INTERNATIONAL TABLES for CRYSTALLOGRAPHY

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Volume

X-ray absorption spectroscopy and related techniques

Edited by Christopher T. Chantler, Federico Boscherini and Bruce Bunker

First edition

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

Volume I

X-RAY ABSORPTION SPECTROSCOPY
AND RELATED TECHNIQUES

Edited by

C. T. CHANTLER, F. BOSCHERINI AND B. BUNKER

First Edition

Published for

THE INTERNATIONAL UNION OF CRYSTALLOGRAPHY

by

WILEY

2024

A C.I.P. Catalogue record for this book
is available from the Library of Congress
ISBN 978-1-119-43394-1 (acid-free paper)
ISSN 1574-8707

This edition first published 2024
© 2024 International Union of Crystallography

Published for the International Union of Crystallography by John Wiley & Sons, Ltd

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Printed and bound by CPI Group (UK) Ltd, Croydon CR0 4YY, UK

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INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Foreword

Sofia Diaz-Moreno*‡

Diamond Light Source, Harwell Science and Innovation Campus, Didcot, OX11 0DE, United Kingdom. *Correspondence e-mail: sofia.diaz-moreno@diamond.ac.uk

‡ Chair of the International Union of Crystallography's Commission on XAFS and Vice-Chair of the International X-ray Absorption Society.

Keywords: *International Tables for Crystallography*; International Union of Crystallography; X-ray absorption spectroscopy; XAS; X-ray emission spectroscopy; XES.

Volume I of *International Tables for Crystallography*, *X-ray Absorption Spectroscopy and Related Techniques*, is a welcome and very timely addition to this encyclopaedic series of volumes, fitting well with the statement of purpose of the International Union of Crystallography (IUCr), 'Advancing structural science globally', that was revisited as part of the 75th anniversary of the organization in 2023. X-ray absorption spectroscopy (XAS) and related techniques such as X-ray emission spectroscopy (XES) complement other structural techniques that are the subject of previous volumes well, expanding the reach and coverage of *International Tables*.

Although there are many excellent books and manuals describing XAS and related techniques, including both practice and theory, there are none as complete or comprehensive as Volume I. The range of topics covered by the present volume is extremely extensive, from the instrumentation needed to perform the experiments, describing the data reduction and analysis, discussing important considerations when preparing samples, presenting theoretical approaches and the statistical significance of the results, and highlighting applications. Each of the nine parts in the volume addresses a specific aspect that is relevant to those who regularly use XAS and related techniques, but also to those who are novices and who would like to understand the potential of using spectroscopy for detailed structure determination. The three Editors have done an exceptional job in attracting many contributions from world experts on the topics covered by the volume, and this is shown in the quality of the final product. The overall result is a very coherent and self-contained volume.

I believe the contents of Volume I will attract interest from a wide variety of researchers. Scientists working on synchrotron beamlines will find that the *Experimental methods* part (Part 3) is an excellent manual describing the instrumentation needed to perform X-ray spectroscopy measurements, and the detectors needed for optimal experiments. It will also serve as a guide for experimentalists interested in improving data quality by optimizing sample preparation and data-collection methods. For those more interested in the fundamentals of the technique, I would recommend Part 2, *Theory*, which includes the theoretical approaches and approximations most often used for the interpretation of XAS and other techniques such as diffraction anomalous fine structure and X-ray magnetic circular/linear dichroism. In my opinion, researchers interested in using XAS for the first time will enjoy Part 5 (*Analysis of experimental data)*, which is an excellent compendium of the many steps required for XAS data reduction and analysis. Personally, as a spectroscopist and expert XAS and XES user, I have found Part 6, *Packages and approaches for data collection and data reduction*, very useful. Descriptions of many of the most frequently used software packages for XAS and XES data analysis and simulations are included, with most of the chapters written by the developers of the codes, and openly discussing their strengths and their limitations. This is a unique feature of the volume, and no other publication exists where all this information can be found in one place. The *Applications* part (Part 8), which focuses on examples showing the applicability of the techniques, will attract the interest of scientists working in many different scientific areas, from catalysis to battery materials, environmental science, bioscience, cultural heritage and many more.

Volume I is consequently a very comprehensive compilation of the fundamentals, state of the art and future directions of XAS and related techniques. I have every expectation that it will become a classic reference text for any expert in the field, but also as a starting manual for those who would like to learn more about the techniques and use them in their research.

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Preface

Christopher T. Chantler,[a]* Federico Boscherini[b] and Bruce Bunker[c]

[a]School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia, [b]Department of Physics and Astronomy 'Augusto Righi', Alma Mater Studiorum – Università di Bologna, Viale C. Berti Pichat 6/2, 40127 Bologna, Italy, and [c]Department of Physics and Astronomy, University of Notre Dame, Notre Dame, IN 46556, USA. *Correspondence e-mail: chantler@unimelb.edu.au

Keywords: X-ray absorption spectroscopy; XAS; X-ray fluorescence; X-ray emission spectroscopy; XES; *International Tables for Crystallography*; International Union of Crystallography; IUCr.

In May 2010, during a meeting of the International Programme Committee for the Twenty-Second Congress and General Assembly of the International Union of Crystallography (IUCr), discussions started between C. J. Gilmore and Isabella Ascone (then Chair of the IUCr's Commission on XAFS) about the possibility of including XAFS-related information in a new volume of *International Tables for Crystallography* that would cover mainly powder-diffraction techniques. After the IUCr decided to dedicate one volume to powder diffraction (subsequently published in 2019 as Volume H of the series) and a separate one to the XAFS technique, the Commission on XAFS submitted a detailed document with suggestions for the content of this Volume I to the IUCr Editorial Office at the beginning of December 2010.

This first proposal was composed primarily by I. Ascone with assistance from C. T. Chantler (then Secretary of the Commission). As Chair of the Commission, I. Ascone started many challenging projects, including looking at XAFS data formats, the standardization of XAFS experimental procedures, contributing XAFS-related definitions to the IUCr's Online Dictionary of Crystallography at https://dictionary.iucr.org ('the XAFS dictionary'), work towards this volume of *International Tables*, and fostering close cooperation with other IUCr commissions and with the International XAFS Society (IXAS) at IUCr Congresses and in the organization of workshops. These projects progressed well as the XAFS Commission was a highly functioning team. The data-format work led to the inauguration of a series of Q2XAFS (Quality and Quantity in XAFS Spectroscopy) conferences as a joint project with IXAS, then led by Hiroyuki Oyanagi, resulting in many publications in IUCr journals as an outcome of the meetings.

Great support for the *International Tables* project was provided by the IUCr Executive Committee, including Sine Larsen and M. L. Hackert; Michael Dacombe; Samar Hasnain; and indeed the Chair of the Commission on *International Tables*, Carol Brock. From early on, it was planned that, as far as possible, different experimental and theoretical backgrounds and regional approaches should be presented, in particular to bring the whole international XAFS community together to share their amassed knowledge. In 2013, three editors for the volume were appointed: Professor Christopher Chantler (Australia), Professor Bruce Bunker (USA) and Professor Federico Boscherini (Italy). The final version of the proposal for the volume was approved by the IUCr's Executive Committee in 2014. The first submissions started to arrive in 2015 and were subsequently fully reviewed and revised before acceptance.

Many chemists, bioscientists and crystallographers often need the supporting evidence and investigations afforded by XAS and XES. Our deliberate purpose is that this volume should be self-contained and, as far as possible with any developing live technique, we intend it to be complete. It has been written for the worldwide XAS community of thousands of practitioners, user communities, beamline scientists, experts and academics, and for the neophyte user who wishes to know what XAS and XES can do for them and how they may use these techniques for their particular purposes. The volume is therefore intended to be an authoritative resource that can be used for training, learning or teaching, providing practical guidance for readers of all levels of experience. It also provides full discussions of the many questions and practical issues that can arise at all stages of XAS or XES experiments and data processing. In addition, it can simply be used as a reference work like a normal *Handbuch* or encyclopaedia, and dipped into for insightful discussion of or solutions to problems or questions.

There are smaller-scale works, including textbooks and books, that have provided much insight into XAS and XES, but there is certainly a need for an authoritative and more comprehensive summary such as the present volume. Several authors of these valuable smaller or focused works are also authors of chapters in this volume, which has thus benefitted from their expertise.

