1} for Fc and dFc respectively, in comparison to numerous theoretical treatments and past experimental studies. For the first time, we obtain agreement of the model with the complex spectral evolution of profiles. These new techniques are sensitive discriminants of alternate models and chemical systems, which argues for wider application to other complex or impenetrable problems across fields arising for numerous other solutions, frozen or at room temperature.

1. Motivation

Ferrocene (Fc, $[Fe(C_5H_5)_2]$) is the iconic molecule of organometallic chemistry, where the ferrous sandwich structure exemplifies metal-aryl bonding, yet is also one of the most subtle. A serendipitous discovery of Fc more than sixty years ago, reported by two groups in late 1951 [4] and early 1952 [5], ultimately proved to be a breakthrough introducing a new era of organometallic chemistry. Wilkinson and coworkers proposed the structure of Fc to be a *sandwich compound* (a metal atom sandwiched between two cyclopentadienyl rings), possessing a symmetry point group of D_{5d} (staggered) [6]. Independently, Fischer and co-workers proposed an iron (II) atom to be confined between staggered cyclopentadienyl (Cp) rings in the ferrocene molecule [7]. Subsequent X-ray crystallography studies [8–10] confirmed the sandwich form of the structure. A recent Nature Chemistry commentary [11] explained that key papers were insightful and generational without providing high standards of analysis.

New development of the understanding of ferrocene is of very broad interest and significance as it relates to the nature of the organometallic bond and advanced quantum chemistry. Fc, extended structures and

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Low-energy electron properties: Electron inelastic mean free path, energy loss function and the dielectric function. Recent measurements, applications, and the plasmon-coupling theory

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A R T I C L E I N F O

Keywords:
Electron energy loss spectra
Inelastic mean free paths
Dielectric function
Electron spectroscopy

A B S T R A C T

We review new self-consistent models of inelastic electron scattering in condensed matter systems for accurate calculations of low-energy electron inelastic mean free paths (IMFPs) for XAFS and low energy diffraction. The accuracy of theoretical determinations of the electron IMFP at low energies is one of the key limiting factors in current XAFS modeling and Monte Carlo transport. Recent breakthroughs in XAFS analysis show that there exist significant discrepancies between theoretical and experimental IMFP values, and that this can significantly impact upon extraction of other key structural parameters from both XANES and XAFS. Resolution of these discrepancies is required to validate experimental studies of material structures, and is particularly relevant to the characterization of small molecules and organometallic systems for which tabulated electron scattering data is often sparse or highly uncertain.

Novel models implement plasmon coupling mechanisms for the first time, in addition to causally-constrained lifetime broadening and high-precision density functional theory, and enables dramatic improvements in the agreement with recent high profile IMFP measurements. We discuss a theoretical approach for IMFP determination linking the optical dielectric function and energy loss spectrum of a material with its electron scattering properties and characteristic plasmon excitations. We review models inclusive of plasmon coupling, allowing us to move beyond the longstanding statistical approximation and explicitly demonstrate the effects of band structure on the detailed behaviour of bulk electron excitations in a solid or small molecule. This interrogates the optical response of the material, which we obtain using density functional theory. We find that new developments dramatically improve agreement with experimental electron scattering results in the low-energy region (30 eV → 200 eV) where plasmon excitations are dominant. Corresponding improvements are therefore made in Low Energy Electron Transport, LEEM, theoretical XAFS spectra and detector modelling.

1. Background for low energy electron properties

The origins of quantum oscillators and resonance scattering and losses is found in Drude and Einstein models extended to Debye and Drude-Sommerfeld models with Fermi-Dirac statistics for the electron by 1928 [1–4]. Much of the understanding of scattering, Compton scattering and inelastic scattering has also been based upon a free electron gas model [5,6]. Perhaps surprisingly, extensions of the Drude-Sommerfeld model into angle-dependent inelastic scattering and q-space extensions are still active and prevalent in 2018.

Major and dramatic advances were made [7,8] over the intervening decades, still based on a free electron gas model. Meanwhile of course the understanding of the solid state, regular arrays of atoms, conductors and dielectrics developed apace. In particular the idea of a plasmon as a plasma oscillation and propagation developed, with the observation of plasmons by energy losses in units of $\hbar\omega_p$ when electrons pass through thin metallic films [9].

Much of this core understanding is presented in classical texts [10–12]. As early as 1982, Levine and Louie attempted to modify the Drude-Sommerfeld basis away from the free electron gas model to account for the band gap in semiconductors [13].

The major breakthrough in the understanding and modelling of electron properties came with Penn in 1987 [14] which was then able to link up arbitrary solid state structure and behaviour from experimental or theoretical optical limit data to evaluate electron and plasmon inelastic scattering from band theory. In the same period there has been development of a plethora of density functional theories (DFTs), effective band theories and plasmon theories with many

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Structural Insight into Redox Dynamics of Copper Bound N-Truncated Amyloid-*β* Peptides from *in Situ* X-ray Absorption Spectroscopy

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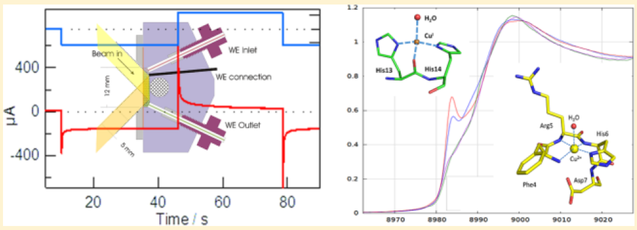
Supporting Information

