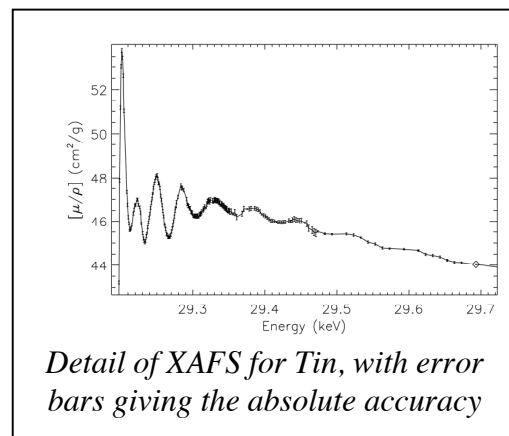


Chris. Chantler, Professor, FAIP; Room 713
X-ray Synchrotron & atomic physics, Quantum
Electrodynamics & X-ray Laboratories
Topics for Masters & Higher Degree Students

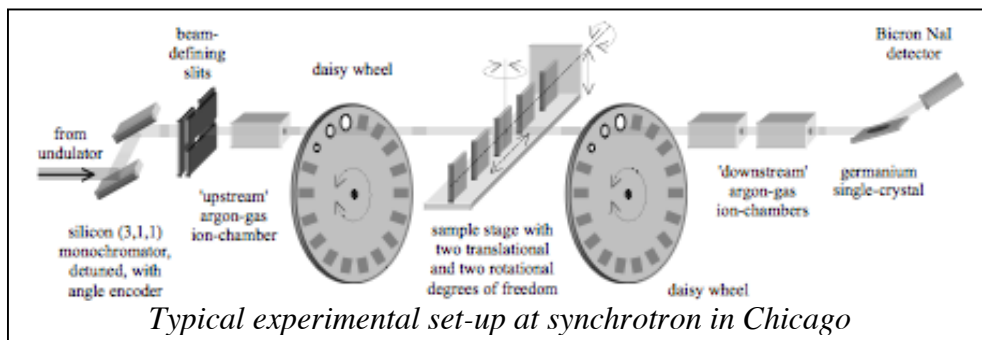


Detail of XAFS for Tin, with error bars giving the absolute accuracy

- 1. Can we test QED? Is it true?** We are the only group to test QED in Australia and have just had a breakthrough reported in Physics Today and New Journal of Physics. This was an international team effort and doctoral thesis work but also with contributions from an Honours/Masters student.
- 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.
- 3. Can I develop or invent a new field of physics?** Yes but probably not in Masters! Recent doctoral students have developed new fields of non-destructive nanoroughness measurement; and electron inelastic scattering (mean free path) experiment and theory; or made major developments in dominant fields of X-ray science or relativistic Quantum Mechanics.

- 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.

- 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.



Typical experimental set-up at synchrotron in Chicago

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 scattering² & synchrotron bandwidth in photoabsorption experiments, have redefined the international standards for (powder) diffraction³, and have placed the field of X-ray Absorption Fine Structure (XAFS) on an absolute footing for the first time. Our *relativistic atomic theory* and tabulation⁴ 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' approximations⁵ & the largest (organometallic) XAFS modelled without this assumption,⁶ with major implications for biological

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. B* **37** (2004) 3163-3176; de Jonge *et al.*, *Phys. Rev. A* **69** (2004) 022717

³ C. T. Chantler *et al.*, *Phys. Rev. A* **69** (2004) 042101

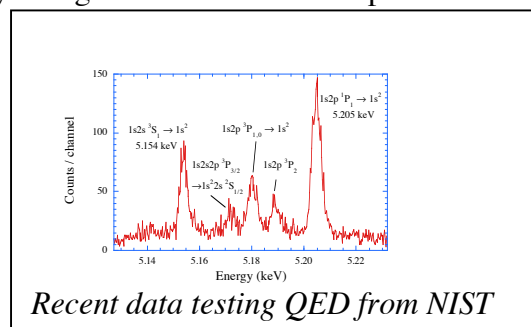
⁴ C.T. Chantler, *Theoretical form factor, attenuation and scattering tabulation for Z=1-92 from E=1-10 eV to E=0.4-1.0 MeV*, *J.Phys.Chem.Ref.Data* **24**, 71-643 (1995); C.T. Chantler, *J. Phys. Chem. Ref. Data*. **29** (2000)

⁵ J. D. Bourke *et al.*, *Phys. Lett. A* **360** (2007); also Cosgriff *et al.*, *Phys. Lett. A* **343** (2005) 174

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

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 edge⁷ 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 – 2008 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.