The Editors would like to express particular thanks:

To all the expert authors and referees who have contributed outstandingly to so much of this work, and in some cases have not lived to see the fruition of their extensive efforts.

To our fellow Editors, without whom this would not have been possible. We have worked collaboratively and collegially on all aspects of the project.

To the team at the IUCr's Editorial Office (Simon Glynn, Nicola Ashcroft and Peter Strickland) for their many hours, months and years of work. We are amazed at their continued energy, enthusiasm and the level of care they have shown for the project.

To Isabella Ascone, whose drive and initiative inspired the Commission, IXAS and the push towards producing this volume.

To Ted Maslen, who guided many of us within and outside crystallography towards the path of accuracy and insight in science.

To the close and warm relations between crystallography, X-ray spectroscopy and all techniques, that we may understand one another better!

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 1.1

Keywords: X-ray absorption spectroscopy; XAS; X-ray fluorescence; X-ray emission spectroscopy; XES.

Overview of *International Tables for Crystallography* Volume I

Christopher T. Chantler,[a]* Federico Boscherini[b] and Bruce Bunker[c]

[a]School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia, [b]Department of Physics and Astronomy 'Augusto Righi', Alma Mater Studiorum – Università di Bologna, Viale C. Berti Pichat 6/2, 40127 Bologna, Italy, and [c]Department of Physics and Astronomy, University of Notre Dame, Notre Dame, IN 46556, USA. *Correspondence e-mail: chantler@unimelb.edu.au

An overview of *International Tables for Crystallography* Volume I and a brief description of the processes behind X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) are provided. The complementary nature of the information that can be obtained using either XAS or XES to information that can be obtained using crystallography is discussed, and some of the many fields of application of X-ray absorption spectroscopy and related techniques are outlined.

1. Introduction

The techniques of X-ray absorption and emission spectroscopy (XAS and XES, respectively) are used in more than 5000 major scientific publications each year. There is a very close synergy and overlap with the techniques of crystallography: X-ray diffraction, neutron diffraction and electron diffraction. While X-ray powder diffraction and X-ray single-crystal diffraction can be seen as defining much of crystallography, condensed-matter science, crystal and chemical and physical structure and nanostructure, XAS and XES come into their own in a complementary and overlapping manner for materials science structure, nanostructure and in quantum systems of partial disorder and partial local order, including in particular solutions, gases, liquids, frozen solutions, glasses and powders, and also including ideal perfect crystals. These techniques and areas of physics allow scientists to seek the answers to questions that are very hard to approach by other or more conventional techniques. Hence XAS and XES synchrotron beamlines are the among the most productive scientific research facilities in materials science, second only to synchrotron and laboratory X-ray crystallography facilities.

This volume is part of *International Tables for Crystallography* for these reasons. The series now comprises Volumes A–I, including A1, and a symmetry database. Together these summarize and encapsulate much of the science of nanostructure, crystallography, three-dimensional and two-dimensional space groups, physical crystallography and matter–photon interactions, particularly in the X-ray regime, but also for neutron and electron interactions with matter. Volumes A, A1, E and G contain extensive mathematical and data tabulations of great value. This volume, *X-ray Absorption Spectroscopy and Related Techniques*, is an encyclopaedic volume with tabulations, much like Volumes B, D, F and H. Volume C comprises an approximately equal mixture of fundamental tabulations and encyclopaedic articles.

This volume has 152 chapters across nine parts, plus additional online supplementary material.

Part 1 (*Introduction*, four chapters) provides a brief overview and introduction to the background of X-ray absorption spectroscopy (XAS) and experimental facilities, particularly at synchrotrons.

Part 2 (*Theory*, 25 chapters) discusses the quantum theory of XAS and related approaches. This goes well beyond that found in past reviews, works and texts, and so can be particularly useful in understanding the reasons why the techniques and the data they yield are so valuable.

Part 3 (*Experimental methods*, 49 chapters) discusses widely used standard and advanced experimental techniques for XAS, X-ray emission spectroscopy (XES) and related techniques. Many of the chapters can be used as a guidebook, introduction or manual, while others explain what is possible, pointing to future standards and additional opportunities using these techniques.

Part 4 (*Spectral distortions and data pre-processing*, seven chapters) discusses standard and more advanced pre-processing of data, especially for common XAS techniques.

Part 5 (*Analysis of experimental data*, 19 chapters) provides an overview of stages and types of data analysis.

Part 6 (*Packages and approaches for data collection and data reduction*, 25 chapters) discusses software packages for different approaches to data collection and data reduction.

Part 7 (*Exchange of data and deposition*, four chapters) discusses the importance in science, reporting and hypothesis testing of the exchange of input and processed output data, and data deposition. Exemplar tables and table formats for data deposition, exchange and reference are presented of data and supplementary material for X-ray absorption spectroscopy, pre-edge, XANES and XAFS. These tables are also available in full as online supporting information.

Part 8 (*Applications*, 18 chapters) discusses the wide range of applications of XAS and its uses in many fields.

Part 9 (*Definitions*) presents XAS definitions as developed by the International Union of Crystallography's Commission on XAFS.

2. What are XAS and XES?

As discussed fully in Part 2 (*Theory*), X-ray absorption spectroscopy is based around an incident photon, an X-ray, being absorbed by the material of interest. The absorption is strongly energy-dependent, especially above any absorption edge, and notably for *K*-shell and *L*-shell edges. This means that the physical process and techniques of XAS are applicable to every element in every material. For low-atomic-number elements, the energies move into the ultraviolet through vacuum ultraviolet to soft X-rays from neon to aluminium ($Z = 10$ to 13). The process behind and the origin of the measured absorption coefficient is the same throughout.

Whereas X-ray absorption spectroscopy depends upon the mass absorption coefficient and represents a loss of X-ray flux to a downstream detector, X-ray fluorescence depends upon a secondary, characteristic photon that is emitted upon relaxation of the excited or ionized system. The spectrum of the emitted, characteristic photon defines X-ray emission spectroscopy. Hence, XAS and XES are closely related processes, as discussed in Part 2. Other secondary modalities including electron emission are discussed in Part 2 and provide great insight into particular areas of study.

Most of these techniques observe fine structure, which arises from the quantum interference of the outgoing photoelectron wave from the ionized absorbing atom with the returning wave from scattering off the charge (electron) density of the material.

3. Why are XAS and XES useful?

Because the scattering of the photoelectron by the charge (electron) density is local, XAS and XES signals can be used to measure the distances between and densities of electron charge carriers in the material. Because XAS and XES are local in space and time, they provide detailed signals irrespective of the crystallinity of the material, and in particular these techniques can be applied to solutions, glasses, liquids and any disordered material with partial local order. The data can be used to solve local structure and study local binding and local orbitals, and can also solve the crystallographic structure for regular solids. By determining the charge density, XAS and XES also determine the atomic and molecular structure.

In this short introduction, we only note that the processes of bound–bound excitation and de-excitation form additional structure in the pre-edge peaks and spectra, which are also part of XAS and XES. Analysis of this structure can be particularly valuable for defining the oxidation state, valence and local geometric symmetry, and for deriving numerous other important parameters. The physical and chemical information content of X-ray absorption spectra is both considerable and detailed.

4. Fields of application

The fields of application of XAS and related techniques span from mathematics, theoretical physics, applied atomic and condensed matter science, physics, chemistry, biophysics and biochemistry, medical science and engineering to, for example, art and the humanities. Part 8 describes a range of these applications and their current status including, for example, catalysts, the study of chemical reactions, atomic photoexcitation studies, semiconductors, magnetic materials, glasses and amorphous solids, earth sciences, environmental studies and cultural heritage, to name a small selection.

XAS and related techniques have the capacity to measure dynamic bonding and dynamic bond distances rather than, for example, the mean separation of lattice positions obtained from crystallography. In this sense, they provide complementary information to that of crystallography for the characterization of materials and the chemistry of bonding. In the past, distances between atoms obtained using crystallography were better defined than those obtained from XAS or X-ray

fluorescence. However, many examples over the last 20 years or so show that bond distances are able to be defined as or more accurately using XAS.