ABSTRACT: X-ray absorption spectroscopy of Cu^{II} amyloid-*β* peptide (A*β*) under in situ electrochemical control (XAS-EC) has allowed elucidation of the redox properties of Cu^{II} bound to truncated peptide forms. The Cu binding environment is significantly different for the $A\beta_{1-16}$ and the N-truncated $A\beta_{4-9}$, $A\beta_{4-12}$, and $A\beta_{4-16}$ ($A\beta_{4-9/12/16}$) peptides, where the N-truncated sequence ($F_4R_5H_6$) provides the high-affinity amino-terminal copper nickel (ATCUN) binding motif. Low temperature (ca. 10 K) XAS measurements show the adoption of identical Cu^{II} ATCUN-type binding sites ($Cu^{II}{}_{ATCUN}$) by the first three amino acids (FRH) and a longer-range interaction modeled as an oxygen donor ligand, most likely water, to give a tetragonal pyramid geometry in the $A\beta_{4-9/12/16}$ peptides not previously reported. Both XAS-EC and EPR measurements show that Cu^{II}:$A\beta_{4-16}$ can be reduced at mildly reducing potentials, similar to that of Cu^{II}:$A\beta_{1-16}$. Reduction of peptides lacking the $H_{13}H_{14}$ residues, Cu^{II}:$A\beta_{4-9/12}$, require far more forcing conditions, with metallic copper the only metal-based reduction product. The observations suggest that reduction of $Cu^{II}{}_{ATCUN}$ species at mild potentials is possible, although the rate of reduction is significantly enhanced by involvement of $H_{13}H_{14}$. XAS-EC analysis reveals that, following reduction, the peptide acts as a terdentate ligand to Cu^{I} (H_{13}, H_{14} together with the linking amide oxygen atom). Modeling of the EXAFS is most consistent with coordination of an additional water oxygen atom to give a quasi-tetrahedral geometry. XAS-EC analysis of oxidized Cu^{II}:$A\beta_{4-12/16}$ gives structural parameters consistent with crystallographic data for a five-coordinate Cu^{III} complex and the $Cu^{II}{}_{ATCUN}$ complex. The structural results suggest that Cu^{II} and the oxidation product are both accommodated in an ATCUN-like binding site.



1. INTRODUCTION

Alzheimer's disease (AD) is a progressive neurodegenerative disorder, characterized by the presence of amyloid plaques in the brain. The major constituent of AD plaques is the amyloid-*β* peptide (A*β*), which is cleaved from the membrane-bound amyloid precursor protein (APP). Further evidence for A*β* involvement in AD ranges from genetic studies indicating that mutations which increase A*β* production or decrease A*β* clearance enhance disease progression[1] to cellular toxicity assays indicating that the A*β* peptide can form neurotoxic structures.[2] Despite this evidence for a role for A*β* in the disease state, there is no consensus on the specific forms of the peptide responsible for the pathogenesis of AD. The degree of synaptic loss correlates more with the small soluble/diffusible species of A*β* oligomers,[3] which in turn are in equilibrium with insoluble A*β* aggregates.[4] The current, most widely accepted theory for A*β* toxicity is that small, soluble, diffusible A*β* oligomers of undefined stoichiometry and composition cause synaptic damage.[5]

Recent biophysical characterization of A*β* aggregates showed that the full length $A\beta_{1-42}$ peptide tends to aggregate into inert amyloid plaques in contrast to N-truncated $A\beta_{4-42}$ and pyroglutamate $A\beta_{3-42}$ (A*β* $pyroE_{3-42}$) peptides, which have a higher tendency to stay soluble and maintain their toxic profile over a longer time period.[6,7] N-terminal deletions such as $A\beta_{4-42}$ enhance generation of toxic soluble and stable A*β* oligomers.[8] The first protein sequencing studies of the amyloid plaque core (APC) from AD brains identified N-terminal heterogeneity and the majority (~64%) of the APC-AD begins with an F_4 residue corresponding to position 4 of the full 42-length sequence.[9,10] Mass spectrometry analyses supported these findings, demonstrating that $A\beta_{4-42}$ and $A\beta_{1-42}$ are the dominant isoforms present in the hippocampus and cortex of sporadic and familial AD patients as well as in healthy controls.[11,12]

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FDMX: extended X-ray absorption fine structure calculations using the finite difference method

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Keywords: X-ray absorption; finite difference methods; fine structure; XAFS; *FDMNES*; *FDMX*.

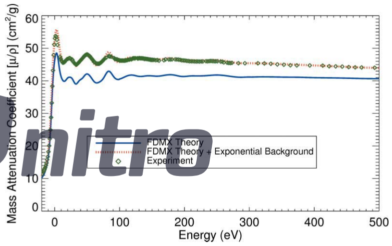
A new theoretical approach and computational package, *FDMX*, for general calculations of X-ray absorption fine structure (XAFS) over an extended energy range within a full-potential model is presented. The final-state photoelectron wavefunction is calculated over an energy-dependent spatial mesh, allowing for a complete representation of all scattering paths. The electronic potentials and corresponding wavefunctions are subject to constraints based on physicality and self-consistency, allowing for accurate absorption cross sections in the near-edge region, while higher-energy results are enabled by the implementation of effective Debye–Waller damping and new implementations of second-order lifetime broadening. These include inelastic photoelectron scattering and, for the first time, plasmon excitation coupling. This is the first full-potential package available that can calculate accurate XAFS spectra across a complete energy range within a single framework and without fitted parameters. Example spectra are provided for elemental Sn, rutile TiO_2 and the FeO_6 octahedron.