<http://optics.ph.unimelb.edu.au/~chantler/home.html> &

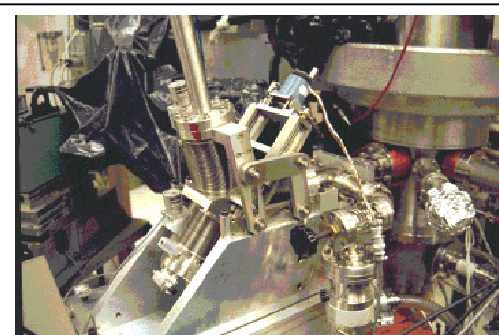
optics.ph.unimelb.edu.au/xrayopt/xrayopt.html. Recent

developments & papers can be collected from Chris Chantler.

Masters will be more successful than earlier honours projects & would expect that results 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. Applications include precision measurements, crystallography, medical physics, tomography, fundamental X-ray experiments & new types of test of Quantum Electro-Dynamics.



Melbourne detector and spectrometer at NIST, USA

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 in 2003-11. Major limitations of current theory *can be addressed within a Masters project*.

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 recently 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.

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

⁷ C.T. Chantler *et al.*, *Phys. Rev. A*62 (2000) 042501; C. T. Chantler *et al.*, *Phys. Rev. A*71 (2005) 032702

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.

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.

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. Two students are involved in separate humanitarian activities where physics crosses boundaries into real-world problems.

2.1 Effect of excitation energy on characteristic radiation: a new ruler in atomic and condensed matter science. A recent invitation from the major international labs in the world has asked us to be involved in determining new standards of energy determination and accuracy. This involves both the preparation of new experiments with $K\alpha$ sources, and leads to 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*]**

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 could be part of a Masters or higher degree. Several doctoral students have worked in this area.

2.3 Absolute measurement of absorption coefficients of gold and zinc using local and international sources [Chris Chantler & Zwi Barnea]. We have the best data in the world to investigate new physics in XAFS (near edge atomic and solid state structure).

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. Post-doctoral students are working on this.

2.5 Biophysics links with labs & analysis to probe X-ray irradiation, biological structures and catalysis.

2.6 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 recently made the highest precision tests of QED for Vanadium atoms ($Z=23$) using a device called 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.

2.7 X-ray Extended Face Crystal measurement of absolute intensities for extinction and bonding redistribution of electron density [Zwi Barnea & Chris Chantler]. Diffraction processes require careful measurements on an absolute scale to reveal new physical and structural insights. The X-ray facility can address these issues directly. Associate Professor Barnea originated these techniques. Questions about how structures bind together, of current international interest, can be resolved. A major dilemma over decades has been the inequivalence of symmetric Bragg diffraction peaks

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 electron-beam ion trap*, *Phys. Rev. A* 29 (2000).

which impact upon the popular biological MAD techniques used by state-of-the-art facilities in the US, Japan and Europe.

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?)

Each experimental topic is a fundamental research area. This work is both in-house and in collaboration with NIST (Washington DC), the University of Oxford & Synchrotrons (Japan, Chicago). Other research on X-ray experimental measurement⁹ 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.

