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Grant Bunker
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Introduction

1.1 What is XAFS?

X-ray Absorption Fine Structure (XAFS) spectroscopy is a unique tool for studying, at the atomic and molecular scale, the local structure around selected elements that are contained within a material. XAFS can be applied not only to crystals, but also to materials that possess little or no long-range translational order: amorphous systems, glasses, quasicrystals, disordered films, membranes, solutions, liquids, metalloproteins – even molecular gases. This versatility allows it to be used in a wide variety of disciplines: physics, chemistry, biology, biophysics, medicine, engineering, environmental science, materials science, and geology.

The basic physical quantity that is measured in XAFS is the X-ray absorption coefficient $\mu(E)$, which describes how strongly X-rays are absorbed as a function of X-ray energy E. Generally $\mu(E)$ smoothly decreases as the energy increases (approximately as $1/E^3$), i.e. the X-rays become more penetrating. However, at specific energies that are characteristic of the atoms in the material, there are sudden increases called X-ray absorption edges. These occur when the X-ray photon has sufficient energy to liberate electrons from the low-energy bound states in the atoms. The cross section, a quantity that is proportional to $\mu(E)$, is shown in Figure 1.1 for the element platinum. Experimental data for MnO and $KMnO_4$ are shown in Figures 1.2 and 1.3.

Absorption edges were first measured in 1913 by Maurice De Broglie, the older brother of quantum mechanics pioneer Louis De Broglie. In 1920, using M. Siegbahn's vacuum spectrograph, Hugo Fricke first observed the "fine structure" – energy-dependent variations in the $\mu(E)$ – in the vicinity of the X-ray absorption edges of a number of elements. Despite some early successes and intermittent progress, for another fifty years the correct

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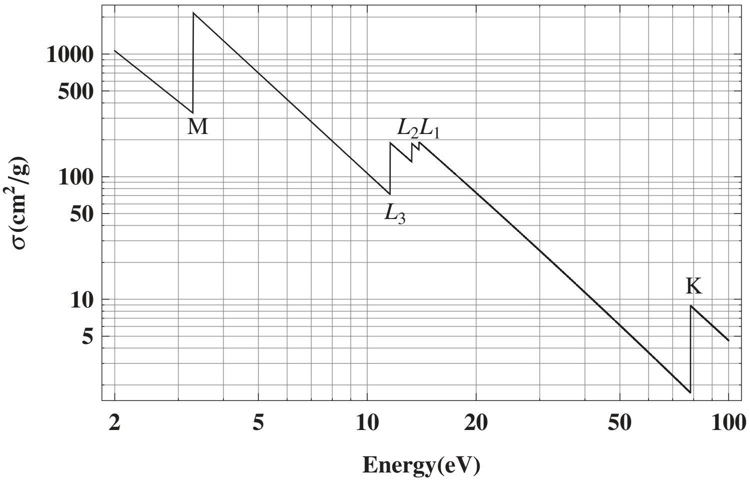

Fig. 1.1 Log-log plot of the (semiempirical) X-ray absorption cross section of platinum (Z = 78) vs. X-ray energy. The K, L_1, L_2, L_3, and M edges are shown; fine structure is *not* shown.

theoretical explanation of XAFS remained obscure. In particular, a controversy existed as to whether a model based on the long-range order (LRO) or short-range order (SRO) in the sample was more appropriate. This confusion was cleared up around 1970 when Stern, Sayers, and Lytle [1, 2, 3, 4] synthesized the essential aspects of a viable theory of XAFS, and further demonstrated that XAFS could be a practical tool for structure determination. A detailed historical account is given in the article by Stumm von Bordwehr [5].

The term "XAFS" is a broad one that comprises several different techniques: EXAFS (Extended X-ray Absorption Fine Structure); XANES (X-ray Absorption Near Edge Structure); NEXAFS (Near Edge XAFS); and SEXAFS (Surface EXAFS). Many papers are published simply as XAS (X-ray Absorption Spectroscopy). Although the basic physics of these techniques is fundamentally the same, different approximations, techniques, terminology, and theoretical approaches may be employed in different situations, particularly in the low-energy (soft X-ray) and high-energy (hard X-ray) regimes. These aspects will be discussed in the experiment and theory chapters of this book.