1. Introduction

X-ray absorption fine structure (XAFS) refers to the oscillations in the energy-dependent photo-absorption coefficient of a condensed matter system, commonly seen at energies up to a few hundred eV above an ionization edge. These oscillations are the result of self-interference of photoelectron excitations, which have scattered elastically from one or more local atoms in the material. The precise form of an XAFS spectrum is directly determined by the spatially dependent elastic and inelastic electron scattering coefficients of the material, and therefore is a function of the complex electronic potential within a critical region near the ionized atom.

The most obvious determinant of this potential is the position of neighbouring atoms, and particularly their associated electron densities. This makes XAFS an excellent probe of local molecular structure, not only for simple elements and solids but also for large compounds, aqueous samples, gases and amorphous materials. The physical structure around a central atom can be probed by tuning the X-ray energy to be near an inner-shell ionization energy for a specific element, and in this way co-ordination numbers, crystal groups and bond lengths can be measured routinely for materials which do not lend themselves to effective study with other crystallographic methods.

The relationship between XAFS and the local complex potential has many other significant consequences. At energies very close to the absorption edge (*i.e.* photoelectron energies less than 60 eV), the XAFS spectrum is highly sensitive to minor changes in the potential that may be associated with changes to ionization state, oxidation state and



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Letter

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Momentum-Dependent Lifetime Broadening of Electron Energy Loss Spectra: A Self-Consistent Coupled-Plasmon Model

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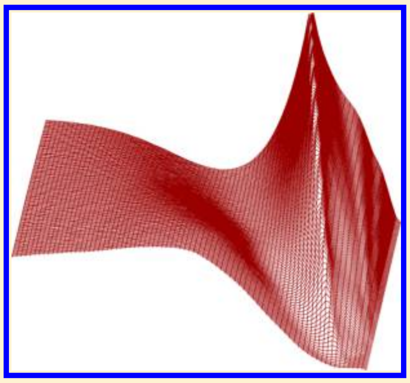

ABSTRACT: The complex dielectric function and associated energy loss spectrum of a condensed matter system is a fundamental material parameter that determines both the optical and electronic scattering behavior of the medium. The common representation of the electron energy loss function (ELF) is interpreted as the susceptibility of a system to a single- or bulk-electron (plasmon) excitation at a given energy and momentum and is commonly derived as a summation of noninteracting free-electron resonances with forms constrained by adherence to some externally determined optical standard. This work introduces a new causally constrained momentum-dependent broadening theory, permitting a more physical representation of optical and electronic resonances that agrees more closely with both optical attenuation and electron scattering data. We demonstrate how the momentum dependence of excitation resonances may be constrained uniquely by utilizing a coupled-plasmon model, in which high-energy excitations are able to relax into lower-energy excitations within the medium. This enables a robust and fully self-consistent theory with no free or fitted parameters that reveals additional physical insight not present in previous work. The new developments are applied to the scattering behavior of solid molybdenum and aluminum. We find that plasmon and single-electron lifetimes are significantly affected by the presence of alternate excitation channels and show for molybdenum that agreement with high-precision electron inelastic mean free path data is dramatically improved for energies above 20 eV.

The low-energy inelastic scattering behavior of electrons in a medium is of fundamental and critical importance to many spectroscopies and microscopies used in modern materials analysis. Electron energy loss spectroscopy (EELS),[1] low-energy electron diffraction,[2] X-ray absorption spectroscopy,[3] and electron microscopy[4] all demand detailed knowledge of electron scattering, inelastic mean free paths (IMFPs), and the dielectric response of the medium being probed. This work aims to incorporate new physical processes into a causally constrained model of the dielectric response of materials in order to improve our understanding and quantification of critical material properties.

We are interested in developing theory to calculate the electron IMFP in the low-energy region (below ~100 eV), where recent experimental results have demonstrated deficiencies in the established literature.[5,6] It has become apparent that existing models of the dielectric response of materials to low-energy electrons systematically overestimate the electron IMFP. Recent theoretical works suggest that this is due to either a poor account of single- and bulk-electron excitation lifetime broadening[7] or a lack of consideration for exchange and correlation effects in the dielectric theory of solids.[8] It is plausible that both of these effects contribute to the discrepancy, but without properly constrained theoretical models, it is not possible to definitively assess the contribution of each.

Attempts to resolve the discrepancy using variations in lifetime broadening parameters for optical resonances have shown that this approach may yield good agreement for energies higher than 50 eV. Recent work of this nature by Da et al. achieved particularly strong success with a model using many fitted resonance terms possessing both positive and negative oscillator strengths.[9] They were subsequently able to achieve excellent agreement with experimental results across all energies studied by using an additional empirical reduction parameter. Although successful, such an approach is ultimately insufficient, however, as it lacks a well-defined physical justification and utilizes an unconstrained representation of optical resonances that are constructed using a potentially overcomplete basis set.