Electron microscopy (EM) and related recent developments, including cryo-EM, have been able to define atomic positions in particular materials to an impressive level. It is less well known that a range of key systematic errors can be measured using XAS in advanced modes, which can thereby correct for errors in or inform the calibration of results from EM. Equally, XAS is able to define bond lengths and atomic positions to a fraction of an ångström and hence 'visualize' the local system, the active site or other characteristics of a noncrystalline or complex nanosystem. The potential applications of XAS and XES and the insight they provide are far more extensive than the illustrations provided in this handbook.

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 1.3

Keywords: deposition; data management.

Deposition of XAFS data

Sydney R. Hall,[a] James R. Hester[b] and Brian McMahon[c]*

[a]School of Molecular Sciences, University of Western Australia, 35 Stirling Highway, Perth, WA 6009, Australia, [b]Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia, and [c]International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, United Kingdom. *Correspondence e-mail: bm@iucr.org

Best practice in modern research data management argues for the deposition of validated experimental data sets in publicly accessible repositories. Such depositions should meet the FAIR principles (that scientific data should be findable, accessible, interoperable and reusable), on which funding bodies increasingly insist. In so doing, they will include sufficient metadata to allow verification and reproducibility of published research results, and provide the scientific community with a curated collection of valuable data. The benefits of such a collection include independent validation, reanalysis and the ability to extract new science from existing data as new techniques appear.

1. Introduction

It has become fashionable in the late twentieth and early twenty-first centuries to speak of 'data-driven science' in response to developments in instrumentation, computation and storage. The term is certainly a misnomer, as observational and experimental sciences have always relied upon the collection, evaluation and analysis of data to confirm or suggest hypotheses and models. Nevertheless, it reflects the recognized scale of the quantity of current scientific research, and the potential for greater collaboration, data sharing and knowledge discovery that modern technologies provide (Hey *et al.*, 2009).

Funding bodies began to require that scientific research groups in receipt of their support should formulate and work to data-management plans, so that observational and experimental data sets were organized and preserved to allow their reuse, both to validate original research results and to make possible other studies based on those data sets, which were often collected at significant expense. A consortium of scientists and research organizations formulated a set of principles intended to develop best practice in such reusability (Wilkinson *et al.*, 2016). These principles used the acronym FAIR to emphasize the need for findability, accessibility, interoperability and reusability of collected data sets. That is, in order for them to be reusable, scientists need to become aware of the existence of useful data sets, and they need to be able to retrieve these data sets and process them with their own software tools. Missing from the acronym FAIR, but implicit in the intention to facilitate reuse, is the notion that the data should be trustworthy according to some agreed criteria, and that they should therefore be validated against those criteria.

We shall consider the application of all of these principles to XAFS data, but here we shall concentrate on the best approach to making experimental data sets accessible to other

Related chapters

Volume I: 1.4, 4.6, 7.1, 7.2, 9.1

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY
ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 2.5

Keywords: XANES; theory.

XANES: theory and approaches

Takashi Fujikawa*

Graduate School of Advanced Integration Science, Chiba University, Yayoi-cho 1-33, Inage, Chiba, Japan. *Correspondence e-mail: tfujikawa@faculty.chiba-u.jp

A brief review of XANES theories is given which focuses on the basic theoretical framework rather than the technical details.

1. Introduction

Several useful computer programs are now available for XAFS data analyses, which unfortunately means that we may have become unfamiliar with the basic theory behind them. Here, the theory of XAFS is briefly reviewed. A more comprehensive discussion is given by Rehr & Albers (2000). Here, we focus on the theoretical basic features of XANES analyses. There are several methods to calculate the X-ray absorption intensity $I(\omega)$ for excitation by monochromatic X-ray photons with energy ω. The basic method is given by the use of Fermi's golden rule,

$$I(\omega) = 2\pi \sum_{\rm f} |\langle {\rm f}|H_{\rm ep}|0\rangle|^2 \delta(E_0 + \omega - E_{\rm f}), \tag{1}$$

where $|0\rangle$ and $|{\rm f}\rangle$ are the initial and the final states of the target, with energies of E_0 and $E_{\rm f}$, respectively. The electron–photon interaction operator $H_{\rm ep}$ is written in the first and second quantizations,

$$H_{\rm ep} = \sum_i \Delta(\mathbf{r}_i) = \int {\rm d}x\, \psi^\dagger(x)\Delta(x)\psi(x),$$
$$x = (\mathbf{r}, \sigma), \tag{2}$$

where ψ and $\psi^\dagger$ are the electron annihilation and creation field operators. In the electric dipole (E1) approximation Δ is written for the linear polarization parallel to the z axis:

$$\Delta(\mathbf{r}) \propto rY_{10}(\hat{\mathbf{r}}). \tag{3}$$

For practical calculations of the ground state $|0\rangle$, some useful methods have been developed, for example Hartree–Fock (HF), density-functional theory (DFT) and configuration interaction (CI) methods; CI methods can also be applied to the final core-hole states $|{\rm f}\rangle$ (Kosugi *et al.*, 1984). The above direct approaches have been used to study XANES analyses excited from small systems such as molecules. For localized magnetic systems such as 3*d* transition-metal compounds or rare earths, multiplet and ligand field theory are quite useful to calculate both the $|0\rangle$ and $|{\rm f}\rangle$ states. These approaches provides us with simple physical pictures with low computational cost, but rely on semi-empirical calculations (van der Laan, 2006). The multichannel generalization of real-space multiple-scattering (MS) theory was developed to study XANES spectra by Natoli and coworkers (Natoli *et al.*, 1990). They combined MS theory and CI approaches, and discuss shake-up effects. It is however difficult to include bosonic excitations. Applications to $L_{2,3}$-edge XANES spectra show excellent

Related chapters

Volume I: 2.1, 2.8, 2.10, 2.14

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 2.13

Keywords: Bethe–Salpeter equation; excited core hole; FCH; NRIXS; screening; *StoBe*; XAS; XCH; X-ray Raman scattering.

Core-hole potentials and related effects

Eric L. Shirley,[a]* Lars G. M. Pettersson[b] and David Prendergast[c]

[a]Sensor Science Division, NIST, 100 Bureau Drive MS 8441, Gaithersburg, MD 20899-8441, USA, [b]Department of Physics, Stockholm University, S-106 91 Stockholm, Sweden, and [c]Molecular Foundry, Lawrence Berkeley National Laboratory, One Cyclotron Road, Building 67, Berkeley, CA 94720, USA. *Correspondence e-mail: eric.shirley@nist.gov

The constrained-occupancy and (linear-response) self-consistent-field methods for the screening of core-hole potentials that affect core-excitation near-edge spectra are considered. The methods are not exact, but each has distinct advantages and limitations. The excitation spectra which are referred to include X-ray absorption spectroscopy (XAS), electron energy-loss spectroscopy (EELS) and nonresonant inelastic X-ray scattering (NRIXS). The screening of interactions that arises is always accompanied by self-energy or lifetime-damping effects of electron and hole states, which are also discussed briefly.

1. Introduction

Core-excitation spectroscopies, such as electron energy-loss spectroscopy (EELS), X-ray absorption spectroscopy (XAS) and nonresonant inelastic X-ray scattering (NRIXS), probe states of a physical system that involve a core hole and a concomitant excited electron. In a one-electron picture, this is a consequence of the promotion of a core electron to an unoccupied electron level because of the experimental probe. However, electron–electron and electron–core hole interactions must also be addressed. The electron–core hole interaction can be treated by considering a two-particle equation of motion (the Bethe–Salpeter equation) for the electron–hole pair, by treating the unoccupied electronic level scheme as perturbed by the core hole, or by other techniques. In all of these approaches it is necessary to evaluate the effective screened potential of the core hole. In Section 2, we discuss the treatment of the screening of the core-hole potential.

The mutual electron–hole interaction is accompanied by interactions with the rest of a system by either particle. (Obviously, the fact that the interaction is screened already implies interactions with the rest of the system.) Individually, the electron and core hole experience self-energy effects that shift and broaden the energies of their states because of lifetime damping. We discuss these effects and their treatments in Section 3. Other effects, including vibrational effects, are beyond the present scope.

2. Core-hole potential calculation methods

The accurate inclusion of core-hole effects requires their computation in a system-specific fashion. In practice, a variety of approximations are used. One class of approximations that we consider here is the constrained-occupancy type, including the 'full core-hole' (FCH) and 'excited-electron and core-hole' (XCH) methods, which usually involve a fixed-occupancy pseudopotential or all-electron site that has a core vacancy,

Related chapters

Volume I: 2.6, 2.10, 2.12

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 2.18

Keywords: magnetism; sum rules; spin and orbital moments.