1.2 Physics of XAFS

XAFS is an intrinsically quantum mechanical phenomenon that is based on the X-ray photoelectric effect, in which an X-ray photon incident on an atom within a sample is absorbed and liberates an electron from an inner

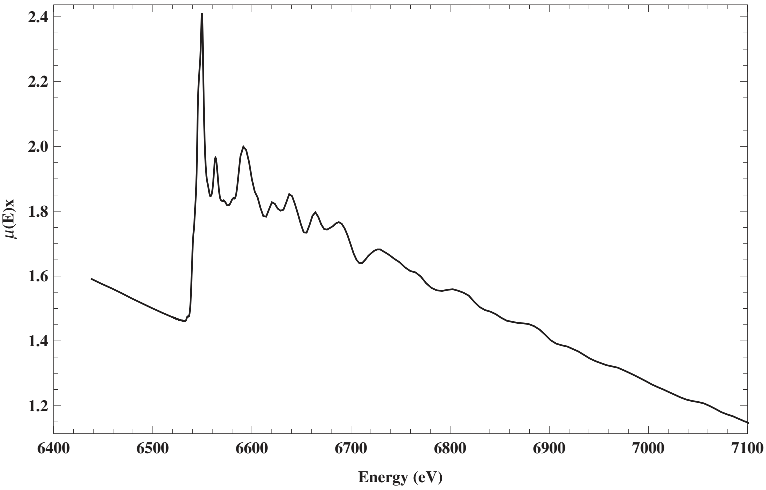

Fig. 1.2 Experimental K-edge XAFS spectrum $\mu(E)x$ of MnO at $T = 80$K.

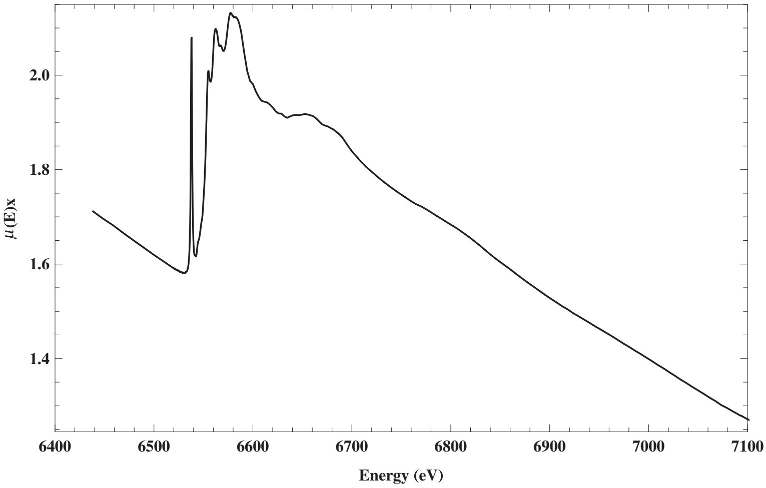

Fig. 1.3 Experimental K-edge XAFS spectrum $\mu(E)x$ of $KMnO_4$ at $T = 80$K.

atomic orbital (e.g. 1s). The "photoelectron" wave scatters from the atoms around the X-ray absorbing atom, creating interferences between the outgoing and scattered parts of the photoelectron wavefunction. These quantum interference effects cause an energy-dependent variation in the X-ray absorption probability, which is proportional to the X-ray absorption coefficient, a measurable quantity. When properly decoded these modulations provide information about the structure, atomic number, structural disorder, and thermal motions of neighboring atoms.

In addition, the XAFS technique is an *electronic* spectroscopy that measures transitions between bound initial states and bound and continuum final states. This has much in common with familiar techniques such as UV-Vis spectroscopy. As such, it also can be used to probe the nature of bound states near the Fermi level, or in molecular orbital language, the partially occupied HOMO[1], and LUMO orbitals. Use of polarized X-ray beams (which are easy to come by) permits dichroism experiments, much like those in optical spectroscopy.

1.3 Synchrotron radiation

XAFS spectroscopy has developed hand in hand with the growth of synchrotron radiation research. The first useful synchrotron X-ray facilities were developed around 1970, about the time of Stern, Sayers, and Lytle's modern synthesis. XAFS requires an X-ray beam of finely tunable energy; although it is possible to do limited experiments with a laboratory X-ray source, most experiments benefit enormously from the availability of synchrotron radiation. As a consequence, nearly all modern XAFS experiments are performed at Synchrotron Radiation Sources (SRSs).

SRSs are shared regional research facilities that, with few exceptions, are operated under government support. At present there are more than 60 rings of various sizes more or less equally distributed between the Americas, Europe, and Asia; and Australia has its own. A listing of these sources can be found at www.lightsources.org/. Often complementary research facilities such as nanotechnology centers are adjacent to the facilities.

SRSs are based on technology originally developed for high-energy physics experiments, but subsequently they have been adapted to reliably produce high-energy electromagnetic radiation such as X-rays with desirable spectral characteristics. Electrons moving close to the speed of light within an evacuated pipe are guided around a closed path of 100–1000 meter circumference by vertical magnetic fields. Wherever the trajectory bends, the electrons accelerate (change velocity vector). Accelerating charged particles emit electromagnetic radiation, and the fact that the electrons are moving at nearly the speed of light implies that relativistic effects are important. In this case they profoundly affect the properties of the emitted radiation: the average energy of the X-rays and the total radiated power are greatly increased, and the radiation pattern becomes more directional, making it much easier to employ X-ray optics such as monochromators. Often

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[1] Highest Occupied and Lowest Unoccupied Molecular Orbitals.