This work focuses instead on the momentum dependence of the lifetime broadening of single-electron and bulk-electron (plasmon) excitations, developing an earlier discussion on the extension of the widely used optical data model for calculations of the electron energy loss function (ELF) and electron IMFP.[10] We will demonstrate how a model may be developed to incorporate these effects in both a physical and uniquely constrained way. These developments will be applied to the test cases of elemental molybdenum and aluminum, allowing us to probe their effects for a free-electron-like material with a single dominant resonance peak and a material with more complex band structure and many optical resonances. In the case of molybdenum, our improvements result in dramatic improve-

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X-ray measurements in helium-like atoms increased discrepancy between experiment and theoretical QED

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Abstract

A recent 15 parts per million (ppm) experiment on muonic hydrogen ($p^+\mu^-$) found a major discrepancy with quantum electrodynamics (QED) and independent nuclear size determinations. Here we find a significant discrepancy in a different type of exotic atom: a medium-Z nucleus with two electrons. Investigation of the data collected is able to discriminate between available QED formulations and reveals a pattern of discrepancy of almost six standard errors of experimental results from the most recent theoretical predictions, with a functional dependence proportional to Z^n where $n \simeq 4$. In both the muonic and highly charged systems, the sign of the discrepancy is the same, with the measured transition energy higher than predicted. Some consequences are possible or probable, and some are more speculative. This may give insight into effective nuclear radii, the Rydberg, the fine-structure constant, or unexpectedly large QED terms.

Keywords: helium-like quantum systems, relativistic atomic physics, x-ray spectroscopy, QED

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Convergence of the Breit interaction in self-consistent and configuration-interaction approaches

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Much discussion in relativistic atomic physics and quantum optics has related to the interaction of gauge and perturbation of the Hamiltonian or Dirac operator. It has been commented that Lorentz and gauge independence requires different forms of the perturbation operator in shifting from one gauge to another. Equally, it has been commented that gauge convergence is not possible without different operator forms in different bases and without the operator being embedded within the self-consistent kernel. We explore the logic and self-consistency of these arguments, applied to the well-known Breit operator in an area of continuing discussion. We find that convergence is now possible to a remarkable degree including a Breit interaction operator in a form consistent with the gauge for length and velocity relativistic forms of the multipole operator, implemented at the configuration-interaction level. Excellent convergence is obtained for Breit interaction energies, interaction mixing coefficients, interaction transition probabilities and eigenenergies and transition probabilities in complex open shells (transition metal K α transitions and shake satellites), and forbidden transitions.

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I. INTRODUCTION

Relativistic quantum mechanics has been a powerhouse and mainstay for the development of science since Dirac and Sommerfeld. As a cornerstone of atomic physics it has led via quantum electrodynamics to one of the two beautiful theories of our natural world [1]. Recently, this has gained dramatic recognition in small-molecule inorganic theoretical and quantum chemistry as a tool for molecular dynamics. Transition energies, probabilities, and profiles have been predicted with outstanding accuracy, especially for the hydrogen atom [2–4].

In the VUV and x-ray regimes the dominant bound-bound transitions are the characteristic inner-shell transitions of $K\alpha$ and $K\beta$ for $1s-2p$ and $1s-3p$ transitions. Not only are these the most recognizable features of the spectra, but also they evince complex questions of relativistic quantum mechanics which remain unresolved to date. If we begin with the Dirac operator, we recognize early on that the three-body problem of a helium nucleus with two electrons is a formidable challenge and that a neutral or singly ionized system of medium atomic number is an immense challenge to theoretical computation. High-accuracy experimental data are a starting point, but complex shake processes and transition probabilities lead to the need for multiconfigurational Dirac-Hartree-Fock (MCDHF) approaches to begin to address the interesting complexity of the spectra, which, in a nonrelativistic perspective, can be represented by two diagram lines ($K\alpha_1$ and $K\alpha_2$) at a ratio of 2:1. Not so in reality.

At the heart of the problem is the determination to convergence and self-consistency of perhaps 1000 to 200 000 configuration state functions (CSFs), the effective and exchange potentials, and the treatment of correlations within that framework. This has been a target of many people for many years, including I. P. Grant, C. Froese-Fischer, P. Jonsson, and the GRASP atomic code package; for two-electron systems it has been a particular concern of groups such as those of G. W. F. Drake. Despite the long-standing need to understand these transitions, due to the difficulty of atomic structure calculations in complex atoms we have only recently been able to properly investigate these processes theoretically, taking into account such effects as relativity and electron-electron correlation [5,6]. For complex, open-shell atoms, these calculations are discrepant from experiment by up to an order of magnitude. For example, Anagnostopoulos found that the $3p$ satellite contributes 15% to the scandium $K\alpha$ spectrum, compared to Kochur's *ab initio* calculation of 6.0% [7], and Mukoyama's 7.8% [8]. The $3d$ satellite was found experimentally to contribute 38%, compared to the 5.0% predicted by the two previous sources. At present it is not clear whether the theoretical values or the experimental analysis needs further work, but a reasonable expectation is that both need further investigation [9]. A recent paper has provided a new approach to shake-off calculations [10]. Large, relativistic, multiconfiguration calculations have been performed for the $3d$-transition metal series. These atomic models have been used in a multiconfiguration shake-off calculation and have provided new *ab initio* shake-off intensities which appear to be in better agreement with experiment than anything prior [9]. One of the first key observations within this framework is, of course, the treatment of correlation and, ergo, the derivation of the Moller or Breit interaction.