Magnetic X-ray techniques

Gerrit van der Laan*

Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, United Kingdom. *Correspondence e-mail: gerrit.vanderlaan@diamond.ac.uk

The underlying theoretical aspects of X-ray spectroscopies are recapitulated with special emphasis on applications to magnetic systems. Prominence is placed on common conceptual aspects, while highlighting the differences in information that they may offer. X-ray scattering can be used to investigate the electronic and magnetic long-range order in crystals and ordered materials. The crystal symmetry of the sample and the X-ray polarization state have a profound effect on the scattering amplitude of X-ray resonant magnetic scattering (XRMS). Expressions for X-ray magnetic circular and linear dichroism (XMCD and XMLD, respectively) can be derived directly from those for XRMS. The photon–matter interaction for electric and magnetic multipole fields is presented from a general point of view, which reveals the physical implications of the various terms in the cross section for X-ray absorption. X-ray optical activity is due to mixed terms of different multipole rank of the electric and magnetic fields. The different optical effects, such as XMCD, X-ray natural circular dichroism (XNCD) and X-ray magnetic chiral dichroism (XMχD), can be distinguished by their properties under space inversion and time reversal.

1. Introduction

The theoretical concepts behind magnetic synchrotron techniques are based on quantum mechanics and provide very rich grounds for experimental exploration. The aim of this chapter is to present a general framework that shows the current and future capabilities, although many details are skipped due to page-length considerations. We will first present the general expressions for the scattering amplitude in nonresonant and resonant elastic scattering. From this, expressions for X-ray magnetic circular and linear dichroism (XMCD and XMLD, respectively) are obtained using the optical theorem. Taking crystal-field interaction into account leads to a remarkable result for XMLD.

The advantage of X-ray resonant magnetic scattering (XRMS), compared with other absorption spectroscopies, is that the scattering amplitudes from the various sites interfere coherently, which gives a sensitivity to long-range order. XRMS allows us to investigate the physics of higher order multipoles for the study of strongly correlated electron systems.

We review the interaction of electric and magnetic multipole fields with matter and explain the origin of X-ray optical activity.

Related chapters

Volume I: 2.1, 2.10, 2.12, 2.17, 3.33

2. X-ray magnetic scattering

2.1. Scattering amplitude

The first magnetic scattering experiment was carried out on NiO under nonresonant conditions (de Bergevin & Brunel, 1981). Subsequent magnetic scattering at resonance (Hannon

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INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 3.7

Keywords: X-ray beam drift; beam movement; feedback; polarization.

Beam drift, control and polarization

Sofia Diaz-Moreno* and Roberto Boada

Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, United Kingdom. *Correspondence e-mail: sofia.diaz-moreno@diamond.ac.uk

The main factors that cause the X-ray beam to drift are discussed in this chapter. Issues such as movement of the source or mechanical and thermal instabilities of the main optical elements of the beamline are translated into movement of the X-ray beam at the sample, intensity drifts and nonlinearities on the energy scale, affecting the quality of the data collected. The main steps that need to be taken to prevent and/or minimize the effects of these drifts are described, and approaches such as feedback systems are presented. The polarization of the beam delivered by the different types of X-ray sources used for synchrotron-based spectroscopy experiments is also presented. The on-axis and off-axis polarizations of the bending magnet and insertion devices such as wigglers and undulators are discussed.

1. Beam drift

An X-ray beam that is stable in position, intensity and energy is a fundamental requirement for the performance of robust and reliable spectroscopic measurements. The variation of the beam position at the sample, fluctuations in the intensity of the radiation and the nonlinearity of the energy scale on the time scale of the experiment are factors that will affect the quality of the data collected.

Although beam drift is an important issue for all spectroscopic beamlines, the delivery of a stable beam is particularly critical in the case of the dispersive variant of the technique (Matsushita & Kaminaga, 1980). This is because it is currently not possible to collect a simultaneous incident-beam intensity measurement while the absorption spectrum is collected on the position-sensitive detector, and thus instabilities in the beam are not as effectively normalized (Pascarelli, Neisius & De Panfilis, 1999; Pascarelli, Neisius, De Panfilis *et al.*, 1999). This means that extra care needs to be taken in the design and implementation of energy-dispersive spectrometers to mitigate the impact of beam drift on the measurements.

1.1. Sources of beam drifts

The drifts observed in the X-ray beam at the sample position have many different origins, but in general can be divided into two main categories: (i) drifts originating at the source and (ii) drifts due to instabilities in the optical components of the beamlines.

1.1.1. Electron-orbit stability. Variations in the electron orbit in the storage ring affect the stability of the beam delivered to the sample. This issue was a very significant factor in the case of second-generation sources, but the advent of third-generation sources considerably improved the situation. On modern synchrotrons the movement of the electron beam in the storage ring should no longer be a significant factor affecting the stability of the X-ray beam at the sample

Related chapters

Volume I: 3.10, 3.11, 3.38, 3.39, 3.42, 3.43

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 3.14

Keywords: sample absorption; sample thickness; accuracy.

Accurate data: mapping sample absorption and thickness effects

Stephen P. Best[a]* and Christopher T. Chantler[b]

[a]School of Chemistry, University of Melbourne, Parkville, Victoria 3010, Australia, and [b]School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia. *Correspondence e-mail: spbest@unimelb.edu.au

The systematic and random errors associated with any measurement are dependent upon experimental design and directly, or indirectly, constitute a compromise between the physics of the measurement, the questions to be addressed and the beamtime available. The processing of experimental measurements to correct for instrumental and sample-dependent phenomena so as to obtain observations with a defined accuracy underpins any subsequent analysis and assessment of the reliability of the conclusions. Here, strategies for the correction and statistical analysis of experimental data are presented, yielding point-by-point estimates of the measured accuracy which can then be used to assess alternate models of the coordination geometry of the absorbing atom. A particular focus is placed on sample absorption and thickness effects. These methods are particularly valuable for the study of species at low concentration and sample forms lacking long-range order.

1. Introduction

Analytical methods describe protocols which, when implemented, yield results with a quantified accuracy and are valuable because they can be communicated and accepted by others inside and outside the field. During the development of experimental methods there is a period of instrumental, computational and sampling advances which significantly increase the quality–cost quotient. When the method is mature, the balance shifts from method development to applications, including a more advanced understanding of signal and information content. Methods such as IR, UV–Vis and NMR spectroscopy, gas chromatography, mass spectrometry and laboratory-based small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD) may be argued to fall into this mature category. X-ray absorption spectrospcopy (XAS) does not yet fit into the mature category and is a field that is undergoing exciting dynamic development.

XAS experiments are highly demanding and the establishment of beamlines that allow the routine collection of spectra is a significant achievement that is too often taken for granted by the user community. In what we define as conventional operation, the beamline is optimized at different times during the user cycle, but uncertainty estimation and the measurement of diagnostics of systematic errors are not embedded into the measurement of individual spectra. Depending on the stability of the beamline and its associated electronics, such an approach can allow the efficient collection of spectra by a higher number of users on oversubscribed beamlines; however, such an approach does not allow the quantification of systematic errors. Measurements of this sort do not have a statistically defined uncertainty. High-accuracy measurements of XAS spectra may be categorized as those where individual observations within a spectrum are obtained with a measured

Related chapters

Volume I: 3.13, 3.38, 3.39, 3.42, 3.46, 3.47, 4.6, 4.7

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 3.27

Keywords: electrochemical cells; *in situ* XAS.

Electrochemical cells for *in situ* XAS studies

Kotaro Sasaki*

Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, USA. *Correspondence e-mail: ksasaki@bnl.gov

The present chapter provides a brief overview of electrochemical cells for *in situ* X-ray absorption (XAS) studies, together with the advantages and disadvantages of the existing cells and some requirements for new cell designs to perform experiments. Understanding of electrochemical reactions at the electrode–electrolyte interface is crucial not only for fundamental electrochemical research, but also for the development of electrochemical devices such as fuel cells, batteries, electrolyzers, supercapacitors and so on. *In situ* XAS with appropriate electrochemical cells provides information on atomic structures, oxidation/electronic states and adsorbate species of the catalytic surface during the course of an electrochemical reaction and thus is an indispensable tool for electrocatalytic/corrosion studies. Many electrochemical cells for *in situ* XAS have been developed. In this chapter, the focus will mainly be on electrochemical cells employed for electrocatalytic studies.