"insertion devices" such as "wigglers" and "undulators" also are used to further enhance the characteristics of the emitted radiation.

Beamlines are large (usually tens of meters in length) and complex instruments that include a variety of components such as X-ray monochromators; X-ray mirrors; slits; ultrahigh vacuum pumps, valves and gauges; photon shutters; shielding; safety interlocks; X-ray detectors; UHV chambers; cryostats, furnaces, reaction cells, magnets; motorized sample stages; goniometers; and data acquisition systems. All of these are under remote computer control from outside the experimental radiation enclosure. Remote control is necessary when the beam is on because ambient radiation levels are too high for experimenters to be present inside the experimental radiation enclosure.

Since the facilities are shared resources, policies are established that regulate access for experimenters. Individual beamlines may be operated by the institution that operates the ring. Alternatively they may be operated through an arrangement with one or more separate institutions that contribute resources. Generally there is some mechanism by which an outside experimenter (general user) can submit a beamtime proposal and, if it is approved, obtain days or weeks of beam time per year for their project. In most cases, if the scientific results are to be published in the open literature (i.e. the work is not proprietary), only minimal (or no) user fees will be applied for beamtime. This mechanism makes access to these outstanding research instruments available to a wide community of scientists. Usually the facilities run 24 hours per day (three 8 hour shifts) when they are operating so experimenters must have a team of several workers in order to use the beamtime effectively.

The usual mode of experimentation is as follows: samples are prepared ahead of time at the experimenter's home institution, they are transported to the beamline, spectra are measured over a period of minutes, hours, or days, and the spectra are analyzed in detail during and after the experiment. In simple cases data analysis can be done immediately, even while acquiring data, but for complex samples, analysis may take considerably more time and effort. For some systems, it may be necessary to prepare the samples on-site, or even prepare them *in situ* – i.e. right in the beam. Usually preparing and characterizing the samples, and analyzing the data are steps that take much longer than acquiring the data at the beamline. The care taken on sample preparation and measurement can have a great impact on how long it takes to interpret the data, however.

The multidisciplinary nature of XAFS and synchrotron radiation techniques, in combination with long hours at the beamline often has an unexpected benefit: experimenters working in widely different areas find themselves colliding over coffee and talking with each other. This has generated many productive collaborations.

1.4 Purpose of this book

This book has several aims. First, it is to provide an accessible, practical introduction to the basics of X-ray Absorption Fine Structure (XAFS) spectroscopy for beginning graduate students and researchers with diverse backgrounds who have a substantial undergraduate preparation in chemistry or physics. To keep the book accessible, the use of advanced mathematics has been kept to a minimum. Second, it is to provide clear explanations of certain topics that I think are important to grasp if one is to do XAFS reliably, and to remind a newer generation of researchers of useful lessons that otherwise may be forgotten. Third, it is to provide useful reference information, resources, and links for further exploration. The applications and techniques of XAFS are diverse, and it is not possible (or probably, desirable) to comprehensively cover all variants without being both tedious and instantly outdated. Programs written in the *Mathematica 7* language[2] are included to provide illustrative (and I hope, useful) examples of computations. Additional code and supplementary information will be posted from time to time, on my web site `http://gbxafs.iit.edu/` or `www.cambridge.org/9780521767750/`.

Following the Chapter 1 introduction, Chapter 2 describes the basic physics of the interaction of X-rays with matter. The same physical processes apply to the workings of the X-ray optics that are used to prepare the X-ray beams, the interaction of the beam with the sample, and the detectors that are used to measure the signals. Chapter 3 provides a description of the experimental apparatus – sources, optics, detectors – and experimental techniques. Those wishing for more extensive coverage of these topics (or lusting for more equations) may wish to consult the recent books by Als Nielsen and McMorrow [7] and Duke [8]; the venerable and still useful book edited by Koningsberger and Prins [10]; the Handbook on Synchrotron Radiation series [6]; and the X-ray data booklet from Lawrence Berkeley Laboratory [9].

Chapter 4 provides a minimal introduction to the basic theory of XAFS, delves more deeply into the computational methods that are used to calculate theoretical XAFS spectra, using as an example FEFF8. Chapter

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[2] *Mathematica 7* is used because it is powerful, self-contained but extensible, interactive, cross-platform, widely available, has numerous data sources built-in, and powerful programs can be expressed compactly. It is unfortunately not free, but much of the code can be converted to other languages by the motivated reader without great effort.