II. THE BREIT INTERACTION

In the MCDHF method, the atomic wave function becomes a linear combination of solutions to the central-field problem CSFs (symmetrized products of one-electron spinors) corresponding to different electron configurations,

$$\boldsymbol{\psi} = \sum_r c_r \boldsymbol{\psi_r}, \tag{1}$$

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RELATIVISTIC CALCULATION OF TRANSITION PROBABILITIES FOR 557.7 nm AND 297.2 nm EMISSION LINES IN OXYGEN

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ABSTRACT

The 557.7 nm green line and the 297.2 nm ultraviolet line in oxygen have been studied extensively due to their importance in astrophysics and atmospheric science. Despite the enormous effort devoted to these two prominent transition lines over 30 years, and in fact going back to 1934, the ratio of their transition probabilities remains a subject of major discrepancies amongst various theoretical calculations for many decades. Moreover, theoretical results are inconsistent with available laboratory results, as well as recent spacecraft measurements of Earth's airglow. This work presents new relativistic theoretical calculations of the transition probabilities of these two photoemission lines from neutral oxygen using the multi-configuration Dirac–Hartree–Fock method. Our calculations were performed in both length and velocity gauges in order to check for accuracy and consistency, with agreement to 8%. Whilst remaining a challenging computation, these results directly bear upon interpretations of plasma processes and ionization regimes in the universe.

Key words: atmospheric effects – atomic processes – line: identification – methods: analytical – radiation mechanisms: general – techniques: spectroscopic

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1. INTRODUCTION

Oxygen is one of the most abundant elements in the universe, and as a result exists in many astronomical objects. The oxygen spectra observed contain emission lines from both the visible and non-visible (infrared and ultraviolet). Two of the most prominent lines observed in Earth's aurorae and airglow are the 557.7 nm visible green line and the 297.2 nm ultraviolet line. Moreover, the O I forbidden green line has also been identified in planetary nebulae and meteors such as Perseid, Orionid, and Lyrid (Halliday 1960). This allows further investigations into meteor compositions and the chemical processes involved, which is important for prebiotic studies (Jenniskens & Stenbaek-Nielsen 2004). Furthermore, this green line is believed to be the primary source of luminosity of the Leonid persistent train, which enables the investigation of meteoric aerothermal chemistry (Jenniskens et al. 2000). The auroral green line also features prominently in many young, oxygen-rich supernova remnants such as Cas A, G298 + 1.8, and N132D (Victor et al. 1994), as well as T Tauri stars (Pascucci et al. 2011).

Due to the correlation between forbidden line emission and disk accretion in classical T Tauri stars (Hartigan et al. 1995), information on mass-loss rate and mass accretion rate can also be obtained using this auroral green line. Modeling of atomic processes in comets such as the C/1996 B2 Hyakutake has also been based on this green emission line (Bhardwaj & Raghuram 2012). However, these studies depend upon the transitions following the relevant model which they are presenting, which has not thus far been possible. A major achievement of recent time is the detection of the 5577 auroral green line on Venus (Slanger et al. 2001), which serves as a stepping stone toward a better understanding of the dynamics of its upper atmosphere (Witasse & Nagy 2006). The auroral green line is particularly sensitive to solar and geomatic activities (Russell 1981), so the intensity variation of this emission line can be used for studies of solar flare (Kudryashev & Avakyan 2000), the atmospheric system, and geophysical disturbances (Mikhalev 2011). Interest in these particular transition lines, especially the auroral green line, is not confined only to astrophysics and plasma physics, but is also important in other areas such as climatology and aeronomy (Semenov & Shefov 2005; Shefov et al. 2000; Semenov et al. 2002; Mikhalev 2012).

Accurate determination of emission lines transition probabilities is especially important, as it can lead to the deduction of the underlying chemical reactions and therefore a better understanding of the evolution of the associated entity. The auroral green line has been a subject of debate for many decades, particularly arising from the disagreement between theoretical calculations and observations. This anomaly has been encountered in studies of electron energy loss in oxygen plasmas (Victor et al. 1994), oxygen UV airglow (Stegman & Murtagh 1988), quantum yields in the nocturnal F-region (Bates 1992), and supernovae (Ryder et al. 1993).

The 557.7 nm visible green line results from the electric quadrupole ($E2$) transition $1s^2\,2s^2\,2p^4(^1S_0$–$^1D_2)$, which is optically forbidden. The 297.2 nm ultraviolet line is a magnetic dipole ($M1$) transition $1s^2\,2s^2\,2p^4(^1S_0$–$^3P_1)$. The intensity ratio $I_{557.7}/I_{297.2} = A_{557.7}/A_{297.2}$ of these two lines (or equivalently, the transition probability ratio) has been calculated many times previously by a range of authors but without agreement (Table 1). Note that experiments can report either photon-counting ratios corresponding to $A_{557.7}/A_{297.2}$ or energy-deposition ratios (erg s^{-1}, etc.) but that all data reported here follows the photon-counting standard.