1. Introduction

Detailed understanding of electrochemical reactions at the electrode–electrolyte interface is crucial not only for fundamental electrochemical research, but also for the development of electrochemical devices such as fuel cells, batteries, electrolyzers, supercapacitors and so on (Simon & Gogotsi, 2008; Debe, 2012; Chen *et al.*, 2013). *In situ* XAS techniques offer a unique method to investigate the local atomic structures, electronic levels and chemical states of the surface under controlled electrochemical conditions using appropriate electrochemical cells (Russell & Rose, 2004; Sasaki & Adzic, 2009).

When designing a three-electrode electrochemical cell for *in situ* XAS studies, one must consider several points to fulfil the experiments adequately (Sharpe *et al.*, 1990; Russell & Rose, 2004; Watanabe *et al.*, 2007). Some of the requirements are described below.

(i) A relevant amount of specimen material must be loaded to obtain a good signal-to-noise ratio; this depends on whether transmission or fluorescence mode is selected.

(ii) The cell must incorporate windows that are transparent to X-rays and both must be resistant to corrosion by the electrolyte.

(iii) The electrode configuration must (1) ensure a uniform distribution of current density flowing between the working and counter electrodes and (2) minimize the *iR* (ohmic) drop between the working and reference electrodes.

(iv) The X-ray path through the cell must be minimized to reduce its absorption by the electrolyte since water is an attenuator of low-energy X-rays. This point must be taken into account in both transmission and fluorescence modes when a reference foil is simultaneously measured to calibrate the X-ray energy.

Related chapters

Volume I: 3.26, 8.10, 8.18

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 3.45

Keywords: bandwidth; divergence.

Bandwidth and divergence

Grant Bunker*

Department of Physics, Illinois Institute of Technology, Chicago, IL 60616, USA. *Correspondence e-mail: bunker@iit.edu

Methods for characterizing the energy bandwidth and divergence of X-ray beams are discussed.

1. Introduction

The X-ray beams that are produced by double-crystal monochromators are not perfectly monochromatic, even if the harmonics are eliminated. The beams still have a small spread in energy, the bandwidth, which should normally be of the order of an electronvolt or less. The quality of X-ray absorption fine-structure (XAFS) spectra is significantly affected by the energy bandwidth of the X-ray beam. Using a beam with an excessively large bandwidth will broaden out near-edge and pre-edge features, distort the shape of X-ray absorption near-edge structure (XANES) features (and derivative spectra), shift apparent edge energies and reduce extended X-ray absorption fine-structure (EXAFS) amplitudes at low k. When comparing spectra, it is important that the energy resolution of their measurements should be approximately the same or that suitable corrections are made to account for the different resolutions. A simple way to verify the adequacy of energy resolution and other instrumental characteristics is to measure the same reference sample at the start of each experimental run, especially a sample with known prominent and sharp absorption features. Additional background material can be found in Stern & Heald (1983), Koningsberger & Prins (1988) and Bunker (2010).

2. Core-hole lifetime spectral broadening

XAFS spectral features, even bound states nominally of a single energy, have an intrinsic energy broadening owing to the finite core-hole lifetime; this is distinct from any instrumental effects. It is necessary to keep this in mind when using experimental spectral peaks or other features to assess instrumental broadening. It also puts limits on the energy resolution needed for an experiment: there is little utility in striving for a monochromator resolution that is much less than the lifetime broadening.

The lifetime broadening is described by Heisenberg's time–energy uncertainty relation $\Delta E \Delta T \geq \hbar/2$, which relates the energy width ΔE of a quantum state and its lifetime ΔT. In XAFS measurements the relevant lifetime is that of the core hole (*i.e.* the vacancy in the initial state, for example 1*s* for *K* edges), which is filled by an electron from a higher energy level, resulting in the emission of a fluorescence photon or the ejection of Auger electrons. Core-hole lifetime values have been tabulated by Krause & Oliver (1979) and are plotted (for

Related chapters

Volume I: 2.8, 2.25, 3.4, 3.5, 3.11, 3.14, 3.38, 3.39, 3.42, 3.43, 3.46, 3.47

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY
ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 4.2

Keywords: harmonics contamination; geometric misalignment.

XAFS spectral distortions related to optics issues

Hitoshi Abe[a,b]*

[a]Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan, and [b]Department of Materials Structure Science, School of High Energy Accelerator Science, SOKENDAI (The Graduate University for Advanced Studies), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan. *Correspondence e-mail: hitoshi.abe@kek.jp

The influence of harmonics contamination and geometric misalignment is discussed. It is shown how harmonics contamination affects X-ray absorption fine-structure (XAFS) spectra. One of the most important suggestions to avoid harmonics contamination in XAFS analyses is to reduce the third-harmonic contamination level to 10^{-5} of the fundamental. If possible it should be reduced to 10^{-6} of the fundamental, and at least to less than 10^{-4}. Slits and apertures must be set at their correct positions. Otherwise, the absolute energy of the incident X-ray shifts and the resolution becomes worse.

1. The influence of harmonics contamination on XAFS spectra and the handling of harmonics

1.1. The influence of harmonics on XAFS signals

The presence of higher harmonics in the incident X-ray beam distorts XAFS spectra. The amount of harmonics sometimes changes during the measurement of spectra. When the amount of harmonics changes smoothly during a scan, distortions may not be apparent in the spectrum. Even if distortions do not appear in the spectra, spectra measured using X-rays containing higher harmonics are incorrect. Thus, we need to be sure to eliminate harmonics.

How much the harmonics need to be reduced is described. The signal intensities I_0 and I measured by ionization chambers are

$$I_0 = \alpha(I_0, 1) + \sum m\alpha(I_0, m)c_m(I_0, m), \quad (1)$$

$$I = [1 - \alpha(I_0, 1)]\exp(-\mu_1 t)\alpha(I, 1) + \sum mc_m[1 - \alpha(I_0, m)]\exp(-\mu_m t)\alpha(I, m), \quad (2)$$

$$\mu t = -\ln\frac{I}{I_0}. \quad (3)$$

Here, $c_m(I_0, m)$ is the ratio of the mth harmonic to the fundamental (m = 1) for I_0 and $c_m(I, m)$ is that for I. $\alpha(I_0, m)$ denotes the detection efficiency for I_0 and $\alpha(I, m)$ is that for I. The term $\exp(-\mu_m t)$ is the transmission of the mth harmonic through the sample. The mth harmonic has an energy which is m times higher than the fundamental, and yields a current that is m times larger in the ionization chamber. This phenomenon is expressed as m in the second terms of equations (1) and (2). In principle, the second harmonic is not generated by Si(111) and Si(311) double-crystal monochromators, which are widely used, because of the extinction rule. Only the third harmonic (m = 3) should be considered, as harmonics with $m > 3$ are negligible.

In the case in which monochromator crystals are strongly distorted by clamping or heat load, a weak second harmonic

Related chapters

Volume I: 3.11, 3.13, 3.14, 3.38, 3.39, 3.43, 3.46, 4.6, 4.7, 5.12

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 5.4

Keywords: multiple scattering; EXAFS; *FEFF*.

Multiple-scattering EXAFS analysis

Jing Liu and Anatoly I. Frenkel*

Department of Materials Science and Chemical Engineering, Stony Brook University, 100 Nicolls Road, Stony Brook, NY 11794, USA. *Correspondence e-mail: anatoly.frenkel@stonybrook.edu

Advances in multiple-scattering theory play a key role in the ongoing progress of analysis and modelling methods of extended X-ray absorption fine structure (EXAFS). This chapter will focus on the history and development of the multiple-scattering theory, introduce data-analysis and modelling strategies that employ multiple-scattering contributions to EXAFS, and discuss their applications to a variety of systems.

