A Story of Copper

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https://www.ph.unimelb.edu.au/~chantler/opticshome/home.html

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In memoriam Ian Grant

Chanh Tran, Diamond Light Source, UK
Tony Kirk, Minh Dao, Paul di Pascale, Jack Stephens, Ramesh Rijal
Truong Nguyen, Jonathan Dean, Hamish Melia, Scott Thompson

Experimental: Zwi Barnea, Martin de Jonge, Stephen Best, Ryan Trevorah, Martin Schalken, Ruwini Ekanayake, Geoff Cousland, Marcus John, Daniel Sier, Nich Tran, Alexis Illig, Mark N Kinnane, Justin A Kimpton, Lucas F Smale, D Paterson, A Payne

- Diamond: Sofia Diaz-Moreno, J Fred W Mosselmans, Matteo Armani, Shusaki, Nitya
- James Hester [ANSTO], Dudley Creagh, Joel Brugger, Barbara Etschmann

Theory: Jay Bourke, Lucas Smale, Chris Witte, Andrew Hayward, John Lowe, Joni Pham, Feng Wang, Finn Jenssens, Paarangat Pushkarna, Yves Joly [CNRS]

A Story of Copper

The ultimate inner shell transition metal spectra

Copper is the most investigated X-ray source and target, the most studied with X-rays, one of the metals of the ancients. One of the most studied materials in history. Whereas hydrogen has defined and led to quantum mechanics, relativistic quantum mechanics and quantum electro-dynamics, and silicon has been developed as the core of the chip and nanotech industry, copper is one of the most stable and useful of transition metals. So, we should understand it. Really well! So, we should be able to tell a Story of Copper. This presentation will be such a story. However, the ending is complex, the physics is complex, and indeed we do not understand the X-ray spectra of copper yet, nor of any other material less well studied. There is a great and bright future for research and science for copper. We will present past and future challenges with copper and with inner shell X-ray spectra.

My first interactions with **Ian Grant** were during my doctorate with **Josh Silver** 1985-1990.
Some decades of this work on copper were with Ian, with **publications in 2009 through 2023**
14 publications co-authored with Ian.
With **four research students: A L C Hayward, J A Lowe, T V B Nguyen, T L H Pham**

On five main topics:

Cu Kα, Kβ
Ti Kα
Oxygen IR, UV
Self-energy: Welton Approximation for QED, the LCG method [Lowe Chantler Grant]
Convergence of the Breit interaction

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A Story of Copper

The most investigated X-ray source and target, the most studied with X-rays, one of the metals of the ancients. One of the most studied materials in history.

Hydrogen: quantum mechanics, relativistic quantum mechanics and quantum electro-dynamics; **silicon:** core of the chip and nanotech industry; **copper:** one of the most stable and useful of transition metals.

The ending is complex, the physics is complex, and we do not understand the X-ray spectra of copper yet, nor of **any other material** less well studied. There is a great and bright future for research and science for copper. We will present past and future challenges with copper and with X-ray spectra.

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Copper Z=29, Latin cuprum "from the island of Cyprus." Man's oldest metal, >10,000 years.
Copper pendant in northern Iraq dated to 8,700 BC. [Gold, Electrum]
High conductivity, thermal and electrical. Coinage metal, tools.

Copper age: end of Neolithic, New Stone Age.
Beginning of Metallurgy: in Mesopotamia as copper was used to make molds 4000 BC
Brass (Cu, 45% Zinc): 5000 BC
Bronze age (Cu, tin Sn, +) : 3500 BC - 1200 BC

A Story of Copper

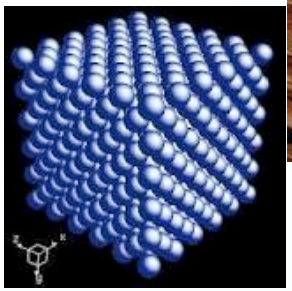
Chemistry: Oxidation state 0 (metals, alloys); +1 (Cuprous oxides etc.); +2 (Cupric oxides, etc.)
IR spectra, UV-Vis spectra, NMR [Valence levels, band structure]
Visible, optical properties … [band structure, relativistic QM, d electron eigenvalues]

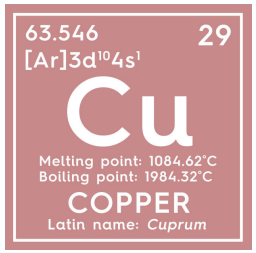
Physics: Group 11A Note Mendeleev [1869], Moseley [1913] K, L + new elements since
Edges: de Broglie [1913]
Ground state $[Ar]3d^{10}4s^1\ ^2S_{1/2}$
Quantum Mechanics [Heisenberg, Schrödinger, Dirac, Feynman, 1930s]

- **Copper anodes and X-ray spectra are well-defined**
- **The quality of experimental Copper Kα characteristic spectra is unmatched in the literature**
- **Important calibration tool**
- **Yet to be adequately theoretically explained!**

Copper isotopes, nuclear processes, gamma-spectra … see later talks from Canada
X-ray Diffraction, Neutron Diffraction [Crystal, space group, atomic sites]

- Space group: Fm-3m.
- Space group number: 225.
- Structure: ccp (cubic close-packed)
- Cell parameters: a: 361.49 pm. b: 361.49 pm. c: 361.49 pm. α: 90.000° β: 90.000° γ: 90.000°





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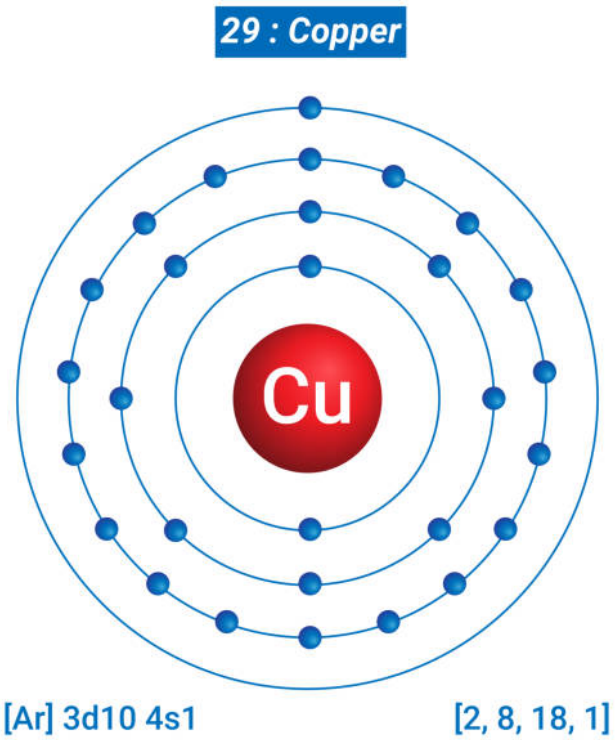
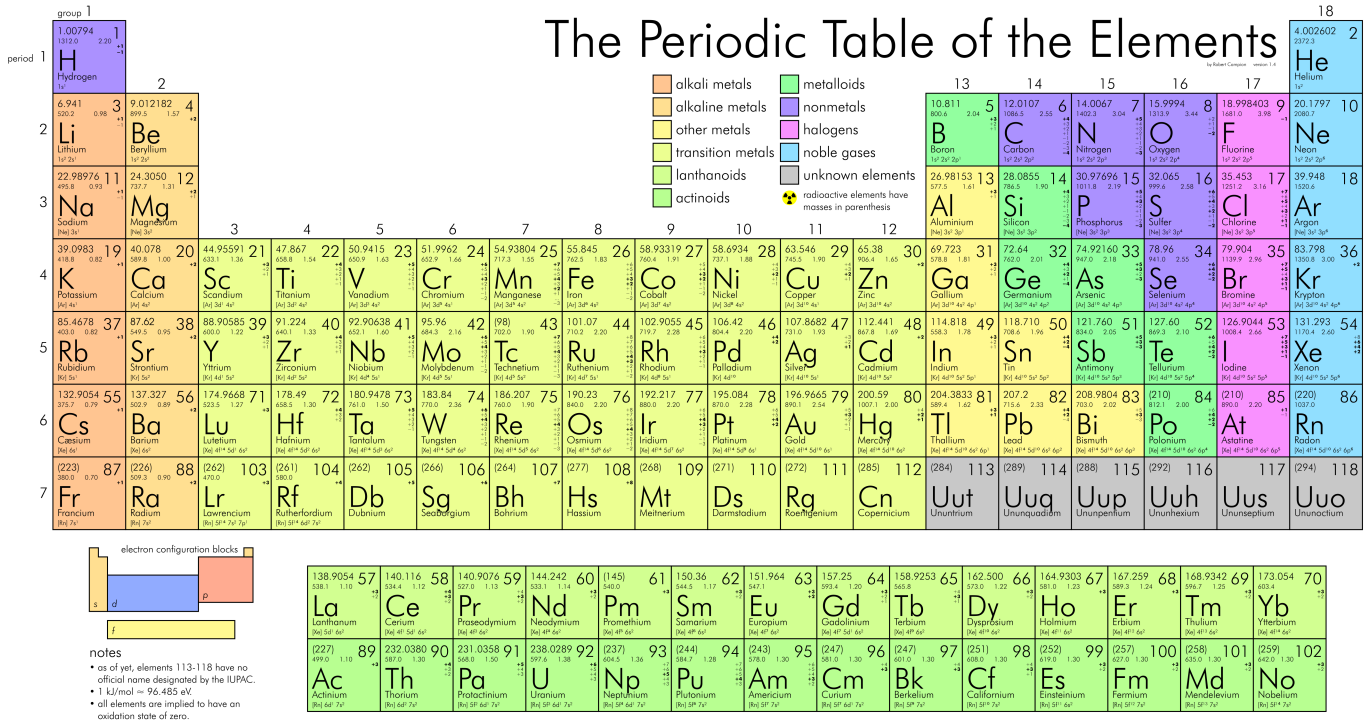
K-edge: 8980.476(20) eV $K\alpha_2^0$ 8027.8416(26) eV $K\alpha_1^0$ 8047.8227(26) eV $K\beta_1^0$ 8905.413(38) eV

LI, LII, LIII, M - edges: [PS you might use the little orange book, but the numbers are often incorrect]

So what do we know about the Relativistic Quantum Mechanics of Copper, and Why do we care?





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Classic [X-ray] spectra of copper: X-ray Absorption Spectra.
K edge. 1s 8.979 keV
L edges. LI $2s_{1/2}$ LII $2p_{1/2}$ LIII $2p_{3/2}$ 1096 - 932 eV Soft X-ray regime e.g. Bianconi 1988 Xu 2013
M edges. MI $3s_{1/2}$ MII $3p_{1/2}$ MIII $3p_{3/2}$ 122.5 eV - 75 eV. Soft X-ray or VUV regime. MIV $3d_{3/2}$ MV $3d_{5/2}$
N - conduction band for copper metal $4s_{1/2}$

XAS Compilations Hubbell[1995] [sparse] Chantler theory [1995, 2000]

[double crystal monochromators] [curved crystal, Johann]

Characteristic Spectra
e.g. Moseley 1914 Siegbahn1931 Parratt1936 BremerSorum1979 Sorum1987 Sauder1997 Deutsch+ 1995-2004 Mendenhall+ 2017
Compilations Bearden-Burr[1967] Desclaux[1973] Deslattes [2003]
Note C T Chantler, L F Smale, L T Hudson, ITC C, 4th edition, Section 4.2.2 X-ray Energies [2025]

Cu $K\alpha_2^0$ 8027.8416(26) eV $K\alpha_1^0$ 8047.8227(26) eV $K\beta_1^0$ 8905.413(38) eV
Cu $K\alpha_{1,2}$ 1s-2p Cu $K\beta_{1,3}$ 1s-3p Cu $K\alpha_{3,4}$ Cu $K\beta_{2,5}$ Cu Kα hypersatellite
Cu $L\alpha_{1,2}$ 2s-3p Soft X-ray regime
Cu $L\beta_{1,3}$ 2s-4p

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First X-ray spectra of copper 1913 - 1948+

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Optical and Quantum Electronics **31:** 495–505, 1999.

Precision X-ray optics for fundamental interactions in atomic physics, resolving discrepancies in the X-ray regime

C. T. CHANTLER, Z. BARNEA, C. Q. TRAN, J. B.
D. PATERSON
School of Physics. University of Melbourne. Parkville. Victoria 3052. Austr

X-RAY SPECTROMETRY
X-Ray Spectrom. 2000; **29**: 449–458

Monitoring fluctuations at a s beamline using matched ion c 1. modelling, data collection, simple measures of associatio

C. T. Chantler,[1]* C. Q. Tran,[1] D. Paterson,[1] Z. Barnea[1] a

X-Ray Spectrom. 2000; **29**: 459–466

Monitoring fluctuations at a s beamline using matched ion cl 2. isolation of component noise sources, and application to attenuation measurements showing increased precision by two orders of magnitude

GAMON

Radiation Physics and Chemistry 61 (2001) 347–350

www.elsevier.com/locate/radphys

Direct observation of scattering contributions in X-ray attenuation measurements, and evidence for Rayleigh scattering from copper samples rather than thermal-diffuse or Bragg–Laue scattering

C.T. Chantler[a,*], C.Q. Tran[a], D. Paterson[a], Z. Barnea[a], D.J. Cookson[b,c]

ELSEVIER

Physics Letters A 286 (2001) 338–346

www.elsevier.com/locate/pla

X-ray extended-range technique for precision measurement of the X-ray mass attenuation coefficient and Im(f) for copper using synchrotron radiation

C.T. Chantler [a,*], C.Q. Tran [a], D. Paterson [a], D. Cookson [b], Z. Barnea [a]

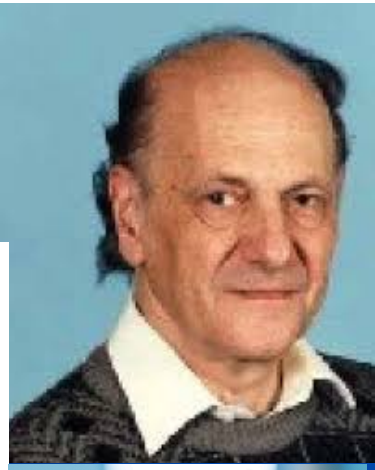
PHYSICAL REVIEW A, VOLUME 64, 062506

Measurement of the x-ray mass attenuation coefficient of copper using 8.85–20 keV synchrotron radiation

C. T. Chantler,[1] C. Q. Tran,[1] Z. Barnea,[1] D. Paterson,[1] D. J. Cookson,[2] and D. X. Balaic[1]
[1]*School of Physics, University of Melbourne, Victoria 3010, Australia*
[2]*ANSTO, Private Mail Bag 1, Menai, NSW 2234, Australia*
and Chem-Mat-CARS-CAT (Sector 15, Bldg 434D), Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois 60439