MSc 2016 – extension and development of new cluster theory - XAFS FDM technique [inelastic mean free paths] [Jay]. Application to new field of inelastic mean free paths; band theory; XANES; EXAFS

MSc 2016 – development of new theory of atomic spectra and continuum regions [Truong, Joni]. Applications to laboratory astrophysics; the fine structure constant; international tables; theory of resonant transitions in relativistic QM; QED

MSc 2016 – new experimental tools for QED. Measurements of relativistic quantum mechanics, X-ray optics, synchrotron science [Bryn, Alexis]. Our new lab has produced several great data sets and developed super-resolution for advanced detectors

MSc 2016 – X-ray Free Electron Lasers. K alpha doublet scaling for hole satellite spectra for copper and Mn... as a function of incident electron or photon energy. Atomic photionisation cross-sections pre- & post- edge [Truong, Joni, John]

MSc 2016 – ideal experimental, biological & organometallic systems [Prof Feng Wang (Swinburne); Bio21; Feiters (Europe); Stephen Best (Chemistry); Stanford, USA; Swiss Light Source, Switzerland]

MSc 2016 – application of molecular codes within the cluster framework [Feng, Swinburne]

MSc 2016 – analysis of XAFS data for Cu₂O anomalies & organometallics [Monash]

MSc 2016 – analysis of XERT data for fluorescence and solutions [Tauhid, Chemistry]

MSc 2016 – powder diffraction analysis & experiments [Ryan/Zwi/CTC]

MSc 2016 – Extended Face experiments, MAD and anomalous dispersion, & modeling [Zwi/Tauhid]

[MSc] Feiters: sequel... complex organometallic clusters by (non-muffin-tin) FDMX

[MSc – Ryan, Tauhid, Lucas] Error analysis and encoding – i.e. making FEFF work

[MSc Theory] FDM Theory and implementation for a least-squares fitting technique to experimental data; AXAFS & unresolved transitional arrays

[MSc Exp] Detector Gas Resolution Study; Crystal Redesign & control; Horizontal Spectrometer; digitization design / study

[MSc Exp] Lab. Scattering; Absolute Absorption Coefficient; analysis; Drosophila

[MSc Exp] Lab. Detector Calibration and Diagnosis for QED, RQM, XERT

[MSc] Chris Howard ... XANES pre-edge, on-edge features for perovskites

[JK] New Si / LaB₆ powder diffraction standard result based upon ZnSe?

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.

Breaking News – Physics Today [December 2012]:

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 $^{22}\text{Ti}^{20+}$ 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 $Z = 27\text{--}31$ 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

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

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Received 2013 March 28; accepted 2013 April 16; published 2013 May 6

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

Online-only material: color figure

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 geomagnetic 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

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 ~ 0.36 MHz pixel⁻¹; the optimized linearity in this configuration has an extended range up to ~ 0.71 MHz pixel⁻¹; these are further correctable with a transfer function to ~ 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.

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.*, 2006a; 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; Gillaspay *et al.*, 2010; Chantler *et al.*, 2009a) 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

Stereochemical analysis of ferrocene and the uncertainty of fluorescence XAFS data

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Methods for the quantification of statistically valid measures of the uncertainties associated with X-ray absorption fine structure (XAFS) data obtained from dilute solutions using fluorescence measurements are developed. Experimental data obtained from 10 mM solutions of the organometallic compound ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, are analysed within this framework and, following correction for various electronic and geometrical factors, give robust estimates of the standard errors of the individual measurements. The reliability of the refinement statistics of standard current XAFS structure approaches that do not include propagation of experimental uncertainties to assess subtle structural distortions is assessed in terms of refinements obtained for the staggered and eclipsed conformations of the C_5H_5 rings of ferrocene. Standard approaches (*XFIT*, *IFEFFIT*) give refinement statistics that appear to show strong, but opposite, preferences for the different conformations. Incorporation of experimental uncertainties into an *IFEFFIT*-like analysis yield refinement statistics for the staggered and eclipsed forms of ferrocene which show a far more realistic preference for the eclipsed form which accurately reflects the reliability of the analysis. Moreover, the more strongly founded estimates of the refined parameter uncertainties allow more direct comparison with those obtained by other techniques. These XAFS-based estimates of the bond distances have accuracies comparable with those obtained using single-crystal diffraction techniques and are superior in terms of their use in comparisons of experimental and computed structures.