1. Introduction

Single-scattering analysis of extended X-ray absorption fine-structure (EXAFS) spectroscopy limited researchers to the first and, rarely, the second nearest-neighbouring shells of atomic species around the X-ray absorbing atoms. The inability to 'peek' beyond the first shell is not much of a limitation for many systems, notably those that are strongly disordered and/or of low dimensionality, where only the first peak in *r*-space can be reliably analyzed. In the case of relatively ordered materials, in particular those possessing relatively open lattices [for example f.c.c. metals (Alayoglu *et al.*, 2009; Frenkel, 1999; Rehr & Albers, 1990), alkali halide salts (Frenkel *et al.*, 1993, 1995) and some perovskites with formula BX_3 (Balerna *et al.*, 1991; Kuzmin & Purans, 1993; Kuzmin *et al.*, 1993)], strong multiple-scattering contributions to EXAFS account for a large portion of the spectrum (Lee & Pendry, 1975; Rehr & Albers, 1990) and are comparable with single-scattering contributions. Therefore, multiple-scattering contributions have to be included in EXAFS calculations and analysis for reliable structural refinement beyond the first nearest-neighbouring shell whenever the experimental data quality allows such analysis. The role of multiple-scattering events has been the subject of extensive and long-term discussions, stimulating the development of theories and data-analysis techniques,

The multiple-scattering effect occurs when the photoelectron wave is scattered more than once by surrounding atoms before returning to the X-ray absorbing atom. Multiple-scattering (MS) paths differ in the number of legs and in the type of scattering geometry. For example, single-scattering paths have two legs. Double-scattering paths (for example MS1 and MS4–MS6 in Fig. 1) have three legs, and triple-scattering paths (MS2 and MS3 in Fig. 1) have four legs. Multiple-scattering paths are very important in the X-ray absorption near-edge structure (XANES) region, because in this region a photoelectron with low kinetic energy has a long mean free path that permits the contribution of extensive multiple-scattering events to the XANES structure (Penner-Hahn, 2001). Multiple-scattering paths can be extraordinarily important when the atoms are present in a linear or nearly

Related chapters

Volume I: 2.1, 2.3, 2.25, 4.6, 4.7, 5.1, 5.2, 5.6, 5.8, 5.9, 5.1, 5.12

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY
ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 5.11

Keywords: cumulant analysis; ratio method.

The cumulant approach and the ratio method

Paolo Fornasini*

Department of Physics, University of Trento, 38123 Trento-Povo, Italy. *Correspondence e-mail: paolo.fornasini@unitn.it

For weak disorder, the distributions of interatomic distances sampled by extended X-ray absorption fine structure (EXAFS) can be parametrized in terms of their leading cumulants. For a sufficiently well isolated first coordination shell, accurate relative values of the cumulants with respect to a reference sample can be obtained by separate analysis of phases and amplitudes (the ratio method). The basics of both the cumulant approach and the ratio method are presented and their strengths and limitations are discussed.

1. Distance distributions and cumulants

An EXAFS experiment samples a one-dimensional effective distribution of interatomic distances for each scattering path

$$P(r, \lambda) = \rho(r) \exp[-2r/\lambda(k)]/r^2, \quad (1)$$

where $\lambda(k)$ is the photo-electron mean free path and $\rho(r)$ is the real distribution of distances, the width and shape of which depend on atomic vibrations and sometimes also on structural disorder.

For disorder that is not too large, an effective distribution can effectively be characterized by the cumulant expansion method (see Appendix *A*), whereby the EXAFS signal for one path is

$$\chi(k) \propto \int_0^\infty P(r, \lambda) \exp(2ikr)\, \mathrm{d}r = \exp\left[\sum_{n=0}^{\infty} (2ik)^n C_n/n!\right], \quad (2)$$

so that, for a single coordination shell,

$$\chi(k) = S_0^2 |f(k, \pi)| N \times \exp\left[C_0 - 2C_2k^2 + \frac{2}{3}C_4k^4 - \frac{4}{45}C_6k^6 + \cdots\right] \times \sin\left[2C_1k - \frac{4}{3}C_3k^3 + \frac{4}{15}C_5k^5 + \cdots + \varphi(k)\right]. \quad (3)$$

Odd and even cumulants C_n separately determine the phase and the amplitude of the signal. C_1 and C_2 are the mean and the variance of the distribution, respectively; higher-order odd and even cumulants measure the asymmetric and symmetric deviations from the normal shape, respectively. In particular, positive or negative values of the third cumulant correspond to a long tail on the positive or the negative side of the distribution, respectively.

The cumulants C_n^* of the real distribution $\rho(r)$ can be recovered from the cumulants C_n of the effective distribution by the recursion formula (Vaccari *et al.*, 2007)

$$C_n^* \simeq C_n + 2C_{n+1}(1/C_1 + 1/\lambda) \quad \text{for} \quad n = 1, 2, 3, \ldots \quad (4)$$

The difference between C_1^* and C_1 can be significant (Bunker, 1983; Freund *et al.*, 1989), $C_1^* = C_1 + 2C_2(1/C_1 + 1/\lambda)$, and the corresponding transformation is included in most data-

Related chapters

Volume I: 2.1, 2.6, 2.8, 2.12, 2.13, 2.14, 3.24, 3.25, 3.29, 4.3, 4.6, 4.7

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ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 6.5

Keywords: *EXCURVE*; EXAFS simulation; multiple scattering; disorder.

Related chapters

Volume I: 3.14, 3.43, 4.7, 5.1, 5.3, 5.4, 5.6, 5.7, 5.13

EXCURVE

Martin C. Feiters,[a]* Richard W. Strange[b] and Norman Binsted[c]

[a]Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands, [b]School of Biological Sciences, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, United Kingdom, and [c]7 Cavendish Close, Romsey SO51 7HT, United Kingdom. *Correspondence e-mail: m.feiters@science.ru.nl

The theoretical background of the EXAFS simulation program *EXCURVE* is described, as well as its simulations, refinement and analysis methods, and these are put in perspective.

1. Introduction: *EXCURVE* in perspective

X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS or XAFS), took off in the 1970s as a technique to study the structures of materials that were not amenable to single-crystal X-ray diffraction. The availability of synchrotrons as a source of brilliant tuneable X-rays coincided with the notion (Sayers *et al.*, 1971) that Fourier transformation of the spectrum yields a radial distribution function that gives the distances of atoms from the absorber atom (see Section 2). An established theoretical framework based on low-energy electron diffraction (Pendry, 1974) served as inspiration for exact theories (Lee & Pendry, 1975; Ashley & Doniach, 1975). Early EXAFS was interpreted using the plane-wave approximation (Teo & Joy, 1981; Koningsberger & Prins, 1988; Stern *et al.*, 1975; Lee & Beni, 1977; Stern, 1974; Citrin *et al.*, 1976; Teo *et al.*, 1977) in either a Fourier-fitting or curve-fitting approach. These neglected the computationally more complex curvature of the electron wave, giving poor agreement between simulation and experiment in the low-energy region. Nevertheless, these early results are reliable insofar as they deal with strong backscatterers in systems where only single scattering is important.

EXCURVE was a joint effort of theoreticians and programmers led by John Pendry at the first dedicated second-generation synchrotron storage ring, the Synchrotron Radiation Source at the Daresbury Laboratory, UK, and its user community. The first interactive version of the program was *EXINT* (Gurman, 1980). The incorporation of fast spherical wave theory into *EXINT* was a major advance because it used exact curved-wave theory with an efficient angle-averaging procedure: the fast spherical wave method (Gurman *et al.*, 1984). Further development by Binsted led to a command-based program, which was named *EXCURVE* by E. Pantos. Before this there were very few examples of EXAFS simulations that did not use the plane-wave approximation: exact calculations of, for example, As_2O_3, were computationally demanding (Gurman & Pettifer, 1979). Subsequent versions of *EXCURVE* included multiple scattering (up to third order; *EXCURV*86; Gurman *et al.*, 1986; subsequently extended to fifth order), the small-atom approximation (*EXCURV*88; Gurman, 1988; Rehr & Albers, 1990), constrained refinement (*EXCURV*90) and restrained refinement (*EXCURV*92;

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 6.8

Keywords: *FEFF*; *JFEFF*; EXAFS; XANES; XES; multiple scattering.

The *FEFF* code

J. J. Kas, F. D. Vila and J. J. Rehr*

Department of Physics, University of Washington, Box 351560, Seattle, WA 98195-1560, USA. *Correspondence e-mail: jjr@uw.edu

FEFF is a real-space multiple-scattering Green's function code for simulating a variety of X-ray spectroscopies as well as ground-state and excited-state electronic structure. It is perhaps best known for its use in extended X-ray absorption fine-structure (EXAFS) calculations, particularly within various analysis codes such as *DEMETER* and *LARCH*. In addition to EXAFS, *FEFF* can also be used to calculate X-ray absorption near-edge structure (XANES), X-ray emission spectroscopy (XES), electron energy loss spectra (EELS) and many other spectroscopic quantities. Here, the basic approach used for the calculations is described, focusing on the most important approximations and aspects of the simulations. The capabilities of the *FEFF* code, including those of the Java-based graphical user interface *JFEFF*, are also briefly described.