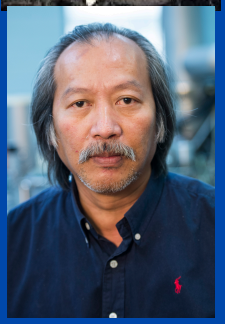
(Received 27 June 2001; published 19 November 2001)

This work presents the x-ray extended range technique for measuring x-ray mass attenuation coefficients. This technique includes the use of multiple foil attenuators at each energy investigated, allowing independent tests of detector linearity and of the harmonic contributions to the monochromated synchrotron beam. Measurements over a wide energy range allow the uncertainty of local foil thickness to be minimized by the calibration of thin sample measurements to those of thick samples. The use of an extended criterion for sample thickness selection allows direct determination of dominant systematics, with an improvement of accuracies compared to previous measurements by up to factors of 20. Resulting accuracies for attenuation coefficients of copper (8.84 to 20 keV) are 0.27–0.5 %, with reproducibility of 0.02%. We also extract the imaginary component of the form factor from the data with the same accuracy. Results are compared to theoretical calcula-



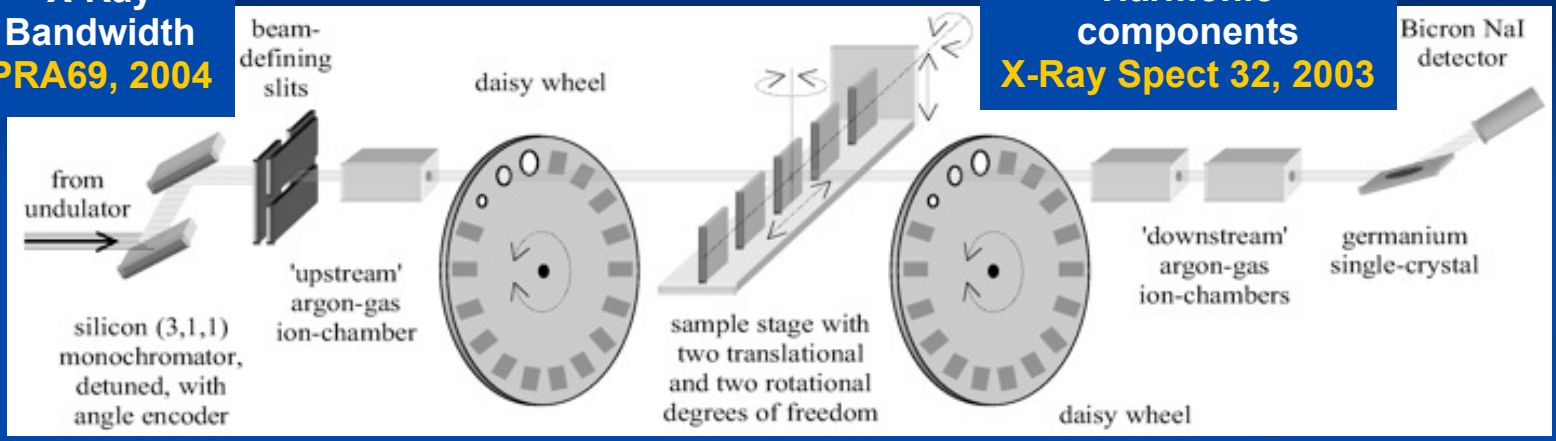
Transmission and Fluorescence X-ray Spectroscopy

X-ray Extended Range Technique: Determine [μ/ρ] accurately & quantify systematics



X-Ray Bandwidth
PRA69, 2004

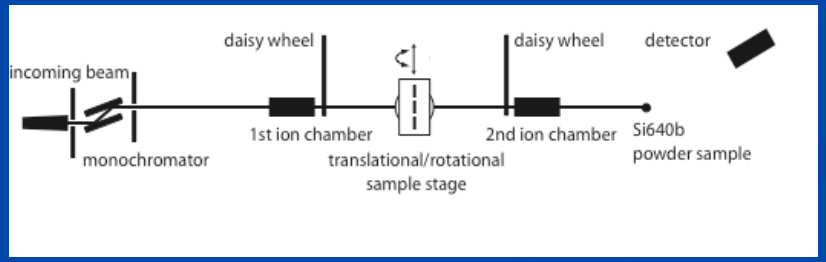
Harmonic components
X-Ray Spect 32, 2003



Optimisation of statistical level
X-Ray Spect 29, 2000

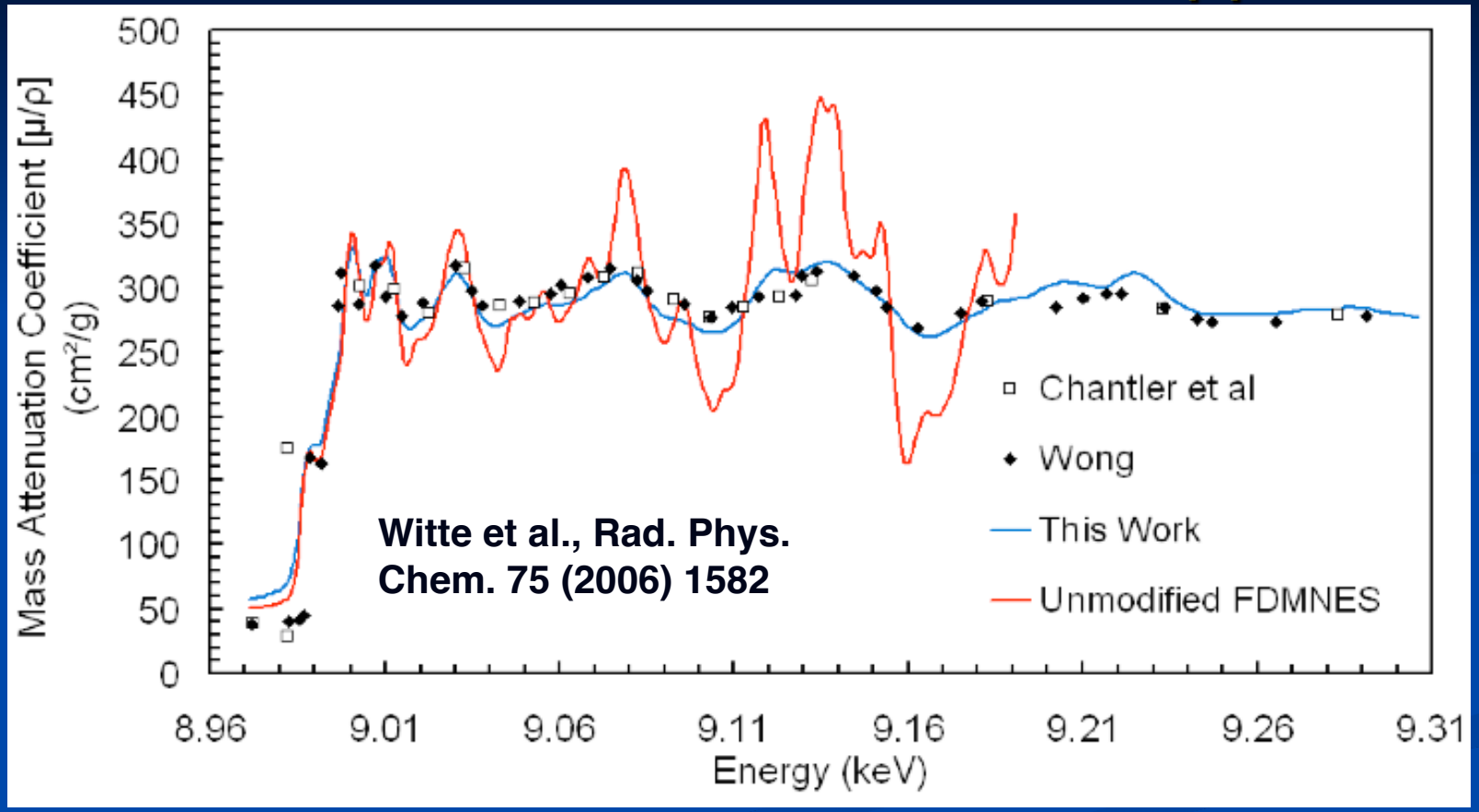
Sample thickness
Meas.Sci.&Technol.15, 2004
RSI 75, 2004

Fluorescence & scattering contributions
Rad.Phys.& Chem. 61, 2001
J.Phys.B37, 2004



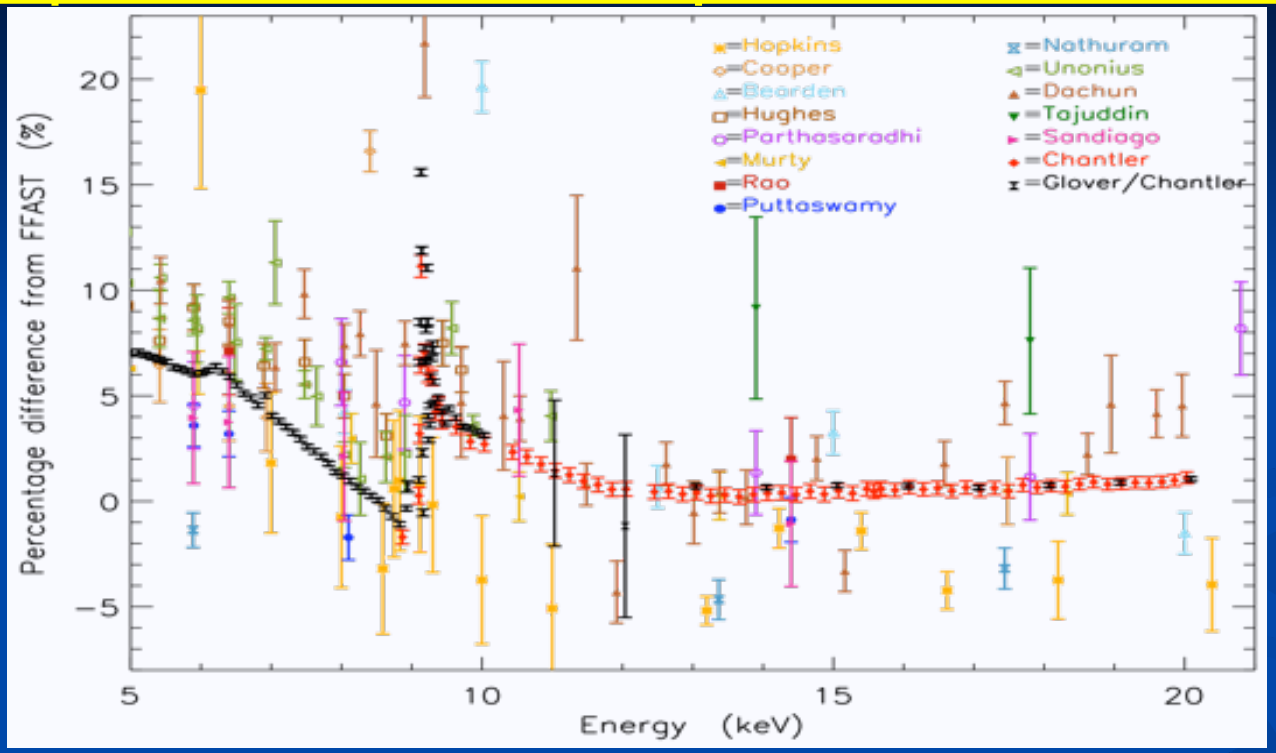
CT Chantler, Rad. Phys. Chem. 79 (2010) 117-123

FDMX: Solid State Structure - Copper



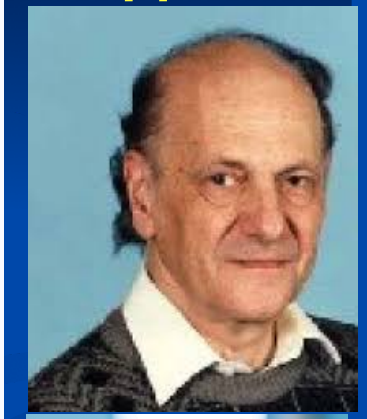
NO fitting parameter: **accurate** experiment and **accurate** theory **CAN** agree! FDMX

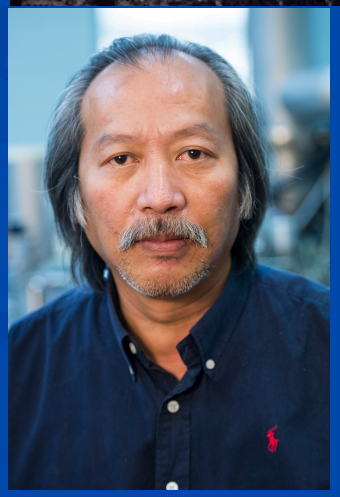
Question: Is it POSSIBLE or USEFUL to have any consistent experiment & beam-line independent method to 0.2% accuracy?