Keywords: fluorescence; X-ray absorption fine structure; ferrocene; standard error.

1. Introduction

The subtle inter-relationship between the electronic and molecular structure of transition metals and the impact on reactivity underpin their proliferation as the catalysts for biological and industrial processes. For homogeneous catalysis in solution it is vitally important to have available methods that determine, reliably, the structural details needed to understand details of the reaction path. This, to some, is the *raison d'être* of spectroscopy. Notwithstanding the possibilities presented by optical, EPR (electron paramagnetic resonance) and NMR (nuclear magnetic resonance) spectroscopy for particular systems, X-ray absorption fine structure (XAFS) provides the best general approach for structural characterization at the molecular level for metal species in low concentration. While there is an extensive literature demonstrating the application of XAFS to the identification of the coordinating atoms and extraction of geometrical information from analysis employing multiple scattering formalisms, any assessment of the derived geometry is limited by difficulties in

assessing the reliability of the individual experimental observations.

The difficulty in assessing the statistical reliability of the XAFS data is greatly accentuated in cases where fluorescence detection is employed, *i.e.* for the study of samples in dilute solutions. This paper is concerned with quantification of the accuracy and precision of fluorescence XAFS measurements. Ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$ (di-cyclopentadienyl iron), discovered in 1951 (Kealy & Pauson, 1951; Miller *et al.*, 1952), is a prototype of sandwich molecular complexes which epitomizes the different bonding interactions possible between metals and organic molecules and is central to the award of the Nobel prize to Fischer and Wilkinson in 1973 (Fischer & Wilkinson, 1993). The molecule has well defined redox chemistry and is a popular reference material for electrochemical studies conducted in non-aqueous solvents and is an ideal test case for *in situ* electrochemical cells for XAFS and X-ray absorption near-edge structure (XANES) studies.

An interesting aspect of the structural chemistry of ferrocene is the orientation of the two cyclopentadienyl rings. The

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

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(Received 11 May 2012; published 10 October 2012)

We report a new test of quantum electrodynamics (QED) for the w ($1s2p^1P_1 \rightarrow 1s^2S_0$) 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 $Z = 16\text{--}92$ 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.

DOI: [10.1103/PhysRevLett.109.153001](https://doi.org/10.1103/PhysRevLett.109.153001)

PACS numbers: 12.20.Fv, 31.30.jf, 32.30.Rj, 34.50.Fa

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 $1s2p^1P_1 \rightarrow 1s^2S_0$ 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

Measurements of Electron Inelastic Mean Free Paths in Materials

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(Received 10 February 2010; published 20 May 2010)

We present a method for determining inelastic mean free paths (IMFPs) in materials using high-accuracy measurements of x-ray absorption fine structure (XAFS). For electron energies below 100 eV, theoretical predictions have large variability and alternate measurement techniques exhibit significant uncertainties. In this regime, the short IMFP makes photoelectrons ideal for structural determination of surfaces and nanostructures, and measurements are valuable for studies of diverse fields such as low-energy electron diffraction and ballistic electron emission microscopy. Our approach, here applied to solid copper, is unique and exhibits enhanced sensitivity at electron energies below 100 eV. Furthermore, it is readily applicable to any material for which sufficiently high accuracy XAFS data can be obtained.

DOI: [10.1103/PhysRevLett.104.206601](https://doi.org/10.1103/PhysRevLett.104.206601)

PACS numbers: 72.15.Lh, 61.05.cj, 73.50.Gr, 78.70.Dm

The electron inelastic mean free path (IMFP) is the average distance travelled between successive inelastic collisions for an electron moving with a particular energy in a given medium [1]. It is of fundamental importance for a quantitative understanding of electron transport, for electron energy loss spectroscopy and for high-resolution transmission electron microscopy—exciting fields capable of imaging materials at an atomic level [2] and sensitive to changes in interatomic bonding [3]. The mean free path is also crucial for investigations of linear dichroism using photoelectron diffraction [4]; structural investigations using auger electron spectroscopy [5] and x-ray photoelectron spectroscopy [6]; organic semiconductor development for spintronics [7]; and even studying Coulomb explosions triggered by femtosecond x-ray pulses in free-electron lasers [8,9].