1. Introduction: what is *FEFF*?

FEFF is a widely used all-electron real-space multiple-scattering Green's function code for simulating a variety of X-ray spectroscopies. However, the code also calculates self-consistent atomic, ground-state and excited-state electronic structure (Rehr & Albers, 2000; Rehr *et al.*, 2009, 2010). The code is highly automated and is applicable to both periodic and aperiodic systems of up to several hundred atoms, throughout the periodic table, which can be defined by a set of atomic coordinates and their atomic numbers. The calculations carried out by *FEFF* include the dominant many-body effects in the spectra including inelastic mean free paths and vibrational damping. *FEFF* is named for the effective scattering amplitude $f_{\rm eff}$ in EXAFS, and is probably best known for its use in extended X-ray absorption fine-structure (EXAFS) calculations, particularly within various analysis codes such as *DEMETER* (Ravel & Newville, 2005) and *LARCH* (Newville, 2013; Newville & Ravel, 2024). In addition, *FEFF* can be used to simulate many other spectroscopies including X-ray absorption near-edge structure (XANES), X-ray emission spectroscopy (XES), electron energy loss spectra (EELS), nonresonant and resonant inelastic X-ray scattering (NRIXS and RIXS) and several others.

2. How does *FEFF* work?

The *FEFF* calculations are broken into several independent steps or modules, which are used sequentially to calculate different properties of the system. The major steps of the calculation are as follows:

(i) Dirac–Fock atomic calculation.
(ii) Potentials and densities.
(iii) Embedded atomic cross sections and phase shifts.
(iv) Calculation of the multiple-scattering Green's function.
(v) Spectral calculations.

Related chapters

Volume I: 2.1, 2.3, 2.6, 2.10, 4.7, 5.1, 5.2, 5.7

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ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 7.1

Keywords: information interchange.

Developing specifications for XAFS information interchange

James R. Hester*

Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia. *Correspondence e-mail: james.hester@ansto.gov.au

A number of data formats in widespread use outside the XAFS community are suitable for comprehensive descriptions of XAFS experiments. The suitability of each data format for particular use cases is assessed.

1. Introduction

As information cannot depend on the way in which it is arranged in a data file, it is always possible to cleanly divide a data-interchange specification into two parts: the *ontology* and the *format*. The ontology defines the scientific meanings of items found in data files. Each individual meaning is labelled for convenience with a *data name*. The format describes the location and arrangement of the values associated with these data names in a data file. A single ontology can therefore be used with multiple file formats, and the ontology developed for use with a particular format can be repurposed and extended for other formats.

The ontologies underlying traditional XAS data formats are simple. A format consisting of a header followed by the absorption spectrum presented in a single table is typically sufficient to capture values for all data names. Notable examples of these formats include XAFS Data Interchange (XDI) and the ICAT XAFS database input format (Asakura *et al.*, 2018). However, as made clear by Sarangi (2018) and Trevorah *et al.* (2019), much richer metadata describing both the experiment and data-modelling process are required in order to properly process, model and assess modern XAS experiments. Recording data values described by ontologies that have been expanded to cover richer metadata requires the adoption of a more complex data format, as discussed in the next section.

A survey of possible data-transfer formats for XAS was presented by Ravel *et al.* (2012). Of the surveyed formats, only the XDI format has seen much subsequent use. A textual XAS Interchange Format (XIF) for biological XAS later outlined by Sarangi (2018) allows more than one table per data file and as such is more suited to a larger ontology.

The following sections briefly assess the way in which a broad-coverage XAFS ontology might be matched to a representative sample of scientific file formats. Each file format is assessed both in terms of its suitability for a scientific ontology and according to other desirable practical features of an interchange format. The analysis below may readily be extended to the hundreds of information-interchange formats that are not covered here.

2. Ontological considerations

The suitability of a particular file format may be evaluated from an ontological perspective according to the arguments of

Related chapters

Volume I: 1.3, 3.14, 3.43, 3.46, 3.49, 4.6, 4.7, 7.2, 7.4

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 7.4

Keywords: XAFS data; XANES data; data quality.

Tables and supplementary material for X-ray absorption spectroscopy, pre-edge, XANES and XAFS

Christopher T. Chantler*

School of Physics, University of Melbourne, Australia. *Correspondence e-mail: chantler@unimelb.edu.au

This chapter attempts to address two challenges: to present a representative set of reduced XAFS data sets, including illustrative pre-edge and XANES; and to discuss scientific purposes to which each may – or may not – properly be put, as we understand at the current time. Comparisons of standards of quality and portability of data sets for different purposes are therefore core to this. The user can happily extract ideas, applications or data for their purposes from this selection, and one hopes this chapter can thereby inform data-collection and quality-control procedures that more readily allow a particular experiment to address a particular scientific purpose. The illustrations herein are arranged mainly in time order. The illustrations and discussion included in tables and the online supporting information can be used as guides towards templates for XAFS, XANES and pre-edge data standards in CIF, *eFEFFit* or *iFEFFit* formats.

1. Introduction

X-ray diffraction and crystallography in general have for a long time defined standards for reporting crystal and diffraction data, allowing these to be checked automatically according to important criteria to judge the suitability, accuracy and self-consistency of the data with the scientific result that was sought and is claimed in a publication. X-ray absorption spectroscopy (XAS) and X-ray fluorescence spectroscopy (XFS) or X-ray emission spectroscopy (XES) have been developing in this respect, and it is the intention of this chapter to discuss and illustrate some of the opportunities, needs and requirements to develop this further, especially for X-ray absorption fine structure (XAFS) studies, X-ray absorption near-edge structure (XANES) studies and pre-edge studies.

The illustrations herein are clearly only a selection, which one hopes will nonetheless be useful and lead to further development and discussion. Since there are several thousand XAFS and XANES publications a year, there is no possibility that this can or should be exhaustive. Many publications do not provide reduced data in a form that is portable for other researchers to use, and in addition the dominant modes of presentation are $\chi(k)$ versus k *plots* or transformed $\chi(r)$ versus r *plots*, thus representing the data after extensive reduction and transformation, and without presentation of the uncertainties. For most purposes, these studies have made many assumptions regarding the science which could and should be questioned, including uncertainties, grid spacing, background subtraction, normalization, interpolation, definition of edge energy and spline fitting, among others. Less common are publications with *plots* of scaled or normalized μ versus E

Related chapters

Volume I: 1.3, 3.14, 3.43, 3.46, 3.49, 4.6, 4.7

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ISSN 1574-8707
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Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 8.3

Keywords: XANES; many-body quantum physics.

Many-body quantum physics in XANES of highly correlated materials, mixed-valence oxides and high-temperature superconductors

Antonio Bianconi[a,b,c,d]*

[a]RICMASS, Rome International Center for Materials Science Superstripes, Via dei Sabelli 119A, 00185 Rome, Italy, [b]CNR, Institute of Crystallography, Consiglio Nazionale delle Ricerche, Via Salaria, 00015 Monterotondo, Rome, Italy, [c]National Research Nuclear University, MEPhI, Moscow Engineering Physics Institute, Kashirskoye sh. 31, Moscow 115409, Russia, and [d]Latvia Academy of Science, Akademijas Laukums 1, LV-1050 Riga, Latvia. *Correspondence e-mail: antonio.bianconi@ricmass.eu

Many-body final states in X-ray absorption near-edge structure (XANES) using synchrotron radiation are a unique tool for probing quantum many-body initial states in complex electronic correlated systems where single-particle descriptions of electronic states in a periodic potential break down. Multi-electron excitations were first observed in the 1960s in X-ray absorption spectra of atoms and subsequently in molecules and complex solids. The applications of XANES many-body final states to probe unique features of electronic correlation in heavy fermions, mixed-valence systems, mixed-valence oxides and high-temperature superconductors are discussed.