Two laboratory measurements were performed by McConkey et al. (1966) and LeBlanc et al. (1966). Their results are given in Table 2. The theoretical results do not agree with each other, and do not agree well with those from available laboratory measurements. The most recent measurements of this intensity ratio are sourced from the Earth's airglow (Table 3). Interestingly, these recent measurements are quite consistent with each other, and yet disagree strongly with those from

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Success and failure of dead-time models as applied to hybrid pixel detectors in high-flux applications

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The performance of a single-photon-counting hybrid pixel detector has been investigated at the Australian Synchrotron. Results are compared with the body of accepted analytical models previously validated with other detectors. Detector functionals are valuable for empirical calibration. It is shown that the matching of the detector dead-time with the temporal synchrotron source structure leads to substantial improvements in count rate and linearity of response. Standard implementations are linear up to $\sim$0.36 MHz pixel^{-1}; the optimized linearity in this configuration has an extended range up to $\sim$0.71 MHz pixel^{-1}; these are further correctable with a transfer function to $\sim$1.77 MHz pixel^{-1}. This new approach has wide application both in high-accuracy fundamental experiments and in standard crystallographic X-ray fluorescence and other X-ray measurements. The explicit use of data variance (rather than $N^{1/2}$ noise) and direct measures of goodness-of-fit (χ_r^2) are introduced, raising issues not encountered in previous literature for any detector, and suggesting that these inadequacies of models may apply to most detector types. Specifically, parametrization of models with non-physical values can lead to remarkable agreement for a range of count-rate, pulse-frequency and temporal structure. However, especially when the dead-time is near resonant with the temporal structure, limitations of these classical models become apparent. Further, a lack of agreement at extreme count rates was evident.

Keywords: hybrid pixel detector; dead-time; single-photon counting; synchrotron fill pattern.

1. Introduction

Fluorescence X-ray absorption fine structure (XAFS), small-angle X-ray scattering (SAXS) and protein crystallography are important applications of synchrotron radiation that require the position and relative intensity of X-rays to be determined to high accuracy. Widespread use of area detectors for high-throughput crystallography, where the weakest reflection, the strongest reflection and the curve of the diffraction spot profile cover many orders of magnitude of flux and brightness, leads to this being a critical consideration. Further, the temporal structure of recorded spots introduces yet another time dependence to the source. A few attempts on laboratory diffractometers have investigated the absolute calibration and hence linearity of diffracted intensities relative to the straight-through beam (Harada *et al.*, 1970). This necessitates the use of detectors with high radiation tolerance, high dynamic range, low noise performance and a small point spread function. Single-photon-counting pixel array detectors (PADs) such as PILATUS have demonstrated an ability to meet these criteria (Broennimann *et al.*, 2006*a*; Sobott *et al.*, 2009).

Many other synchrotron applications benefit from these advanced characteristics. Moreover, these advantages serve well in high-flux operation, including measurements of direct-beam or attenuated beam geometries, but also in medium or low-flux operation, including scattering and fluorescence detection from disordered or dilute systems. A range of critical experiments including tests of QED (Pohl *et al.*, 2011; Gillaspy *et al.*, 2010; Chantler *et al.*, 2009*a*) also depend upon such characteristics of the detector chain. Too often the best measurements are limited by either statistics (detector efficiency and count-rate) or by systematic errors including non-linearities (Chantler & Kimpton, 2009). Hence even modest advances in these areas can lead to dramatic new science. In fact, in several of these fields, an increase in final accuracy by

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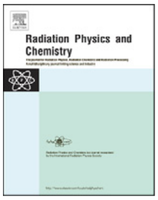

Self-energy screening approximations in multi-electron atoms

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HIGHLIGHTS

- We develop a self-energy screening approximation suitable for multi-electron atoms.
- This approximation is tested in a number of few- and many-electron systems.
- We obtain superior agreement with experiment compared with existing approximations.
- An implementation of this approximation is provided for use with GRASP2K.

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ABSTRACT

Atomic structure calculations have reached levels of accuracy which require evaluation of many-electron QED contributions. Since exact analytic solutions do not exist, a number of heuristics have been used to approximate the screening of additional electrons. Herein we present an implementation for the widely used GRASP atomic-structure code based on Welton's concept of the electron self-energy. We show that this implementation provides far superior agreement compared with a range of other theoretical predictions, and that the discrepancy between the present implementation and that previously used is of comparable magnitude to other sources of error in high-accuracy atomic calculations. This improvement is essential for ongoing studies of complex atomic systems.

1. Quantum electrodynamics and self-energy

Both classically and in quantum field theory, the electromagnetic field of the electron can interact with the electron itself. In both cases, this interaction results in an infinite energy associated with the electron (Sakurai, 1967). In quantum field theory, this interaction corresponds to an electron emitting a virtual photon, which is then reabsorbed by the electron – the Feynman diagram for this interaction is presented in Fig. 1. The energy associated with the interaction between the electron and its own electromagnetic field is the self-energy of the electron.

This self-energy results in observable effects. Most famously it is responsible for the Lamb shift (Lamb and Retherford, 1947; Bethe, 1947). In order to obtain a finite numerical result, the infinite portion of the integral is required to be removed by the process of renormalisation, which can also include a finite energy cut-off. Since the classical electromagnetic self-energy is thereby removed or renormalised, this energy shift is a purely quantum-mechanical phenomenon. It arises due to the interaction of the electron with the quantised electromagnetic field. In quantum field theory, these quantum fluctuations of the electromagnetic field strength are also responsible for spontaneous emission.