However, IMFPs are difficult to determine experimentally, especially at energies below 100 eV–200 eV [10]. As discussed later, different models have predicted large differences in IMFP values in this region, and there has not been a reliable method for assessing the low-energy limits of calculations and predictions which are used for many cognate fields.

Theoretical approaches and computations have large challenges. While theory is well developed for the determination of IMFPs for a free-electron material [11], most solids exhibit complex energy loss functions which require a new approach. It is common to compute IMFPs using experimentally determined optical dielectric functions, or analytic predictive formulae based on these [12]. Empirical curves may also be used when more detailed tabulations are unavailable [13]. These approaches can give applicability at high electron energies, but tend to show discrepancies below 200 eV.

Our work focusses on x-ray absorption fine structure (XAFS) as a solution to this problem. Thousands of papers on XAFS demonstrate its value in probing material struc-

ture down to atomic displacements at the femtometer scale [14]. XAFS theory [15] has shown recent success in the region where it is highly sensitive to the IMFP [16]. We match this theory to experimental XAFS determined by the x-ray extended range technique [17]. This technique provides us with the unprecedented accuracy required to extract the IMFP. In particular, this data is extremely valuable for low-energy electron diffraction (LEED) [18], ballistic electron emission microscopy (BEEM) [19], and experimental configurations where IMFPs for electron energies below 100–200 eV play a role. For much higher electron energies (eg., 200 keV STEM), primary processes will be quite different but secondary scattered photoelectrons may be treated with this new information.

XAFS refers to the complex series of oscillations seen in the photoelectric absorption curve of a material, immediately following an absorption edge. These oscillations convey important structural information about the absorbing material, most notably the relative positions of atoms in the crystal lattice. They are produced by interference between the outgoing photoelectron wave functions from the absorbing atoms, and the returning wave functions back-scattered from atoms in the surrounding region. Since this interference is strongly dependent on the photoelectron energy, the short lifetimes of the photoelectrons cause an energy uncertainty and thus a smearing of the XAFS curve.

The finite IMFP reduces the wave amplitude which diminishes interference (coherence) between the outgoing and incoming waves. Because of the Fourier relationship between the reflected wave function and the resulting XAFS spectrum, this exponential damping leads to a broadening of the XAFS peaks with corresponding energy uncertainty. This effect is particularly clear below 100 eV where the amplitude of the XAFS oscillations is high. To quantify the coherence of the interference, we require knowledge of the photoelectron lifetime or, equivalently, the IMFP.

X-ray mass attenuation coefficients and imaginary components of the atomic form factor of zinc over the energy range of 7.2–15.2 keV

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(Received 16 July 2009; published 22 February 2010)

The x-ray mass attenuation coefficients of zinc are measured in a high-accuracy experiment between 7.2 and 15.2 keV with an absolute accuracy of 0.044% and 0.197%. This is the most accurate determination of any attenuation coefficient on a bending-magnet beamline and reduces the absolute uncertainty by a factor of 3 compared to earlier work by advances in integrated column density determination and the full-foil mapping technique described herein. We define a relative accuracy of 0.006%, which is not the same as either the precision or the absolute accuracy. Relative accuracy is the appropriate parameter for standard implementation of analysis of near-edge spectra. Values of the imaginary components f'' of the x-ray form factor of zinc are derived. Observed differences between the measured mass attenuation coefficients and various theoretical calculations reach a maximum of about 5% at the absorption edge and up to 2% further than 1 keV away from the edge. The measurements invite improvements in the theoretical calculations of mass attenuation coefficients of zinc.