1. Historical introduction to many-body effects in physics: from atomic physics to condensed matter

The origin of many-body quantum physics is usually associated with the publication by Heisenberg in 1926 of the paper in which he provided a theoretical interpretation of the energy splitting of the spectral lines, called orthohelium and parahelium, in helium atomic gas absorption spectra (Heisenberg, 1926). In this work, Heisenberg assumed that the motion of the two electrons in helium is correlated, considering it as the simplest many-body electronic system, made up of only two electrons. Therefore, he described a quantum resonance between two electronic configurations of the two electrons. In this work, he introduced the exchange interaction giving the energy splitting between symmetric and antisymmetric wavefunctions. Following the article on the Fermi statistics for the electron gas in metals (Fermi, 1926), Dirac introduced the distinction of Fermi versus Bose statistics for fermions versus bosons characterized by an antisymmetric versus a symmetric wavefunction, respectively (Dirac, 1926). The exchange interaction between bosons is attractive, giving a quantum Bose condensate at $T = 0$, while the exchange interaction is repulsive for fermions, giving a degenerate Fermi gas at $T = 0$. In 1927, Wentzel proposed a nontrivial extension of the Heisenberg theory to explain the nonradiative Auger effect (Wentzel, 1927).

Majorana (1931) extended the Wentzel theory, focusing on the selection rules for the nonradiative decay of two-electron excitations observed in atomic absorption spectra (Foote *et al.*, 1925; Shenstone, 1931). Following the experiment of Beutler on vacuum ultraviolet absorption spectra of rare gases (Beutler, 1935), in which he observed broad lines due to multi-electron excitations appearing beyond the ionization

Related chapters

Volume I: 2.5, 2.7, 2.11, 2.12, 5.19

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ISSN 1574-8707
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Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 8.5

Keywords: disordered systems; liquids; EXAFS.

Liquids, glasses and amorphous solids

Andrea Di Cicco[a] **and Adriano Filipponi**[b]*

[a]Physics Division, School of Science and Technology, Università degli Studi di Camerino, Via Madonna delle Carceri, I-62032 Camerino, MC, Italy, and [b]Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila, Via Vetoio, I-67100 L'Aquila, Italy. *Correspondence e-mail: adriano.filipponi@aquila.infn.it

The nature of the structural information that can be obtained by XAFS in disordered (amorphous, liquid and glassy) systems is discussed with emphasis on the physical processes and current computational approximations and compared with established diffraction techniques. Early results and applications as well as more recent achievements are briefly reviewed.

1. XAFS in disordered systems

The photoabsorption process involved in X-ray absorption spectroscopy (XAS) can be regarded as the excitation of a core electron to a continuum level (well above the Fermi energy for the XAFS range) occurring on timescales that can be considered instantaneous with respect to atomic motion. The lifetime of the excited state is determined by the core-hole lifetime and the finite electron mean free path, which is usually limited to a few ångströms due to the strong electron interaction at the typical kinetic energies of the XAFS range (20–1000 eV). As a result, this technique is insensitive to long-range order and atomic dynamics, but is ideally suited to probe the average local structure around selected photoabsorbing atomic species in systems lacking long-range order such as glasses, amorphous solids and liquid substances.

XAFS experiments are analyzed by looking at the structural signal $\chi(k)$, which is the normalized modulation of the X-ray absorption cross section as a function of the photoelectron wavevector k, which is usually measurable in an extended range up to 10–30 Å^{-1}. In condensed systems lacking translational symmetry, the description of the average structure is usually performed by defining the n-body distribution functions $g_n(\{r\})$, of which the first nontrivial function is the pair distribution $g_2(r)$. These distributions are temperature-dependent ensemble-averaged properties and include the effect of atomic thermal motions. In amorphous systems or glasses 'thermal disorder' and 'static disorder' are sometimes considered as separate effects affecting signal damping, with the latter being associated with the classical $T = 0$ K inherent structure of the system. A general expression (Filipponi *et al.*, 1995) for the XAFS structural signal $\chi(k)$ is given in terms of the n-body distribution functions $g_n(\{r\})$ (where $\{r\}$ is a generic set of n-body coordinates):

$$\begin{aligned}\langle\chi(k)\rangle = &\int_0^\infty \mathrm{d}r\, 4\pi r^2 \rho g_2(r)\gamma^{(2)}(r,k)\\ &+\int \mathrm{d}r_1\,\mathrm{d}r_2\,\mathrm{d}\varphi\, 8\pi^2 r_1^2 r_2^2 \sin(\varphi)\rho^2 g_3(r_1,r_2,\varphi)\gamma^{(3)}(r_1,r_2,\varphi,k)\\ &+\int \mathrm{d}r_1\mathrm{d}r_2\,\mathrm{d}\varphi\,\mathrm{d}r_3\,\mathrm{d}\Omega\, 8\pi^2 r_1^2 r_2^2 r_3^2 \sin(\varphi)\rho^3 g_4(r_1,r_2,\varphi,r_3,\Omega)\\ &\times\gamma^{(4)}(r_1,r_2,\varphi,r_3,\Omega,k)\ldots \qquad (1)\end{aligned}$$

Related chapters

Volume I: 2.5, 2.11, 2.12, 3.15, 5.14, 5.15, 5.18, 5.19

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

ISSN 1574-8707
it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques
ISBN: 978-1-119-43394-1

Chapter 9.1

Keywords: X-ray absorption spectroscopy (XAS); X-ray absorption fine structure (XAFS); absorption edge; absorption coefficient; mass attenuation coefficient; linear attenuation coefficient; cross section; extended X-ray absorption fine structure (EXAFS); multi-electron excitations; absorption threshold; selection rules; secondary-process detection; X-ray emission spectroscopy (XES); inelastic X-ray scattering (IXS); X-ray excited optical luminescence (XEOL); high-energy-resolution fluorescence detection (HERFD).

X-ray absorption spectroscopy definitions

Christopher T. Chantler*

School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia. *Correspondence e-mail: chantler@unimelb.edu.au

The definitions given in this chapter were developed by a Working Group of the Commission on XAFS of the International Union of Crystallography (IUCr), and now form part of the IUCr's Online Dictionary of Crystallography at https://dictionary.iucr.org. The aims of the project were to identify ambiguous or incorrect usage of XAFS expressions in the scientific literature and to propose currently used definitions that could eventually be improved through open debate.

More than 2000 papers concerning X-ray absorption techniques are published every year. In 2009, the Commission on XAFS (CXAFS) of the International Union of Crystallography (IUCr) created a Working Group on XAFS Nomenclature to identify ambiguous or incorrect usage of XAFS expressions in the scientific literature. Our objective was not to formulate 'perfect' definitions, but to propose currently used definitions that could eventually be improved through open debate. To ensure a clear connection between CXAFS and IXAS (The International X-ray Absorption Society), both communities were represented in the membership of the Working Group: P. Glatzel (CXAFS and IXAS, Germany), C. T. Chantler (CXAFS, Australia), A. M. Molenbroek (CXAFS, Denmark), M. Newville (IXAS, USA), J. Rehr (Theory, USA), Tsun-Kong Sham (IXAS, Theory, Canada) and R. Strange (Biology, UK). The proposed definitions were then reviewed by the seven members of the Advisory Committee: C. Brouder (France), D. Creagh (Australia), J. Garcia (Spain), C. Natoli (Italy), J. Penner-Hahn (USA), R. Sarangi (USA) and E. I. Solomon (USA). The members of Working Group and the Advisory Committee were experimentalists and/or theoreticians having a physical or chemical or chemical–physical background. These different backgrounds resulted in the description of the same phenomenon with different approaches and different terminology. For example, the item 'absorption threshold', which is currently used by all XAFS experts, was considered tricky to define by nearly all Working Group and Advisory Committee members. Consequently, several definitions, reflecting theoretical or experimental approaches, have been proposed. The definitions below now form part of the IUCr's Online Dictionary of Crystallography at https://dictionary.iucr.org.

Related chapters

Volume I: 2.5, 2.7, 2.8, 2.14, 2.19, 2.25, 3.14, 3.31, 3.32, 3.43, 4.7, 7.4

1. X-ray absorption spectroscopy (XAS)

Definition: X-ray absorption spectroscopy (XAS) is a technique for measuring the linear absorption coefficient $\mu(E)$ of a substance as a function of the incident photon energy E in the X-ray regime. This technique is element- and orbital-specific and determines the local atomic and electronic structure of

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