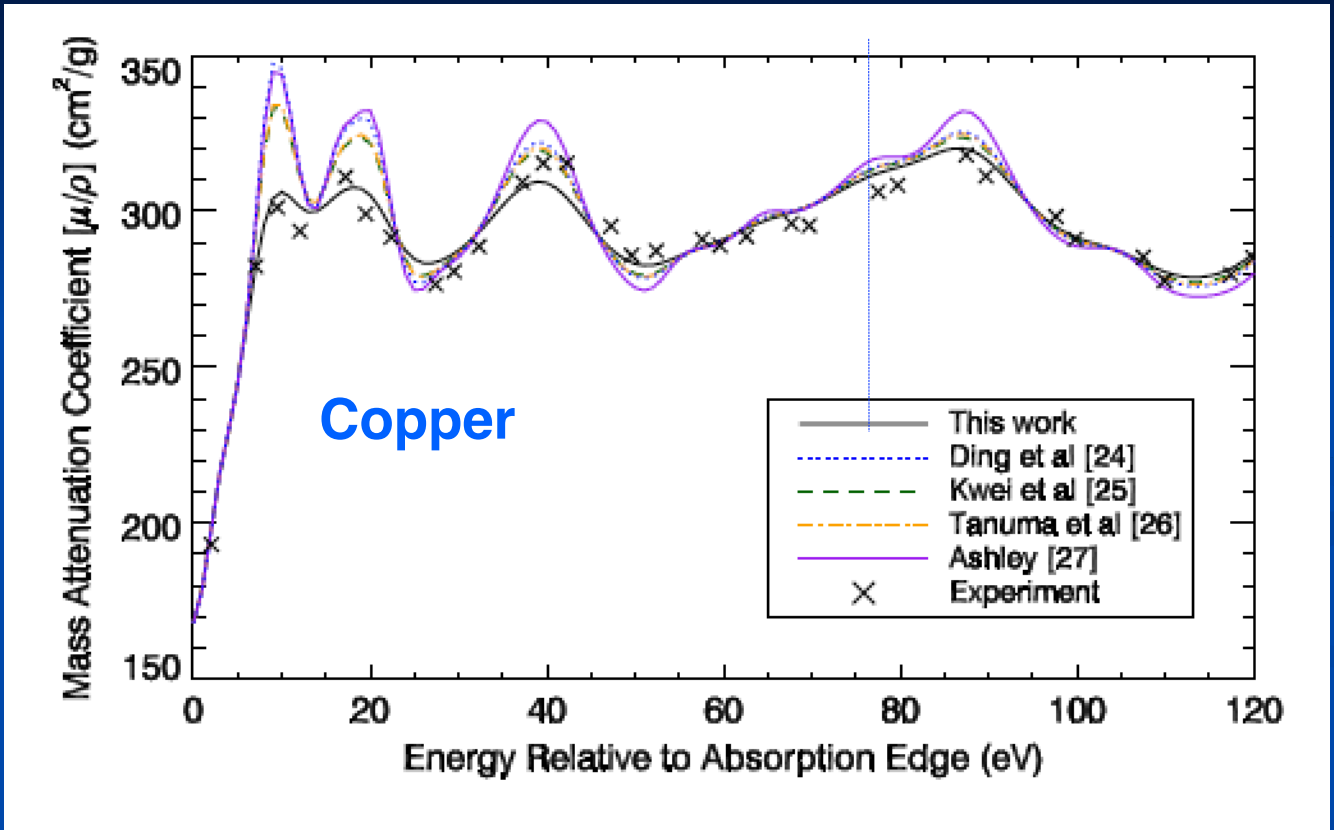
JL Glover, CT Chantler, Z Barnea, NA Rae, CQ Tran, DC Creagh, D Paterson, BB Dhal, Phys. Rev. A78 (2008) 052902

Copper:





Measurement with Uncertainty



- CQ Tran, CT Chantler, Z Barnea, Physical Review Letts 90 (2003) 257401-1-4
- JD Bourke, CT Chantler, Measurements of Electron Inelastic Mean Free Paths in Materials, Phys. Rev. Letters 104 (2010) 206601-1-4

Developing theory for XAFS:

Copper - plot of [μ/ρ] vs E

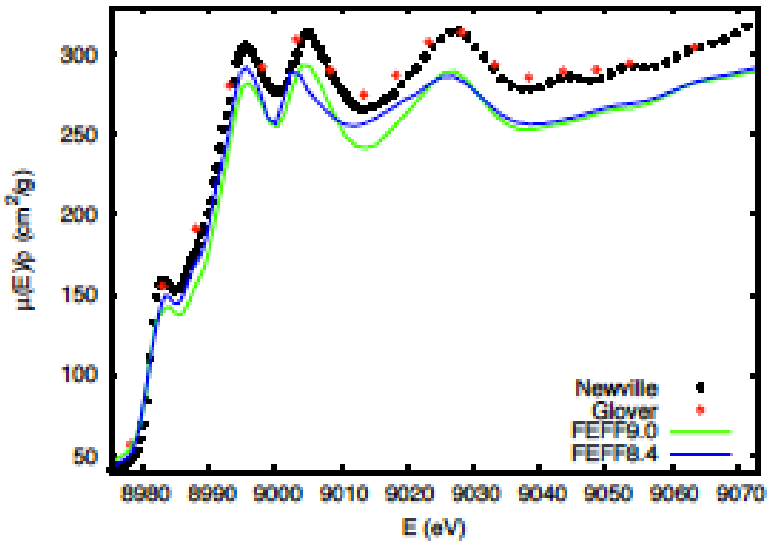


Figure 6: Comparison of experimental (red circles) Cu K-edge XANES [20] with calculations from FEFF90 (green) and FEFF84 (blue). In order to compare the details of the XANES calculation with experiment we have also included additional experimental data (black +) [21, 22], which has been scaled to match absolute measurement.

J. J. Kas, J. J. Rehr, J. L. Glover, C. T. Chantler, Comparison of Theoretical and Experimental Cu and Mo K-edge XAS, NIM A619 (2010) 28-32

Dynamic Bonding from XAFS:

Copper plot of the Fourier transform χ(r) vs r

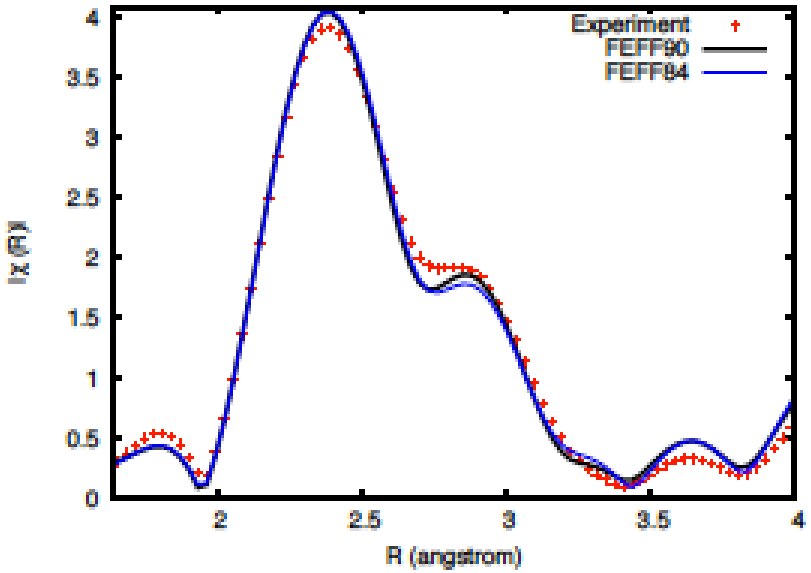
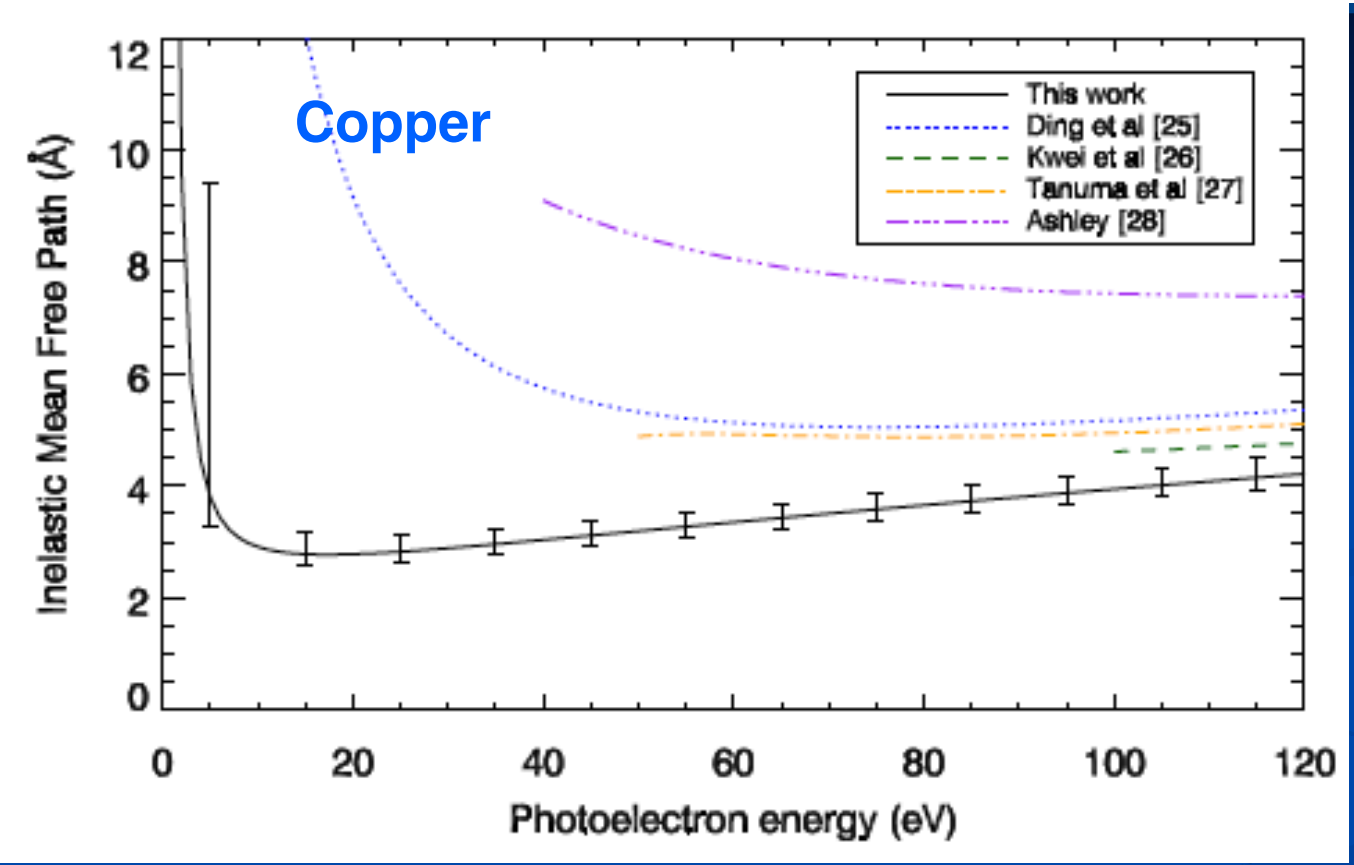


Figure 7: Best first shell fits of FEFF8.4 (blue) and FEFF90 (black) compared to experimental (red) EXAFS signal in R space. The fit range was 1.700 - 3.523 Å

J. J. Kas, J. J. Rehr, J. L. Glover, C. T. Chantler, Comparison of Theoretical and Experimental Cu and Mo K-edge XAS, NIM A619 (2010) 28-32

The first Encyclopaedia on XAFS: International Tables for Crystallography Volume I: XAS, Eds Chantler Bunker Boccherini 2024 > 500 cites

Measurement of plasmon-coupling



- Established theories appeared to overestimate the IMFP below 120 eV
  - JD Bourke, CT Chantler, Measurements of Electron Inelastic Mean Free Paths in Materials, Phys. Rev. Letts 104 (2010) 206601-1-4

MEASUREMENT OF PLASMON-COUPLING

- NEW Plasmon coupling theory (2014) – calculate *γ* using the loss spectrum itself

$$\lambda(E)_N^{-1} = \frac{\hbar}{a_o \pi E} \int_0^{\frac{E-E_F}{\hbar}} \int_{q_-}^{q_+} \int_0^{\infty} \frac{2}{\pi} \frac{\omega'}{q} \times \mathrm{Im}\left[\frac{-1}{\epsilon_{\mathrm{data}}(0,\omega')}\right] \times \mathrm{Im}\left[\frac{-1}{\epsilon_M(q,\omega,\gamma_i(q)_{N-1};\omega_p=\omega_i)}\right] d\omega' dq d\omega$$

$$\gamma_i(q)_N = \hbar \left.\frac{d\omega_q}{dq}\right|_{\omega_q,q} \lambda(E)_N^{-1} \Theta(N-\delta)$$

- **First physical, uniquely constrained optical data model since the Penn algorithm [1987]**
- **Self consistent from successive iterations – broadening comes from coupling between excitation channels**

Measurement of plasmon-coupling

- Broadening contributes a substantial reduction in IMFP from a fully lossless Lindhard model
- The reduction has a strong impact from excitations below the plasma frequency

- Agreement with experiment is improved greatly across all energies
- New predictions for low energy electron transport in any matter. Major differences below 200 - 300 eV, LEED, EELS, Monte Carlo, detector design

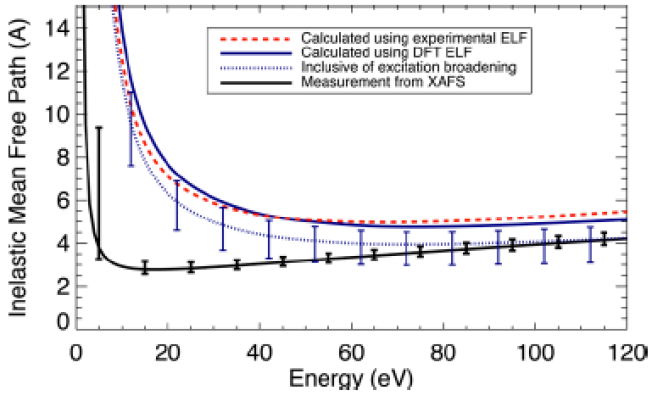


Figure 4. Electron inelastic mean free paths of copper calculated using theoretical optical loss data (solid blue curve) and measured optical loss data from Hagemann et al. (dashed red curve) compared with recent measurements using high-accuracy XAFS spectroscopy (black).[7] Also shown is a result inclusive of plasmon broadening quantified via a previous analysis of copper IMFPs (dotted blue curve),[14] along with a maximum-variational confidence interval.