Early self-energy corrections were carried out to first-order in $Z\alpha$ (Bethe, 1947). In the early 1970s, Mohr provided an atomic self-energy formulation within the bound-state Furry formalism in a suitable form for direct numerical evaluation, used to evaluate the self-energy for ground-state hydrogenic atoms (Mohr, 1974). Later work extended this to include $n=2$ hydrogenic systems (Mohr, 1983) and more recent studies have evaluated hydrogenic self-energies for $n=3$, 4, 5 (Mohr and Kim, 1992; Indelicato et al., 1998; Le Bigot et al., 2001). There have been no generalisations of the self-energy calculations to arbitrary N-electron atomic systems.

Without exact solutions, atomic structure packages use an approximation to the self-energy. This can be obtained by taking the exact hydrogenic results of Mohr and successors and reducing them by some screening factor to allow for multiple electron interactions. These factors aim to represent some scaling from the hydrogenic system to the system of interest, yet their form is of a wide variety. From Mohr (1974) we have that $E_{SE}^{H}=(\alpha/\pi)(Z\alpha)^4 F(Z\alpha)m_e c^2$. Approaches used to derive a multielectron self-energy include using the mean radius to determine an effective Z for that

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Testing Three-Body Quantum Electrodynamics with Trapped Ti^{20+} Ions: Evidence for a *Z*-dependent Divergence Between Experiment and Calculation

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We report a new test of quantum electrodynamics (QED) for the w ($1s2p\,^1P_1 \rightarrow 1s^2\,^1S_0$) x-ray resonance line transition energy in heliumlike titanium. This measurement is one of few sensitive to two-electron QED contributions. Systematic errors such as Doppler shifts are minimized in our experiment by trapping and stripping Ti atoms in an electron beam ion trap and by applying absolute wavelength standards to calibrate the dispersion function of a curved-crystal spectrometer. We also report a more general systematic discrepancy between QED theory and experiment for the w transition energy in heliumlike ions for $Z > 20$. When all of the data available in the literature for $Z = 16$–92 are taken into account, the divergence is seen to grow as approximately Z^3 with a statistical significance on the coefficient that rises to the level of 5 standard deviations. Our result for titanium alone, 4749.85(7) eV for the w line, deviates from the most recent *ab initio* prediction by 3 times our experimental uncertainty and by more than 10 times the currently estimated uncertainty in the theoretical prediction.

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Quantum electrodynamics (QED) is a cornerstone of modern theoretical physics. New activity on this topic has been stimulated by the announcement of a 5σ inconsistency between a 15 ppm measurement of an atomic transition frequency in muonic hydrogen [1] and independent measurements of the proton size, linked together by QED calculations. The high sensitivity of such a measurement to QED is derived in part from the large mass of the bound lepton which shrinks the orbital radius. Another way to reduce the orbital radius and study magnified QED effects is to measure transitions in highly charged ions of increasing Z. QED processes scale as various powers of $Z\alpha$ and significantly affect the quantum observable, namely, transition energies. Moreover, in the high-Z range, some of the perturbative expansions fail, so theoretical methods very different from those used for hydrogen are required. Since QED treatments of low-Z and high-Z systems are undertaken with significantly different starting points and mathematical techniques, precise measurements for ions in the mid-Z range will guide the long-pursued development of a unified computational methodology with very accurate predictions for the entire domain $Z < 100$ [2,3].

Advances in QED theory have been sufficient that one can go beyond one-lepton systems (either free or bound) and explore the three-body quantum problem to high precision, including the investigation of heliumlike atomic systems with two electrons bound to a nucleus. Here, the two-electron QED contributions that are entirely absent in one-electron systems can be probed and compared to various theoretical formulations. In this Letter, we report a measurement of the strongest resonant transition $1s2p\,^1P_1 \rightarrow 1s^2\,^1S_0$ in He-like Ti (Ti^{20+}) and present a divergence that is becoming evident between precision measurements and the most complete theoretical formulations of transition energies for He-like ions in the mid-Z range between S and Kr.

The context of this report is the systematic investigation of medium-Z two-electron systems that is underway by several research groups [4–8]. New results are infrequent, owing to the need to account for all known systematic effects to ever-exacting levels of precision and the scarcity of run time available at the few facilities capable of producing such highly charged ions. Improvements in measurement precision not only help distinguish between theoretical methods which treat few-electron atomic systems but also check the consistency of various experimental approaches that have very different methodologies (using empirical, semi-empirical, relative, or absolute calibration schemes). A very useful outcome would be if measurements that are traceable to the definition of the meter, as the present one, would be found to agree with measurements done relative to transitions in H-like systems (convenient and precise fiducials in many highly charged ion experiments) that themselves have been calculated using two-body QED [4,8,9]. Such a closing of this measurement loop could help establish hydrogenlike lines of highly charged ions as a new class of transfer standards in x-ray spectroscopy [10,11].