DOI: [10.1103/PhysRevA.81.022904](https://doi.org/10.1103/PhysRevA.81.022904)

PACS number(s): 32.80.Aa, 32.80.Fb, 32.30.Rj, 61.05.cj

I. INTRODUCTION

The x-ray atomic form factor is the fundamental parameter describing the interaction of x rays with matter. Accurate values of the mass attenuation coefficient and hence of the dielectric function are vital for many areas such as particle energy loss functions [1], electron energy loss spectroscopy [2], crystallography [3,4], tomography [5], and polarizability and reflectometry [6]. A wide range of atomic [7], molecular [8], and solid-state [9,10] features can be calculated given accurate values of x-ray atomic form factors of the constituent elements.

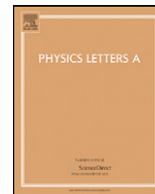
Theoretical estimates of atomic form factors have been tabulated since early in the development of x-ray science for all elements across a wide range of energies. The National Institute of Standards and Technology (NIST) currently supports two such tabulations; XCOM [11,12] and FFAST [13–15]. Significant differences exist in the values of the form factors from these tabulations across a wide range of energies and elements [13,16], the largest being at and immediately above absorption edges [17]. These discrepancies lead to a significant problem when calculating mass attenuation coefficients in these regions.

Figure 1 shows the percentage difference between various experimentally or theoretically determined mass attenuation coefficients of zinc and the corresponding theoretical values calculated using FFAST. Despite experimental errors between 1% and 2% quoted by the various authors, the values are inconsistent, have a spread of about 10%, and generally do not agree with theoretical values. Above the absorption edge

at 9.623 keV, there are few reported measurements of mass attenuation coefficients of zinc. Given these inconsistencies, uncertainty, and spread, existing experimental results cannot be used to distinguish different theoretical approaches (Fig. 1).

The absorption edge region is of particular importance for widely used synchrotron techniques such as x-ray absorption fine structure (XAFS) [22] and x-ray absorption near-edge structure (XANES) [9]. The need for accurate measurements of the mass attenuation coefficient in this region has been noted by other groups [23] and in particular the measurement of K-shell [24] and L-shell [25] jump factors and jump ratios has been of concern. Investigation of photoeffect cross sections for subshells depends upon accurate experimental data and should preferably cover a range of energies to avoid key systematics [26]. In the edge region, accurate values of the mass attenuation coefficient are needed to derive structural and chemical information, such as for example elemental and phase concentrations derived from the edge height [27].

The discrepancies between theory and experiment, between theory and theory, and between experiment and experiment led the International Union of Crystallography (IUCr) to conduct a study of problems associated with the measurement of x-ray mass attenuation coefficients [28,29]. The study found that systematic errors had not been quantified, leading to discrepancies greater than the individual measured uncertainty. Such measurements could not be used to distinguish among different theoretical approaches. The study found that a key tool for determining sources of error was to perform measurements on different thicknesses of absorbing material.



Nano-roughness in gold revealed from X-ray signature

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ARTICLE INFO

Article history:

Received 21 January 2009

Accepted 22 January 2009

Available online 31 January 2009

Communicated by V.M. Agranovich

PACS:

78.70.Dm

32.80.Aa

47.54.Jk

68.35.bd

68.35.Ct

Keywords:

Roughness

Materials characterisation

Synchrotron radiation

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.

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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 measure-

ment 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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Contents lists available at SciVerse ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Self-energy screening approximations in multi-electron atoms

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H I G H L I G H T S

- ▶ 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.

A R T I C L E I N F O

Article history:

Received 31 October 2012

Accepted 3 January 2013

Available online 11 January 2013

Keywords:

QED

Self-energy

GRASP

Screening

Atomic structure

A B S T R A C T

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.