Bourke, Chantler J Phys Chem A 118 (2014) 909

C T Chantler, J D Bourke, Low-energy electron properties: Electron inelastic mean free path, energy loss function and the dielectric function. Recent measuren the plasmon-coupling theory. Ultramicroscopy 201 Mar (2019) 38-48

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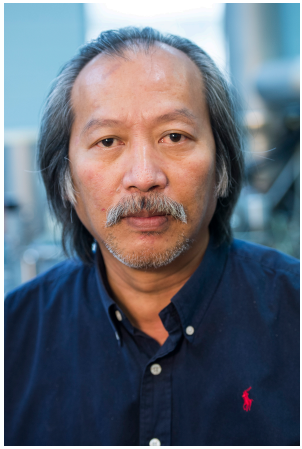
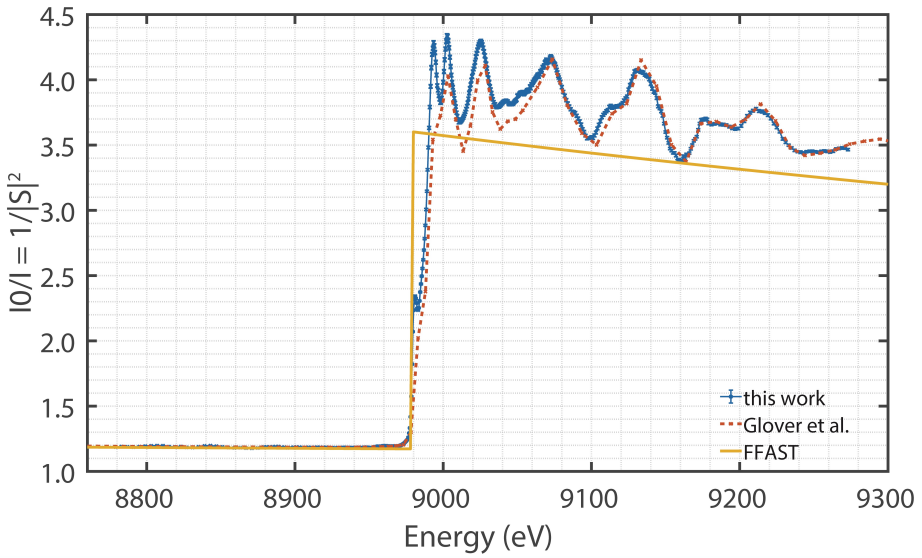
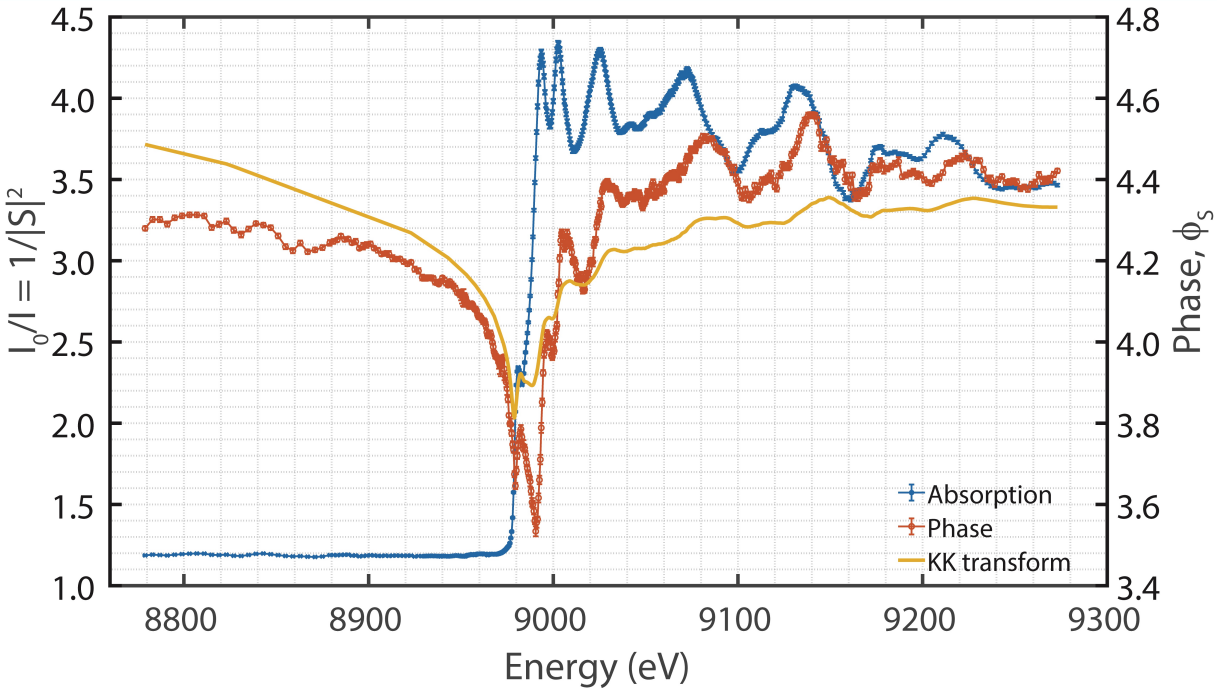
[C Q Tran et al.] the new field of

<u>Complex Atomic Fine Structure</u> measurement







A Story of Copper

1. X-ray Absorption and Fluorescence Spectra. Experiment.
2. X-ray Absorption and Fluorescence Spectra. Theory.
3. **X-ray Characteristic Spectra. Experiment.**
4. **X-ray Characteristic Spectra. Theory.**

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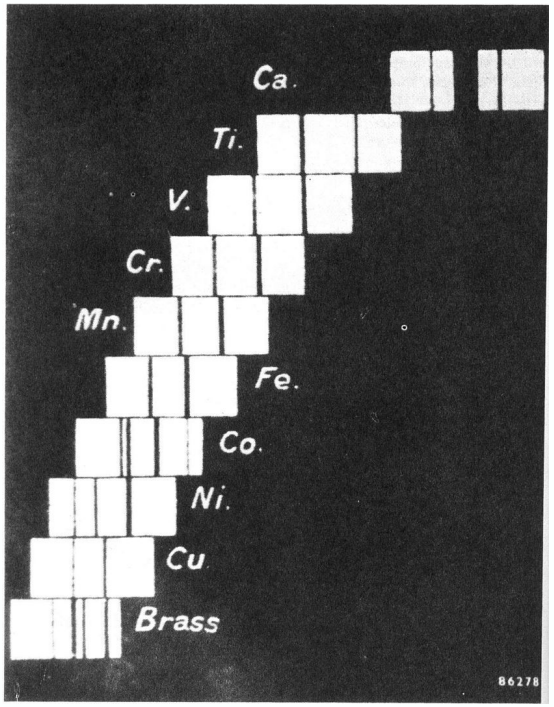

First characteristic spectra of copper
[X-ray] [K, L] 1914 - 1948+

A Story of Copper

Why study Characteristic radiation?

- Characteristic radiation provides a monochromatic, high intensity source of known energy, used in:
  - Astrophysics – e.g. for identifying the processes of star formation and properties of black holes. (Winkler, *The Astro. Journal* 1981), (Nguyen et al., *MNRAS* 2014), (Wilkins et al., *Nature* 2021)
  - Mining Industry - Monitoring and process of metal ores (Tickner et al. 2015 , *Rad. Phys. Chem.* 2015)
  - Environmental applications - measuring microplastics and marine pollutants (Turner et al., *Talanta* 2016), sorting of electronic waste (Bonifazi et al., *Recycling* 2021).
  - Medical research - advancement of medical radioisotopes (Lee et al. *Comp. & Math. Meth. in Med.* 2012)
  - Calibration standard in X-ray fluorescence and many fields – transferable standards for Cu Kα is critical.

- Characteristic radiation is a major international field of research, allowing us to test and understand fundamental physical processes:
  - Shake off process
  - Auger and Coster-Kronig transitions
  - Radiative Auger emission
- Research into Characteristic radiation also allows:
  - Accurate test for multi-configuration Dirac-Fock theory. (Pham et al. *J. Phys. B* 2016)
  - High accuracy tests of QED - Anomalous He-like Ti spectra (Payne et al. *J. Phys. B* 2014)
  - Determination of peak energies to the ppm level (Dean et al., *J Phys. B* 2019)
  - Measuring hole widths, binding energies, fluorescence yields and intensity ratios
  - *Ab initio* calculations of complex, many-body systems (Nguyen et al., *Phys. Rev. A* 2022)
  - Comparison of computational methods and software.

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A Story of Copper

CHARACTERISTIC SPECTRA: A "SIMPLE" PROBLEM

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$$i\frac{\partial}{\partial t}\Psi = \sum_i^N \left(\beta c^2 + c\alpha\cdot p\right)\psi + \sum_{i<j}^N \left(\frac{1}{|r_i - r_j|}\right.$$

$$\left. + c^2(\alpha_i\cdot\nabla_i)(\alpha_j\cdot\nabla_j)\frac{\cos\left(\frac{|\omega_i-\omega_j||r_i-r_j|}{c}\right)-1}{|\omega_i-\omega_j|^2|r_i-r_j|}\right)$$

Calculating many-electron atom wavefunctions MCDHF

Electron correlation → multiconfiguration Dirac Hartree Fock method (MCDHF).

Relativistic → Dirac equation: $$i\hbar\frac{\partial\phi}{\partial t} = \left(c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2 + \frac{Ze^2}{4\pi\epsilon_0 r}\right)\phi \;\rightarrow\; \phi_{E\kappa m} = \frac{1}{r}\begin{bmatrix} P_{E\kappa}(r)\chi_{\kappa m}(\theta,\varphi) \\ iQ_{E\kappa}(r)\chi_{-\kappa m}(\theta,\varphi)\end{bmatrix}$$

Our atomic state wavefunction is approximated as a linear combination of **configuration state functions** (CSFs).

$$\Psi \approx \sum_j^n c_j\phi_j$$

CSFs are obtained by taking the Slater determinants of excited state electron configurations. eg. , the helium atom wavefunction is approximated:

$$\Psi \approx c_1\phi(1s^2)+c_2\phi(1s^12s^1)+c_3\phi(2s^2)+c_4\phi(1s^12p^1)+c_5\phi(2s^12p^1)+c_6\phi(2p^2)\ldots$$

The number of possible CSFs is infinite. Therefore we must limit their number by choosing a cut-off subshell.

The subshells for which excitations are allowed (into and out of) form what we call the **Active Set**. *e.g.:*

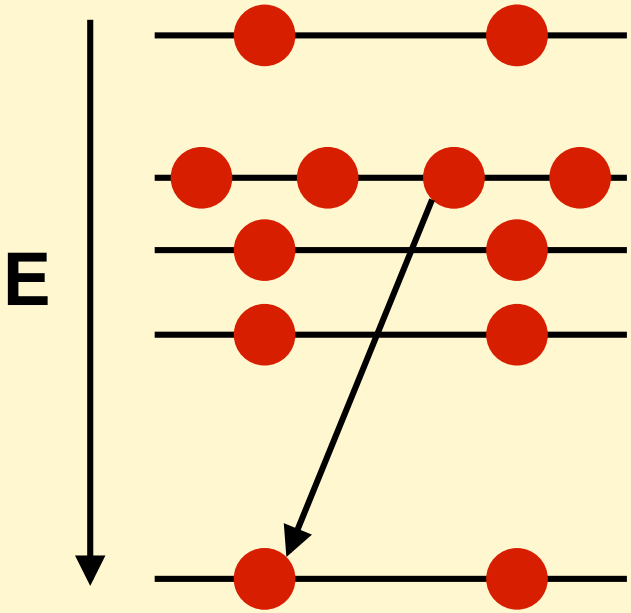
$$\text{Single configuration: } \Psi(He) \approx c_1\phi(1s^2)$$

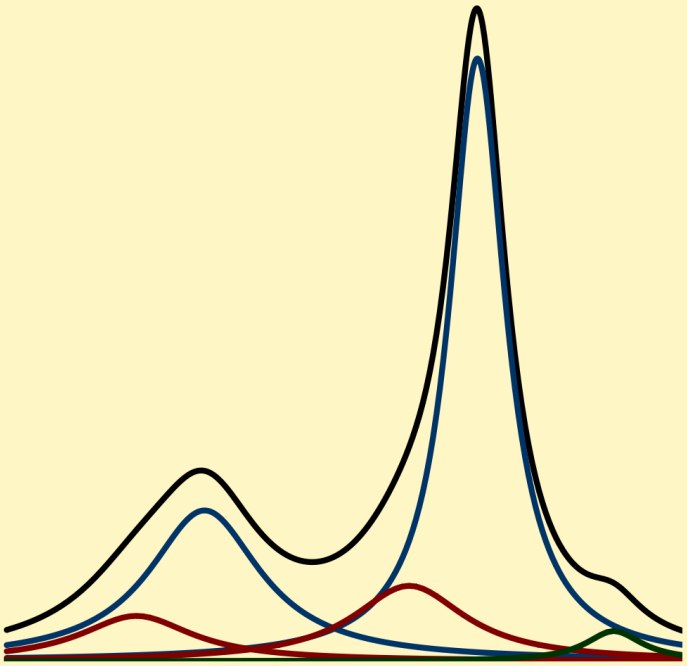
$$\text{Active set up to 2s: } \Psi(He) \approx c_1\phi(1s^2) + c_2\phi(1s^12s^1) + c_3\phi(2s^2)$$

$$\text{Active set up to 2p: } \Psi(He) \approx c_1\phi(1s^2) + c_2\phi(1s^12s^1) + c_3\phi(2s^2) + c_4\phi(1s^12p^1) + c_5\phi(2s^12p^1) + c_6\phi(2p^2)$$

A Story of Copper

The Kα Spectrum





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A Story of Copper

PRL **103,** 123002 (2009) PHYSICAL REVIEW LETTERS week ending 18 SEPTEMBER 2009

Theoretical Determination of Characteristic X-Ray Lines and the Copper $K\alpha$ Spectrum

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I. P. Grant
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(Received 9 May 2009; published 16 September 2009)

Core excitations above the K edge result in $K\alpha$ characteristic x-ray emission. Understanding these spectra is crucial for high accuracies in investigations into QED, near-edge x-ray structure and advanced crystallography. We address unresolved quantitative discrepancies between experiment and theory for copper. These discrepancies arise from an incomplete treatment of electronic interactions. By finding solutions to relativistic multiconfigurational Dirac-Fock equations accounting for correlation and exchange corrections, we obtain an accurate reproduction of the peak energies, excellent agreement of theory with experiment for the line shapes, good convergence between gauges, and account for the $K\alpha$ doublet ratio of 0.522 ± 0.003:1.

A Story of Copper

PHYSICAL REVIEW A **82**, 052505 (2010)

Multiconfiguration Dirac-Fock calculations in open-shell atoms: Convergence methods and satellite spectra of the copper $K\alpha$ photoemission spectrum

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I. P. Grant
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(Received 18 August 2010; published 8 November 2010)

The copper $K\alpha$ photoemission spectra is one of the most widely studied. Recent Dirac-Fock calculations have produced transition energies in good agreement with experiment, though they have relied on approximations that may not be transferable to other complex atoms in which uncertainties in theoretical results are dominated by poor convergence. Through a detailed examination of convergence issues in the copper spectrum, we consider the accuracy obtainable with the multiconfiguration Dirac-Fock (MCDF) method, provide the first determination of fine structure contributions to the spectrum, and demonstrate reliable techniques for modeling spectator states with vacancies in the $3p$, $3d$, and $4s$ shells.

PHYSICAL REVIEW A **83**, 060501(R) (2011)

Ab initio determination of satellite intensities in transition-metal photoemission spectroscopy using a multiconfiguration framework

J. A. Lowe and C. T. Chantler*
School of Physics, University of Melbourne, Australia

I. P. Grant
Mathematical Institute, Oxford University, Oxford, United Kingdom
(Received 8 March 2011; revised manuscript received 11 June 2011; published 30 June 2011)

Following atomic photoionization, the abrupt change in potential can lead to secondary ionization of an outer-shell electron in a phenomenon known as shake-off, a process which gives rise to the asymmetric $K\alpha$ profile and satellite lines. Investigation of chemical effects and relativistic quantum mechanics requires a theoretical determination of these satellite intensities; however, existing theoretical predictions are inconsistent with experimental results by up to an order of magnitude. Previously theoretical modeling required up to 12 fitting parameters to account for transition widths, energy corrections, spectator intensities, and spectator broadening. Using a multiconfiguration atomic model to account for electron-electron correlation, we provide here the first *ab initio* calculations of shake-off probabilities which are in agreement with experimental results (except for copper), an important step toward a complete theoretical profile.