The present work was undertaken at the electron beam ion trap (EBIT) facility at the National Institute

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Hydrogenic Lamb shift in Ge^{31+} and the fine-structure Lamb shift

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Using x-ray diffraction and beam-foil spectroscopy, we have determined precise wavelengths for Lyman α_1 and Lyman α_2 in hydrogenic germanium of 1.166 993 8 ± 33 ± 169 and 1.172 433 6 ± 39 ± 170 Å. Hydrogenic germanium Ge^{31+} $1s$-$2p_{3/2}$ and $1s$-$2p_{1/2}$ Lamb shifts are measured to be 66 080 ± 237 ± 1121 and 67 169 ± 281 ± 1237 cm^{-1}, respectively. This 14 ppm measurement of the wavelengths thus provides a 1.8% measurement of the $2p$-$1s$ Lamb shift and is an improvement by a factor of 3 over previous work. Fitting the full two-dimensional dispersion relation, including Balmer and Lyman series, limits random and systematic correlation of parameters. Dominant systematics are due to diffraction parameters including crystal thickness and alignment, differential Doppler shifts due to the variable location of spectral emission downstream of the beam-foil target, and dielectronic, $2s$-$1s$, and $4f$-$2p$ satellites. Models developed are applicable to all relativistic plasma modeling in beam-foil spectroscopy at accelerators. The technique also reports the germanium $2p_{3/2}$-$2p_{1/2}$ fine structure as 397 617 ± 251 ± 512 cm^{-1}, representing a 0.14% measurement of the fine structure and a 71% measurement of the QED contribution to the hydrogenic germanium fine structure, an improvement of a factor of 6 over previous work. We also report a precise measurement of heliumlike resonances and fine structure.

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I. INTRODUCTION AND OVERVIEW

The use of beam-foil spectroscopy for the production of highly charged ions is well known [1–3]. In particular, the production of one- and two-electron species by this method permits a precise test of QED [4–8]. Theoretical evaluation of the hydrogenic and heliumlike energy levels enables derivation of the Lamb shifts.

Impressive precision of low-Z measurements has led to investigations of nuclear form factors and polarization, which involve interesting physics in their own right [8,9]. Meanwhile, medium-Z techniques have been developed over the last two decades, with a view to probing QED in the regime of high effective coupling strength [10–12]. Motivation arises from the increasing significance of higher-order QED terms, together with the $(Z\alpha)^4$ dependence of the lowest order QED contributions, depending on the formalism used for the theoretical expansions [13,14]. The dependence upon $Z\alpha$ indicates another strong motivation for these investigations, namely, that as $Z\alpha$ approaches unity for high-Z elements, the convergence of higher-order terms may fail, and additional interactions may in principle be observed.

However, rate processes and relative intensities inside and outside the foil have not received the same attention. With sufficient precision, these may be used to deduce dominant interactions within the foil. This corresponds to a dominant uncertainty in beam-foil measurements because of differential source and cascade locations and hence differential Doppler shifts, as we discuss. The effect on absolute and relative x-ray emission intensities as a function of target thickness is compared to model predictions. The observation of one- and two-electron spectra as a function of foil thickness allows

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Nano-roughness in gold revealed from X-ray signature

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ABSTRACT

We present a new method for investigating roughness for surface structure and internal inhomogeneity down to the nano-scale for thin, nano-structured and opaque materials. The method uses careful measurements of the X-ray mass-attenuation coefficient and is applied to measure the magnitude of the roughness of gold foils. The technique is unique, providing insight into both surface and internal roughness. We show that moments of the distribution function of surface and internal structure can be investigated using this method, and discuss observable signatures. The approach is non-destructive and very sensitive as a local in situ measurement and as a diagnostic for accurate characterisation.

1. Introduction

We report a new technique for investigating roughness from the mm to nm scale. This non-destructive technique determines the roughness of a sample by careful measurement of the X-ray mass-attenuation coefficient. The technique provides insight into both surface and internal roughness. It can be applied to a wide class of samples and can be useful in nano-fabrication, surface-science, high-precision optics and in many other areas requiring non-destructive characterisation of internal or surface roughness.

The roughness of a sample can be divided into two components: surface roughness and internal inhomogeneity. Surface roughness is a measure of the small-scale variability in surface height across a sample and is widely studied using numerous existing techniques including stylus [1] and optical profilometry [2], atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) [1,3], transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [4,5] and X-ray reflection [6].

Internal inhomogeneity (which will be referred to as internal roughness) is manifest in the density non-uniformities and voids within the bulk of the sample. X-rays are extremely penetrative and can interrogate the bulk of a sample, allowing the measurement of roughness not only at the surface but also within the bulk. Hence our technique can provide unique insight into internal roughness and open exciting new research opportunities, including studies of nano-structures in cement [7], energy conversion devices [8], and the effects of nano-scale roughness which lead to effects on stresses [9].

Our technique can be summarised as follows. Measurements of the X-ray mass-attenuation coefficient are made over a range of energies on the sample of unknown roughness that is being investigated. Measurements are also made on a set of thicker reference samples of low roughness. The attenuation of the unknown sample is compared to that of the reference samples and the difference is calculated. The magnitude of the roughness can then be determined based on the size and form of this difference.

2. Measuring mass-attenuation coefficients

The X-ray mass-attenuation coefficient $[\frac{\mu}{\rho}]$ quantifies the extent to which a material absorbs and scatters X-rays. In order to measure the mass-attenuation coefficient accurately, we use the X-ray extended range technique (XERT) [10–12], which can correct for a wide range of systematic errors including scattering [13], fluorescence [14], harmonics [15], bandwidth [16], and the attenuation of the ion-chambers and air-path. The XERT has produced the most accurate measurements of the mass-attenuation coefficient in the

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