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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

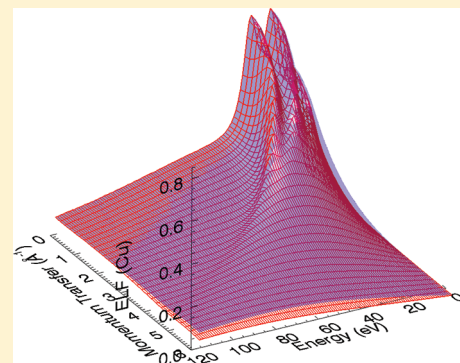
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Electron Energy Loss Spectra and Overestimation of Inelastic Mean Free Paths in Many-Pole Models

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ABSTRACT: We investigate established theoretical approaches for the determination of electron energy loss spectra (EELS) and inelastic mean free paths (IMFPs) in solids. In particular, we investigate effects of alternate descriptions of the many plasmon resonances that define the energy loss function (ELF), and the contribution of lifetime broadening in these resonances to the IMFP. We find that despite previously claimed agreement between approaches, approximations of different models consistently conspire to underestimate electron scattering for energies below 100 eV, leading to significant overestimates of the IMFP in this regime.



INTRODUCTION

The electron energy loss function is a prime quantifier of the interaction between a bulk material and a moving electron. It represents the probability of a scattering event in which the energetic electron transfers energy $\hbar\omega$ and momentum $\hbar q$ into the medium, via plasmon or single-electron excitations. Determination of the energy loss function is crucial for understanding elementary solid-state interactions and, in particular, is the principal determinant of the inelastic mean free path, a critical parameter in X-ray absorption fine structure,¹ X-ray photo- and auger-electron spectroscopy,² electron energy loss spectroscopy,³ imaging,⁴ and nanoscale structural determination.⁵ Through electron energy loss spectroscopy, the energy loss function provides detailed information regarding physical and electrical properties of materials⁶ and has even seen recent application in high profile work investigating the role of aerosols in climate change.⁷

It is standard to express the energy loss function of a given medium as the imaginary part of the negative inverse dielectric function, $\text{Im}[-1/\epsilon(q,\omega)]$. We define the real and imaginary parts of the energy- and momentum-dependent dielectric function as $\epsilon_1(q,\omega)$ and $\epsilon_2(q,\omega)$, so that we have

$$\text{Im}\left[\frac{-1}{\epsilon(q,\omega)}\right] = \frac{\epsilon_2(q,\omega)}{\epsilon_1^2(q,\omega) + \epsilon_2^2(q,\omega)} \quad (1)$$

General expressions for $\epsilon_1(q,\omega)$, $\epsilon_2(q,\omega)$, and $\text{Im}[-1/\epsilon(q,\omega)]$ can prove difficult to obtain for arbitrary solids, with intrinsically q -dependent theory claims typically limited to a few electronvolts above the Fermi level.⁸ First principles calculations may more readily be made, however, for the special case of a nearly free electron gas, in which electron interactions with a lattice potential are neglected.⁹ This result, referred to as the Lindhard equation for $\epsilon(q,\omega)$, can be used as a starting point for a general solid by implementing the statistical approximation.¹⁰ This

approximation treats the solid as a collection of small regions of definite charge density corresponding to nearly free electron gases. Accordingly, we can treat the energy loss function as a sum of Lindhard terms, where the Lindhard dielectric function is defined as follows:

$$\epsilon_L(q,\omega) = 1 + \frac{3\omega_p^2}{q^2 v_F^2} f \quad (2)$$

where

$$f = \frac{1}{2} + \frac{1}{8z} [1 - (z - u)^2] \ln\left[\frac{z - u + 1}{z - u - 1}\right] + \frac{1}{8z} [1 - (z + u)^2] \ln\left[\frac{z + u + 1}{z + u - 1}\right] \quad (3)$$

and

$$u = \frac{\omega}{qv_F} \quad (4)$$

$$z = \frac{q}{2q_F} \quad (5)$$

ω_p represents the plasma frequency of the nearly free electron gas, and v_F and q_F are the Fermi velocity and momentum, respectively. We can use eq 1 to determine the energy loss function (ELF) produced by each Lindhard term and sum together terms based on different ω_p 's, with different relative amplitudes. This allows us, in principle, to produce any arbitrary ELF at a given value of q .

The value of this approach arises from the availability of ELF data at $q = 0$ from either density functional theory¹¹ or, more

Received: October 20, 2011

Revised: February 6, 2012

Published: March 5, 2012