PHYSICAL REVIEW A **85**, 032513 (2012)

Anomalous satellite intensity discrepancy in copper x-ray lines

C. T. Chantler* and J. A. Lowe
School of Physics, University of Melbourne, Melbourne, Australia

I. P. Grant
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(Received 25 October 2011; published 16 March 2012)

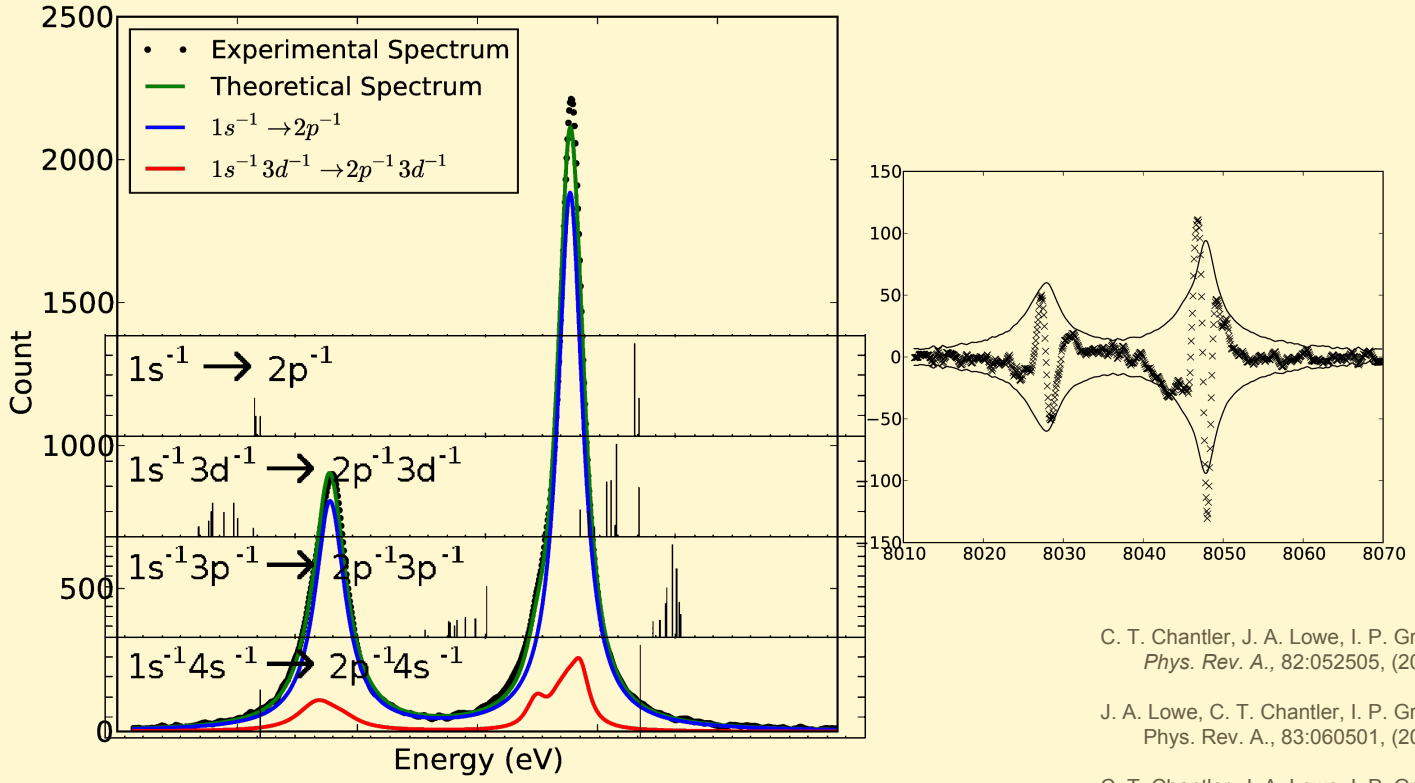
The copper $K\alpha$ spectrum contains asymmetries and satellite features due to secondary electron emission during ionization. Theoretical attempts at determining the intensities of these features are highly discrepant from experimental results. This discrepancy has been the subject of much discussion. In the present work we show that widely applied fitting procedures produce satellite intensities which depend strongly on assumptions regarding parametrization. We also show that recent high-accuracy satellite calculations can provide a copper $K\alpha$ spectrum in good agreement with experiment, thus resolving the discrepancy. This represents a major step toward a complete *ab initio* x-ray spectrum, a goal with significant implications for astrophysics, plasma physics, and tests of quantum electrodynamics.

Jun **2025** CT Chantler CompAS Lund

A Story of Copper

THE UNIVERSITY OF MELBOURNE

Copper Kα Photoemission Spectrum



Experimental Data: Deutsch et al., Phys. Rev. A., 51: 283, (1995)

C. T. Chantler, J. A. Lowe, I. P. Grant. *Phys. Rev. A.,* 82:052505, (2010)

J. A. Lowe, C. T. Chantler, I. P. Grant. Phys. Rev. A., 83:060501, (2011)

C. T. Chantler, J. A. Lowe, I. P. Grant. *Phys. Rev. A.,* 85: 032513, (2012)

A Story of Titanium

Physics Letters A 374 (2010) 4756–4760

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

A new approach to relativistic multi-configuration quantum mechanics in titanium

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Atomic structure
Photoionization
MCDF
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ABSTRACT

Multiply-ionized atoms in plasmas and astronomical systems are predominantly of intermediate atomic numbers with open electron shells. The spectra seen in laboratory plasmas and astrophysical plasmas are dominated by characteristic $K\alpha_{1,2}$ photoemission lines. Modelling these transitions requires advanced relativistic frameworks to begin to formulate solutions. We present a new approach to relativistic multi-configuration determination of $K\alpha_{1,2}$ diagram and satellite energies in titanium to a high level of convergence, allowing accurate fitting of satellite contributions and the first agreement with profile to negligible residuals. These developments also apply to exciting frontiers including temporal variation of fundamental constants, theoretical chemistry and laboratory astrophysics.

IOP PUBLISHING — JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

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High-accuracy reconstruction of titanium x-ray emission spectra, including relative intensities, asymmetry and satellites, and *ab initio* determination of shake magnitudes for transition metals

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Abstract
High resolution x-ray spectroscopy has revealed a complex structure in the spectrum of core-ionized elements. To date, theoretical reproductions must be fitted to experimental results using fitting parameters to account for transition widths, energy corrections, spectator intensities and spectator broadening—up to 12 or more parameters depending on complexity. We provide here the first accurate reconstruction of the $K\alpha$ spectra in titanium using only instrumental broadening widths as free parameters. We also determine structural systematics in observed shake processes in transition metals for the first time.

Jun **2025** CT Chantler CompAS Lund

A Story of Solar and Astrophysics

The Astrophysical Journal, 769:84 (5pp), 2013 May 20 doi:10.1088/0004-637X/769/1/84

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

Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY
MNRAS **440,** 3439–3443 (2014) doi:10.1093/mnras/stu511

Advanced ab initio relativistic calculations of transition probabilities for some O I and O III emission lines

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[2] *Mathematical Institute, Oxford University, Oxford, OX1 3LB, UK*

Accepted 2014 March 11. Received 2014 March 7; in original form 2013 January 21

ABSTRACT

This work presents new ab initio relativistic calculations using the multiconfiguration Dirac–Hartree–Fock method of some O I and O III transition lines detected in B-type and Wolf–Rayet stars. Our results are the first able to be presented in both the length and velocity gauges, with excellent gauge convergence. Compared to previous experimental and theoretical uncertainties of up to 50 per cent, our accuracies appear to be in the range of 0.33–5.60 per cent, with gauge convergence up to 0.6 per cent. Similar impressive convergence of the calculated energies is also shown. Two sets of theoretical computations are compared with earlier tabulated measurements. Excellent agreement is obtained with one set of transitions but an interesting and consistent discrepancy exists between the current work and the prior literature, deserving of future experimental studies.

Jun **2025** CT Chantler CompAS Lund

A Story of LCG Welton Self-energy

Radiation Physics and Chemistry 85 (2013) 118–123

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Radiation Physics and Chemistry

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

Self-energy screening approximations in multi-electron atoms

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[b] Mathematical Institute, Oxford University, Oxford, UK

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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Atomic structure

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.

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Electron self-energy corrections using the Welton concept for atomic structure calculations

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ARTICLE INFO

Keywords:
Self energy
Hydrogenic screening
Atomic structure
QED

ABSTRACT

The high level of accuracy achieved by atomic experiments in recent time has shone a spotlight on the need for a similarly high level of accuracy in atomic structure calculations, and in particular, QED prediction. A method of electron self-energy correction originally derived from the Welton idea by Lowe et al. (2013) (LCG-Welton method) has now been fully incorporated into the popular atomic structural package, GRASP2K, which we have introduced in this paper. A series of benchmark tests and results are presented, which enables the comparison of the implementations of different versions of GRASP2K, and the implementations on different platforms or operating systems. Test results presented in this paper demonstrate that these new implementations maintain the overall consistency and stability of the program across various platforms, while at the same time improve the accuracy of final energies. Our calculations for hydrogenic Ly$\alpha_{1,2}$ transitions show excellent agreement with experiment, to within less than 0.5 eV. On helium-like systems, our calculations show an improvement from the previous GRASP2K screening method. The new results from electronic self-energy contribution using the LCG-Welton method is more consistent with current standards in the literature, where they now fit within experimental variability of up to 0.1 eV. An option for users to adjust the gauge factor in the electric component of the transition rate has also been added to facilitate further investigation of this particular topic.

Jun **2025** CT Chantler CompAS Lund

A Story of Breit in GRASP

PHYSICAL REVIEW A **90**, 062504 (2014)

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

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I. P. Grant
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(Received 15 October 2014; published 8 December 2014)

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.

A Story of Copper

The characteristic radiation of copper $K\alpha_{1,2,3,4}$

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A characterization of the Cu $K\alpha_{1,2}$ spectrum is presented, including the $2p$ satellite line, $K\alpha_{3,4}$, the details of which are robust enough to be transferable to other experiments. This is a step in the renewed attempts to resolve inconsistencies in characteristic X-ray spectra between theory, experiment and alternative experimental geometries. The spectrum was measured using a rotating anode, monolithic Si channel-cut double-crystal monochromator and backgammon detector. Three alternative approaches fitted five Voigt profiles to the data: a residual analysis approach; a peak-by-peak fit; and a simultaneous constrained method. The robustness of the fit is displayed across three spectra obtained with different instrumental broadening. Spectra were not well fitted by transfer of any of three prior characterizations from the literature. Integrated intensities, line widths and centroids are compared with previous empirical fits. The novel experimental setup provides insight into the portability of spectral characterizations of X-ray spectra. From the parameterization, an estimated $3d$ shake probability of 18% and a $2p$ shake probability of 0.5% are reported.

J. Phys. B: At. Mol. Opt. Phys. **49** (2016) 035601 (14pp) doi:10.1088/0953-4075/49/3/035601

Characterization of the copper $K\beta$ x-ray emission profile: an *ab initio* multi-configuration Dirac–Hartree–Fock approach with Bayesian constraints

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[2] Mathematical Institute, Andrew Wiles Building, Radcliffe Observatory Quarter, Woodstock Road, OX2 6GG, UK
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Abstract

We investigate the $K\beta$ characteristic radiation and the complex asymmetric structure of photoemission lines of copper, which provides a benchmark for theoretical and experimental studies of x-ray calibration series in transition metals. *Ab initio* multi-configuration Dirac–Hartree–Fock (MCDHF) calculations have been performed to study the complex open-shell many-electron problem in copper. The biorthogonalization technique permits determination of transition intensities and Einstein A coefficients. The results from our MCDHF calculations demonstrate excellent convergence in transition energies and intensities, as well as gauge invariance to 0.6%. Shake processes caused by single and double spectator vacancies from 3d, 3p, 3s and 4s subshells have also been investigated extensively. MCDHF has been performed to calculate energies and relative intensities of 3d, $3d^2$, 3p, 3s and 4s satellites, resulting in the total number of configuration states exceeding 100 000 and more than 1500 transition components. Our theoretical calculations of shake-off probabilities using the multi-configuration method in the sudden limit have a high degree of internal consistency with the best available experimental data for copper $K\beta$. This supports the validity of relativistic atomic theory and sets a new benchmark even for poorly resolved characteristic spectra using current techniques of analysis.

Jun **2025** CT Chantler CompAS Lund

A Story of Copper

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Physics Letters A

www.elsevier.com/locate/pla

Theory of copper $K\alpha$ and $K\beta$ diagram lines, satellite spectra, and *ab initio* determination of single and double shake probabilities

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ABSTRACT

High-accuracy MCDHF Cu $K\alpha$ and Cu $K\beta$ diagram spectra and major satellites are presented. Spectral eigenvalues reach a theoretical expansion convergence of 0.03 eV or 0.00025%, with gauge and amplitude convergence to 0.7% for Cu $K\alpha$ diagram spectra. Dominant theoretical spectral eigenvalues are shown to be within 0.032 eV of experimental data. *Ab initio* shake-off contributions are presented in terms of total probability from each subshell and as separated single and double shake probabilities. Discrepancies between theory and experiment in copper X-ray spectra arise from profile asymmetries, relativistic terms and shake spectra not yet accounted for. These results and this improved agreement provide key fundamental parameters for processes towards XFEL evolution and resolving key discrepancies between theory and experiment.

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

Ab initio calculations of Auger electron kinetic energies: Breadth and depth

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ARTICLE INFO

Keywords:
Auger electron spectroscopy
X-ray physics
X-ray spectroscopy
Relativistic quantum mechanics

ABSTRACT

Ab initio theoretical calculations for Auger electron kinetic energies are presented for twenty prominent Auger peaks for the 3*d* transition metals ($21 \leq Z \leq 30$). These are the twenty Auger peaks listed for these elemental solids in the National Institute of Standards and Technology (NIST) X-ray photoelectron spectroscopy database. Adding to these values, over one hundred Auger electron kinetic eigenenergies are calculated for titanium. Many of these transition lines are not established in current literature due to their relatively small yields and overlapping widths. These data can be of importance for determination of previously unaccounted Auger electron peaks with titanium and will be useful for X-ray fluorescence studies into the radiative Auger effect. The consistency between our values and the empirical data is an improvement compared with previous binding energy approaches and the methodology is convergent. The methods presented can be extended to other elements for future investigations of Auger electron kinetic energies which is particularly useful where current experimental values do not exist. Furthermore, these calculations provide evidence in the success of multiconfigurational Dirac–Hartree–Fock approaches in complex quantum mechanics.

PHYSICAL REVIEW A **107**, 012809 (2023)

Cu $K\alpha_{3,4}$ satellite spectrum with *ab initio* Auger-rate calculations

H. A. Melia, J. W. Dean, T. V. B. Nguyen, and C. T. Chantler
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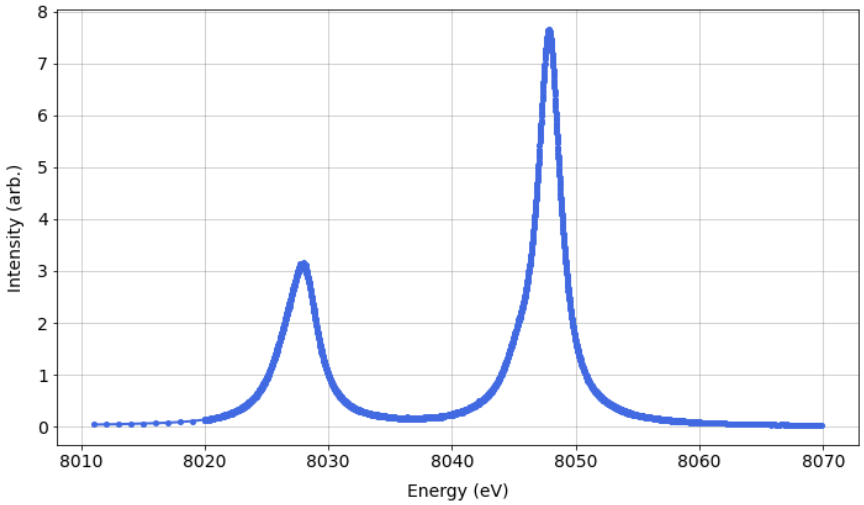
This work investigates the capability of the multiconfiguration Dirac-Hartree-Fock (MCDHF) method in predicting the Cu $K\alpha_{3,4}$ spectrum. *Ab initio* energy eigenvalues, relative intensities, and radiative widths are calculated for the Cu 2*p* and 2*s* satellite transitions. By fitting to the most accurate experimental Cu $K\alpha_{3,4}$ spectra available, we show that our 2*p* satellite energy eigenvalues agree with experiment to within 0.35 eV and that our 2*p* shake probability agrees with the 2*p* fitted intensity to within 0.05%. Our fits suggest a $I(2s)$:$I(2p)$ satellite intensity ratio (as a percentage of the total $K\alpha$ spectrum) of 0.03(1):0.76(1) Theoretical predictions of this ratio can be examined using shake probabilities. We calculate the probability of shake-off due to the sudden creation of a 1*s* hole in Cu, yielding an *ab initio* $I(2s)$:$I(2p)$ shake probability ratio of 0.194:0.742. Using MCDHF, the rates at which hole states, created through the shake processes, depopulate via Auger transitions are determined. These results explain the apparent discrepancy between experimental satellite intensities and shake probabilities, and characterize the Cu $K\alpha_{3,4}$ spectrum with a satellite intensity ratio of 0.04(1):0.76, consistent with the experiment.

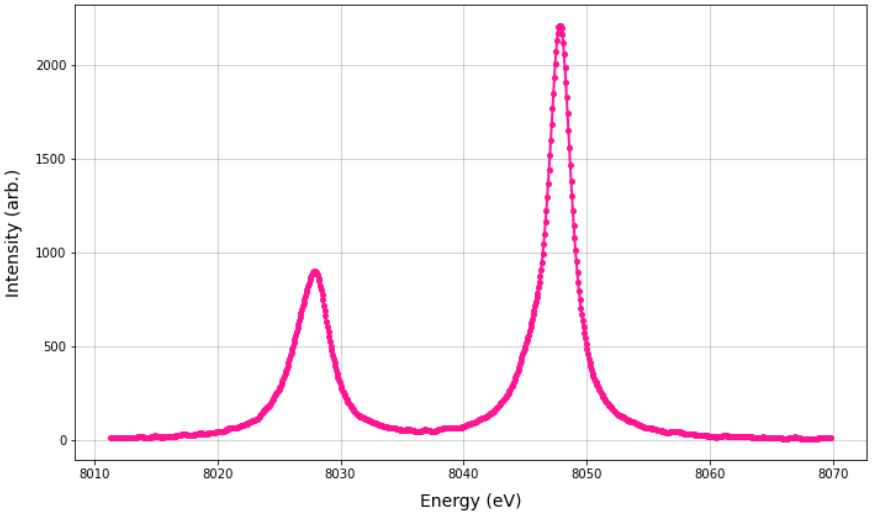
Jun **2025** CT Chantler CompAS Lund

A Story of Copper

Copper Kα Experimental Spectra



Mendenhall et al.



Deutsch et al.

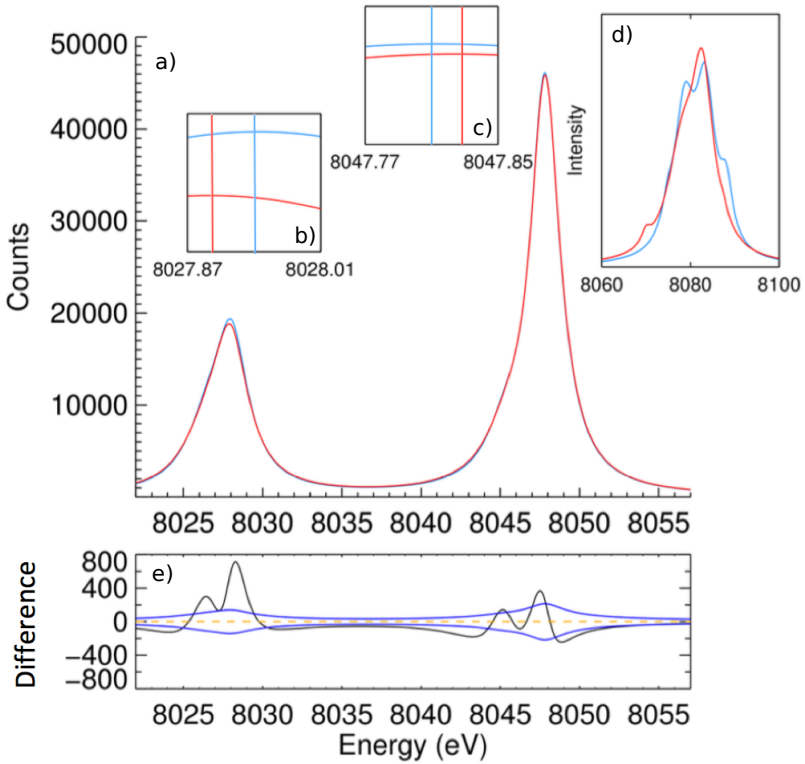
Mendenhall, Marcus H., et al. *Journal of Physics B: Atomic, Molecular and Optical Physics* 50.11 (2017): 115004.
Deutsch, M., et al. Physical Review A 51.1 (1995) 283

A Story of Copper

- **New experiment can see complex Auger and satellite processes for the first time**
- [J W Dean, The Auger effect and its applications. H A Melia, Characteristic Spectral Profiles: Copper Kα and Kβ]

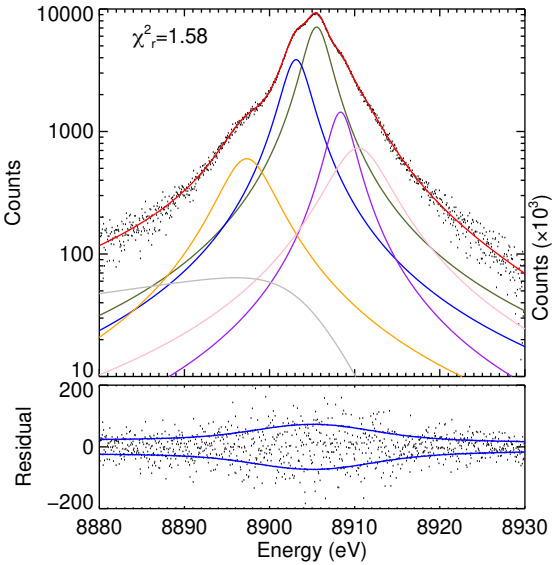
- J W Dean C T Chantler, L F Smale, H A Melia, High Accuracy Characterisation for the Absolute Energy of Scandium Kα, J Phys B 52 (2019) 165002 – 1 -12; H A Melia, C T Chantler, L F Smale, A J Illig, The Characteristic Radiation of Copper Kβ including radiative Auger processes, J Phys B 53 (19) (2020) 195002-1-12; J W Dean C T Chantler, L F Smale, H A Melia, An Absolute Energy Measurement of Scandium Kβ to 2 parts per million, J Phys B53 (2020) 205004 – 1 - 10.

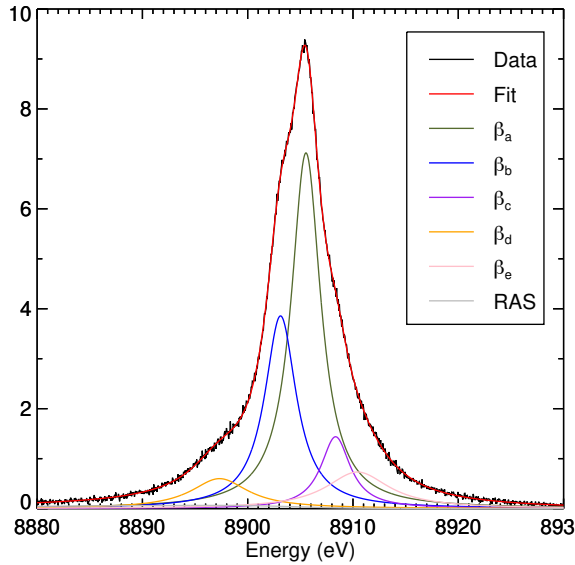
- Mendenhall+: Most accurate characteristic spectrum to date; compared with Deutsch, Fritsch+, the best for 20 years …
- a) Cu $K\alpha_{1,2}$: red line Holzer+ 1997, blue line Mendenhall+ 2017 b) Parametrisations around $K\alpha_2$. The vertical lines indicate the maximum of each profile characterisation c) Parametrisations around $K\alpha_1$. d) Parametrisations of $K\alpha_{34}$ Mendenhall+ 2017 (blue); Fritsch+ 1998 (red) e) The difference between the two characterisations (black line) is structured and larger than the s.e. (dark blue) indicating locations of disagreement between the parametrisations



A Story of Copper

- New experiment can see complex Auger and satellite processes for the first time
- Cu Kβd The origin of the low energy contribution (Kβ') is the least clear feature in the spectrum. The right panel shows 5 Lorentzians including RAS. χ_{2r} reduced to 1.58 by including RAS, indicating the significance for obtaining transferable parameterisations.





- H A Melia, C T Chantler, L F Smale, A J Illig, The Characteristic Radiation of Copper Kβ including radiative Auger processes, J Phys B 53 (19) (2020) 195002-1-12

G. Holzer, M. Fritsch, M. Deutsch, J. Hartwig, and E. Forster, Kα1;2 and Kβ1;3 x-ray emission lines of the 3d transition metals, Physical Review A56 4554-4568, 1997

A Story of Copper

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Physics Letters A

www.elsevier.com/locate/pla

Theory of copper $K\alpha$ and $K\beta$ diagram lines, satellite spectra, and *ab initio* determination of single and double shake probabilities

T.V.B. Nguyen, H.A. Melia, F.I. Janssens, C.T. Chantler *

School of Physics, The University of Melbourne, Melbourne Australia

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Kα

ABSTRACT

High-accuracy MCDHF Cu $K\alpha$ and Cu $K\beta$ diagram spectra and major satellites are presented. Spectral eigenvalues reach a theoretical expansion convergence of 0.03 eV or 0.00025%, with gauge and amplitude convergence to 0.7% for Cu $K\alpha$ diagram spectra. Dominant theoretical spectral eigenvalues are shown to be within 0.032 eV of experimental data. *Ab initio* shake-off contributions are presented in terms of total probability from each subshell and as separated single and double shake probabilities. Discrepancies between theory and experiment in copper X-ray spectra arise from profile asymmetries, relativistic terms and shake spectra not yet accounted for. These results and this improved agreement provide key fundamental parameters for processes towards XFEL evolution and resolving key discrepancies between theory and experiment.

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Ab initio calculations of Auger electron kinetic energies: Breadth and depth

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ABSTRACT

Ab initio theoretical calculations for Auger electron kinetic energies are presented for twenty prominent Auger peaks for the 3*d* transition metals ($21 \leq Z \leq 30$). These are the twenty Auger peaks listed for these elemental solids in the National Institute of Standards and Technology (NIST) X-ray photoelectron spectroscopy database. Adding to these values, over one hundred Auger electron kinetic eigenenergies are calculated for titanium. Many of these transition lines are not established in current literature due to their relatively small yields and overlapping widths. These data can be of importance for determination of previously unaccounted Auger electron peaks with titanium and will be useful for X-ray fluorescence studies into the radiative Auger effect. The consistency between our values and the empirical data is an improvement compared with previous binding energy approaches and the methodology is convergent. The methods presented can be extended to other elements for future investigations of Auger electron kinetic energies which is particularly useful where current experimental values do not exist. Furthermore, these calculations provide evidence in the success of multiconfigurational Dirac–Hartree–Fock approaches in complex quantum mechanics.

PHYSICAL REVIEW A **107**, 012809 (2023)

Cu $K\alpha_{3,4}$ satellite spectrum with *ab initio* Auger-rate calculations

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This work investigates the capability of the multiconfiguration Dirac-Hartree-Fock (MCDHF) method in predicting the Cu $K\alpha_{3,4}$ spectrum. *Ab initio* energy eigenvalues, relative intensities, and radiative widths are calculated for the Cu 2*p* and 2*s* satellite transitions. By fitting to the most accurate experimental Cu $K\alpha_{3,4}$ spectra available, we show that our 2*p* satellite energy eigenvalues agree with experiment to within 0.35 eV and that our 2*p* shake probability agrees with the 2*p* fitted intensity to within 0.05%. Our fits suggest a $I(2s)$:$I(2p)$ satellite intensity ratio (as a percentage of the total $K\alpha$ spectrum) of 0.03(1):0.76(1) Theoretical predictions of this ratio can be examined using shake probabilities. We calculate the probability of shake-off due to the sudden creation of a 1*s* hole in Cu, yielding an *ab initio* $I(2s)$:$I(2p)$ shake probability ratio of 0.194:0.742. Using MCDHF, the rates at which hole states, created through the shake processes, depopulate via Auger transitions are determined. These results explain the apparent discrepancy between experimental satellite intensities and shake probabilities, and characterize the Cu $K\alpha_{3,4}$ spectrum with a satellite intensity ratio of 0.04(1):0.76, consistent with the experiment.

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Ab Initio Shake Probability

- The shake probability can be determined for each satellite spectra
- Shake probability is used to scale the satellite intensity
- The copper Kα satellite intensity, Nguyen *et al.*

Satellite	4s	3d
Shake Probability (%)	11.25	18.39

T V B Nguyen et al. Phys. Rev. A 105 (2022) p022811

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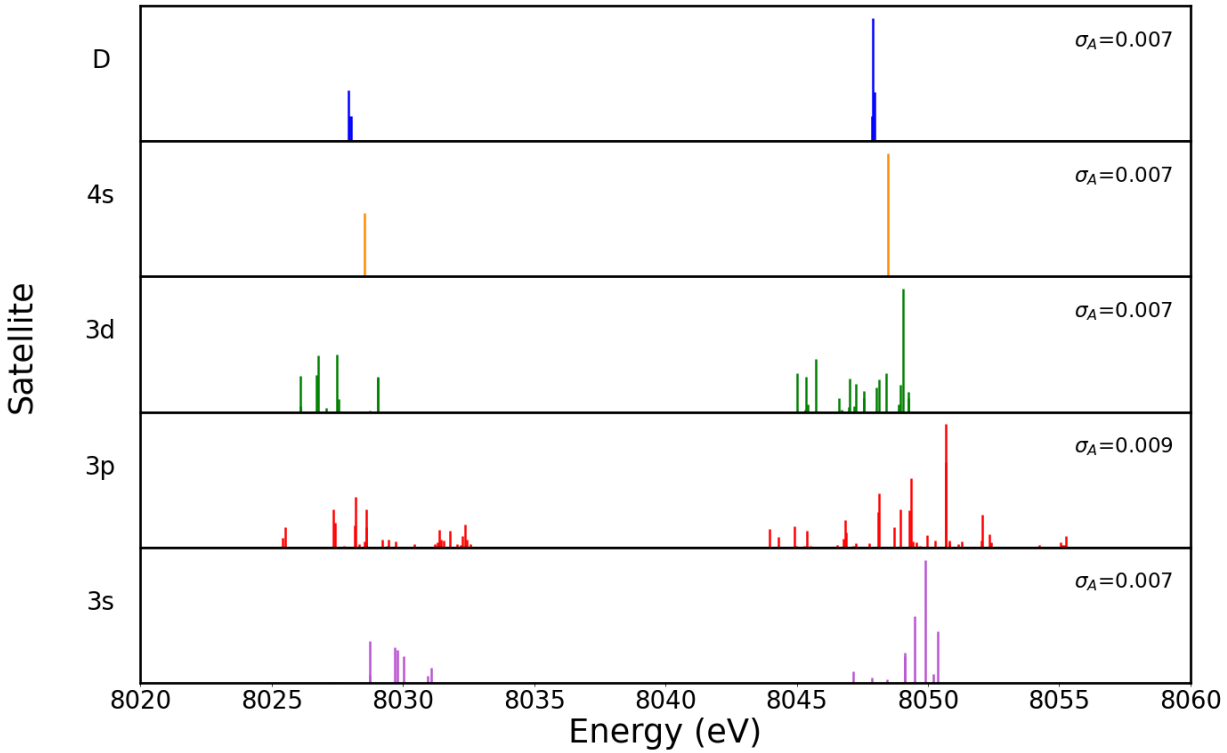
Kα Satellite Spectra



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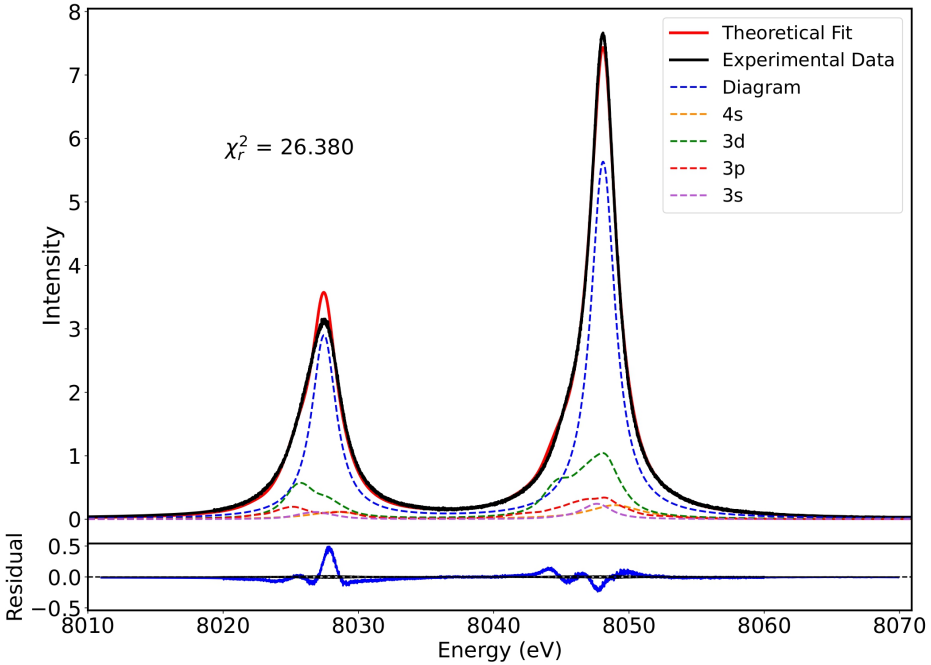
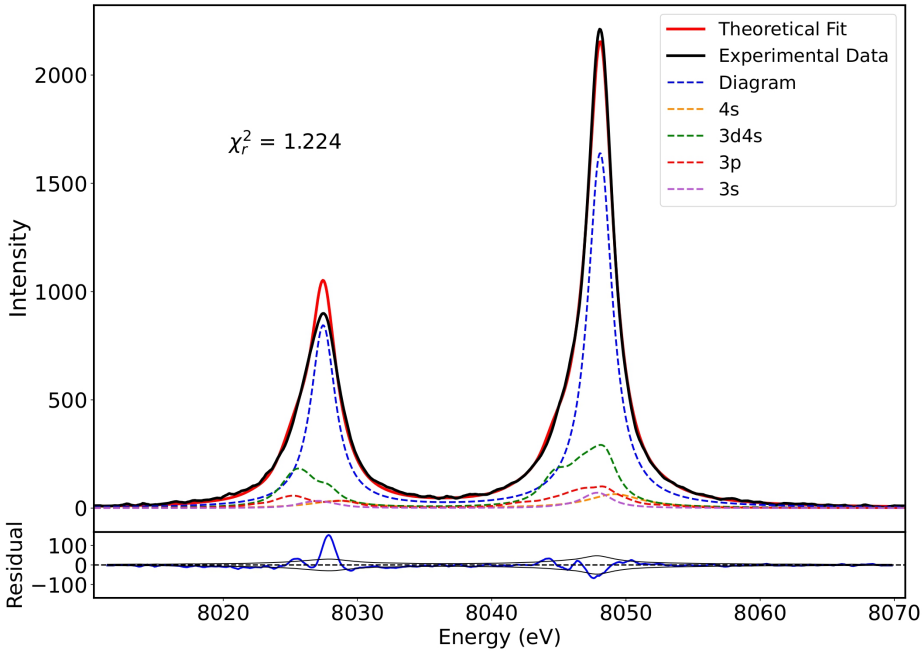
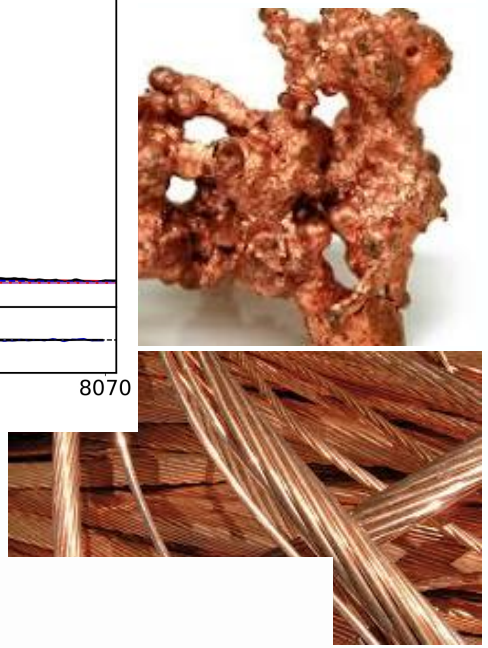
Auger Corrected Theoretical Spectrum



Mendenhall et al.



Deutsch et al.



- By including the Auger effect, the model is improved significantly
- The 4s satellite (Orange) is significantly smaller and broader
- This is the best fit for the experimental features

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- The **most complete theoretical model** for the copper $K\alpha_{1,2}$ profile to date
- Importance of the **shake processes** to modelling characteristic radiation, providing the **first evidence of the 3p and 3s satellite spectra**
- First ***ab initio* lifetime calculations** for the upper states of the copper $K\alpha_{1,2}$ transition
- Development of **new lifetime convergence metric**
- First **Auger rate calculations** for the copper $K\alpha_{1,2}$ profile
- Strong evidence for the **necessity of the Auger Effect** in modelling the copper $K\alpha_{1,2}$ transition through **corrections to the FWHM and satellite intensities**

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Characteristic radiation and Cu Kα$_{3,4}$

Diagram transitions:

$$\mathrm{K}\,\alpha_1 : 2p_{3/2} \rightarrow 1s \qquad [1s] \rightarrow [2p_{3/2}]$$
$$\mathrm{K}\,\alpha_2 : 2p_{1/2} \rightarrow 1s \qquad [1s] \rightarrow [2p_{1/2}]$$

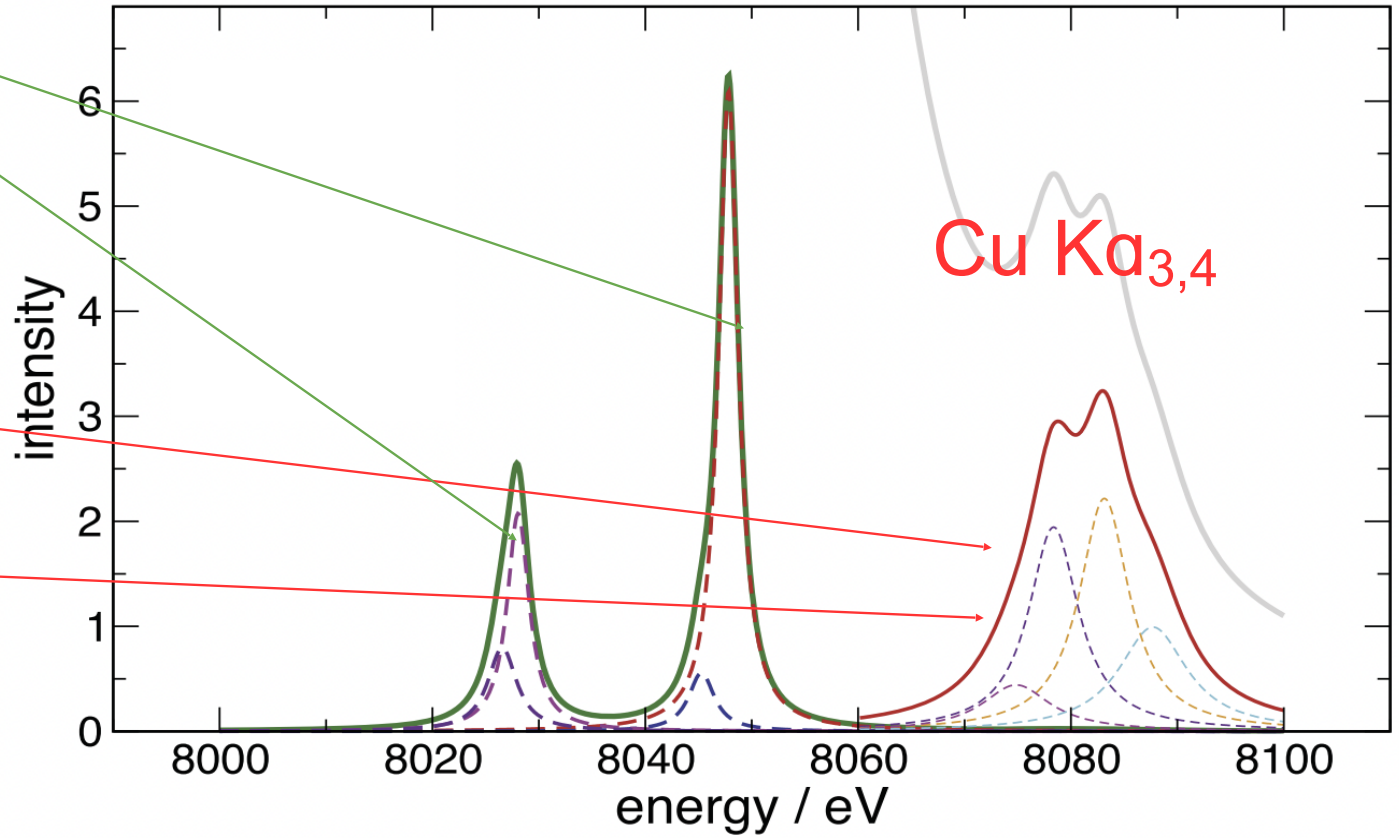
2*p* satellite:

$$[1s2p] \rightarrow [2p2p]$$

2s satellite:

$$[1s2s] \rightarrow [2p2s]$$

The probability of these multi-hole initial states occurring we call the **shake probability**.



Mendenhall, M. H., Henins, A., Hudson, L. T., Szabo, C. I., Windover, D., & Cline, J. P. (2017). High-precision measurement of the x-ray Cu Kα spectrum. JPhysB: Atomic, Molecular and Optical Physics, 50(11), 115004.

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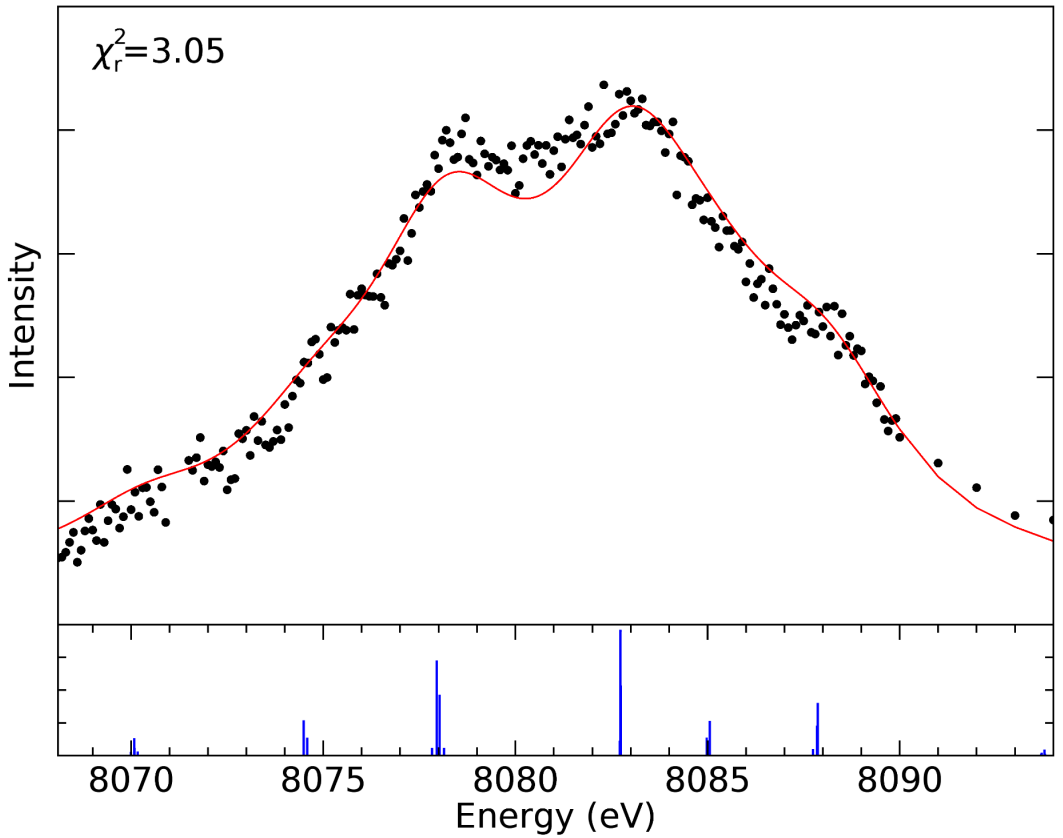
Modelling with only the 2*p* satellite

We can perform 3 Fits using the results of our 3 active sets.

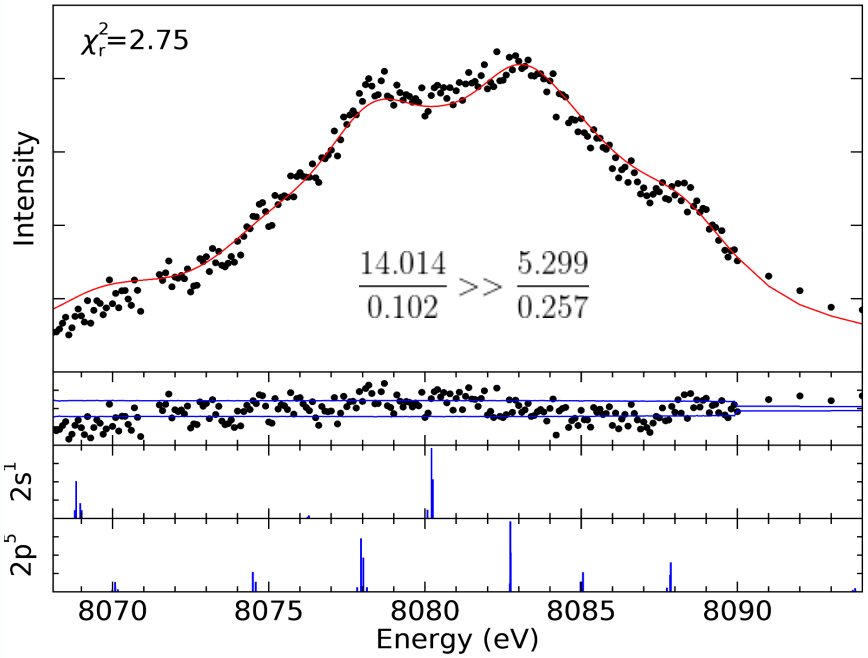
Expanded to:	χ_r^2	Shift	Contribution to Kα (%)
5s	29.055	1.59(3)	0.919(4)
4s	4.777	-0.34(2)	0.856(3)
4f	2.910	-0.73(2)	0.843(3)
5s	3.051	-0.25(2)	0.791(3)

- We have converged to within 0.25 eV of experimental peak energies (0.003 %).
- As we expand the active set our results improve.
- Residuals between the peak point to new physics



Modelling including non-radiative decay channels

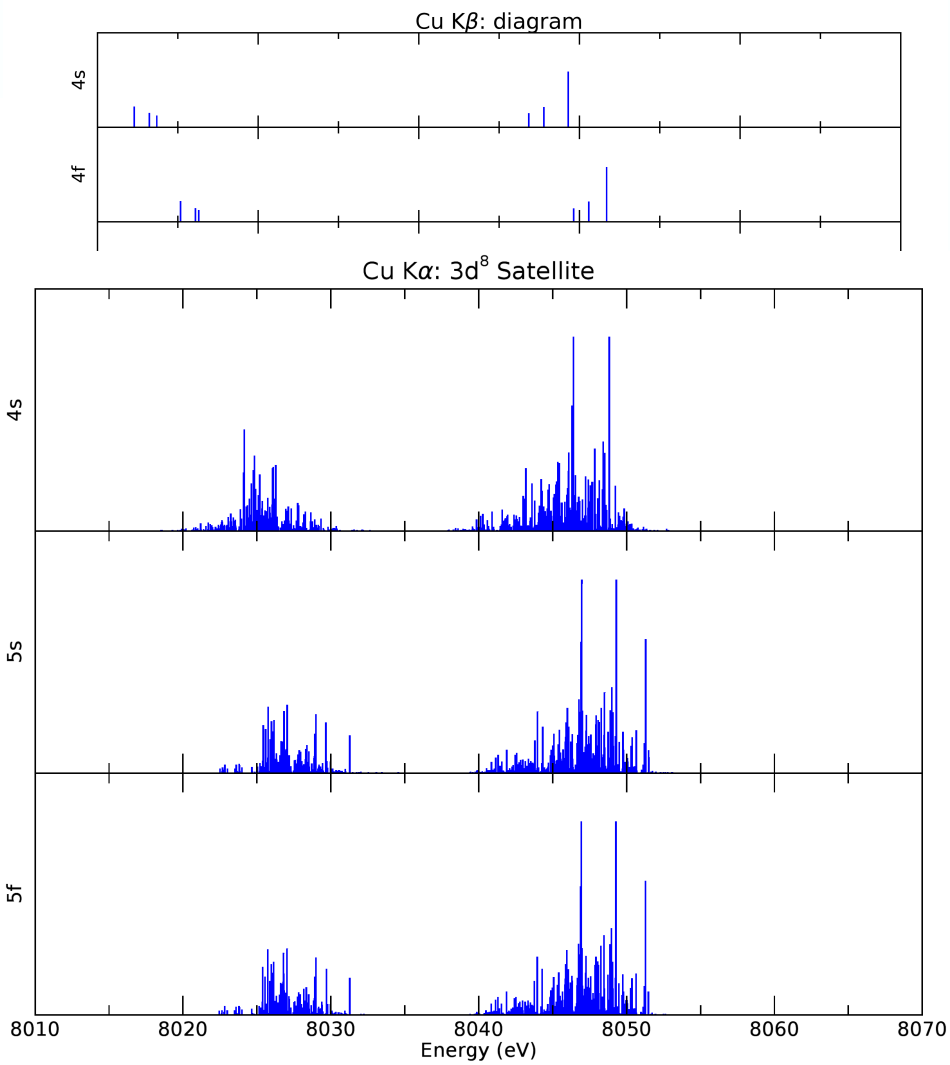
- Non-radiative rates using MCDHF RATIP (Fritzche S. *et al*. (2012) Comp. Phys. Comm.)
- Considering the depopulation of the 2s initial states through non-radiative rates AND the shake probabilities we determine a new *ab initio* satellite intensity ratio: I(2p)/I(2s) = 26



Initial Hole	Final Hole(s)	Type	Name	Rate ($eV/\hbar$)
$[1s]$	$[2p]$	Radiative	Kα diagram	0.256
$[1s2s]$	$[2p2s]$	Radiative	Kα $2s$ sat.	0.102
	$[1s2p3s]$	Auger	$L_1L_{2,3}M_1$	1.342
	$[1s2p3s]$	Auger	$L_1L_{2,3}M_{2,3}$	2.210
	$[1s2p3d]$	Auger	$L_1L_{2,3}M_{4,5}$	3.021
	$[1s2p4s]$	Auger	$L_1L_{2,3}N_1$	0.741
	$[1s3s3s]$	Auger	$L_1M_1M_1$	0.012
	$[1s3s3p]$	Auger	$L_1M_1M_{2,3}$	0.142
	$[1s3s3d]$	Auger	$L_1M_1M_{4,5}$	0.547
	$[1s3p3p]$	Auger	$L_1M_{2,3}M_{2,3}$	1.561
	$[1s3p3d]$	Auger	$L_1M_{2,3}M_{4,5}$	2.833
	$[1s3d3d]$	Auger	$L_1M_{4,5}M_{4,5}$	1.695
	$[1s3\ell4s]$	Auger	Σ LMN_1	<0.01
Total $L_1(2s)$ Auger rate: 14.104				
$[1s2p]$	$[2p2p]$	Radiative	Kα $2p$ sat.	0.257
	$[1s3s3s]$	Auger	$L_{2,3}M_1M_1$	0.019
	$[1s3s3p]$	Auger	$L_{2,3}M_1M_{2,3}$	0.119
	$[1s3s3d]$	Auger	$L_{2,3}M_1M_{4,5}$	0.508
	$[1s3p3p]$	Auger	$L_{2,3}M_{2,3}M_{2,3}$	1.342
	$[1s3p3d]$	Auger	$L_{2,3}M_{2,3}M_{4,5}$	1.240
	$[1s3d3d]$	Auger	$L_{2,3}M_{4,5}M_{4,5}$	1.891
	$[1s3\ell4s]$	Auger	Σ LMN_1	<0.01
$2p$ total Auger rate: 5.299				

A new process … not 1s - 2p in the characteristic spectrum

- **New theory can now see the 100-1000 spectral components of characteristic X-ray radiation for X-ray spectroscopy and fundamental processes**
- Multiconfiguration Dirac-Hartree-Fock (MCDHF). Diagram spectra expanded to 5s with simultaneous convergence of 28000 configuration state functions (CSFs), Kα, and to 6g with simultaneous convergence of 91000 CSFs, Kβ, eigenvalue convergence to ±0.03 eV or 0.00025%, 10x improved upon past work.
- Biorthogonalisation, developments of the active space approach, analysis of markers for theoretical convergence of eigenvalues, and the question of self-consistency for Kα and Kβ.
- Gauge convergence, eigenvalue convergence, A-coefficient convergence. Without the satellite spectra it is not possible to make use of the increased accuracy of the diagram computations.
- Cu Kα $3d^8$ double-shake satellite spectrum: 1506 unique eigenvalues (transitions); simultaneous convergence of 593 000 CSFs



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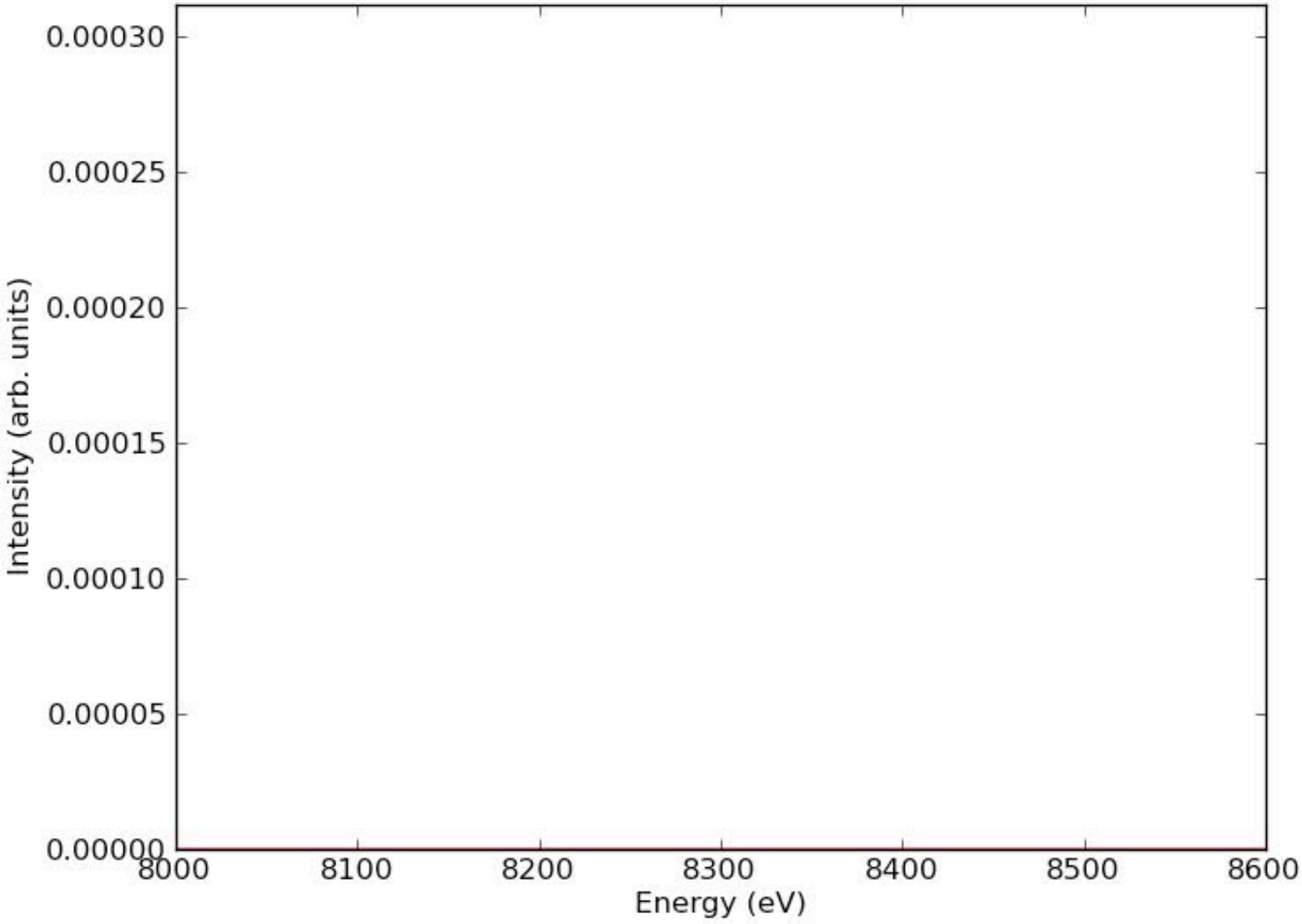
Instantaneous spectrum Copper in an XFEL



Cumulative Spectrum Copper in an XFEL