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5 describes the architecture of XAFS spectra, with the goal of developing some intuition for the spectra. It then presents the principles and rationale behind XAFS data analysis methods, and some examples with code to implement it. Detailed description of the use of various analysis packages is not attempted, since that information has a limited shelf life, there are too many from which to choose, and they are generally well described in the user guides to the programs. Chapter 6 briefly describes a variety of related techniques such as Diffraction Anomalous Fine Structure (DAFS) and Inelastic X-ray Scattering (IXS), and a conclusion. The book concludes with Appendices on Fourier methods, cumulants, X-ray filters, reference spectra, and tables of X-ray properties.

2

Basic physics of X-ray absorption and scattering

2.1 X-rays

This chapter provides a brief description of the basic X-ray physics needed to design XAFS experiments. We start with the basics.

X-rays are short-wavelength electromagnetic (EM) radiation; except for their wavelength, they are essentially the same as radio waves, microwaves, infrared, visible, ultraviolet, and gamma radiation. The frequency f is related to the wavelength λ by $f\lambda = c$, where c is the speed of light, $\approx 3 \times 10^8$ m/s.

In free space, EM waves are transverse: the electric and magnetic field vectors of the wave are perpendicular to each other, and also to the direction of propagation. The electric and magnetic field vectors oscillate in phase, and their magnitudes are proportional to each other. The direction of the electric field is described by the "electric polarization vector" $\hat{\epsilon}$, which is a unit vector in the direction of the wave's electric field vector. The direction of wave propagation is given by the wave vector $\vec{k}$, where $k = |\vec{k}| = 2\pi/\lambda$.

From a quantum perspective, the electromagnetic waves of classical physics consist of swarms of photons, which carry energy, linear momentum, and angular momentum. Such a wave is illustrated in Figure 2.1. The wavelength λ of all particles, including photons and electrons, is related to their momentum p through the De Broglie relation $\lambda = h/p$, where h is Planck's constant. Similarly, the particle frequency f is related to the energy E by $f = E/h$. Defining the angular frequency $\omega = 2\pi f$ and $\hbar = h/2\pi$, for any nonrelativistic quantum particles we have the relations $E = \hbar\omega$, $\vec{p} = \hbar\vec{k}$. The energy and momenta of photons are related by $E = pc$, which gives the relation $E = hc/\lambda \approx 12398.4\,\mathrm{eV\,Å}/\lambda \approx 1240\,\mathrm{eV\,nm}/\lambda$ for photons, a relation worth committing to memory. One eV (electron-volt) is the energy acquired by an electron as it moves between potential difference of 1 volt.

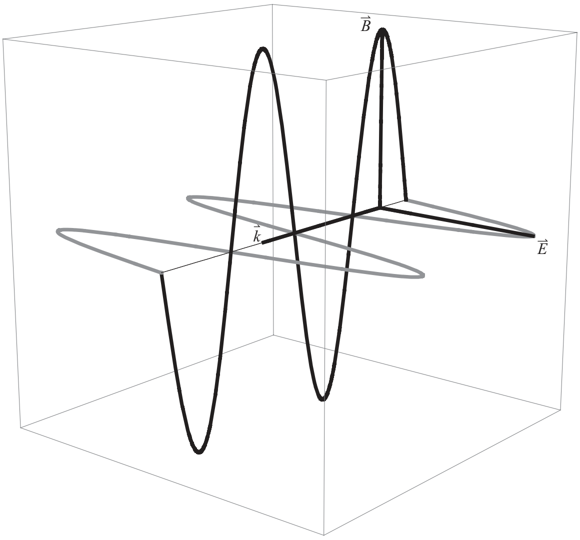

Fig. 2.1 Electric and magnetic fields in a plane EM wave in free space. The direction of propagation is along $\vec{k}$.

The wavelengths of X-rays are on the order of Ångstroms (1Å = 0.1 nm), while the wavelengths of visible light are nearly 10^4 times longer: nominally ≈ 0.4–0.7μm. The relation $E = hc/\lambda$ indicates that the energies of visible photons are a few eV (red is about 2 eV, green about 2.5 eV, blue about 3 eV), while X-rays typically have energies on the order of 10 KeV. The energies of interest for "hard" X-ray XAFS span the range from a few KeV up to about 100 KeV. "Soft" X-rays cover the range from hundreds of eV to a few KeV.

2.2 The structure of atoms

We assume the reader has a basic understanding of the architecture of atoms. Here we briefly review it from the point of view of (nonrelativistic) quantum mechanics – it is essential for understanding the interactions of X-rays and electrons with atoms.

The structure of many-electron atoms is similar to the structure of the hydrogen atom, with a few important differences. Solving Schrödinger's equation for the hydrogen atom (or one electron "hydrogenic" atoms of nuclear charge Z) can be done exactly, something that is worked out in quantum mechanics books [17], and we will not repeat it here.

The various bound state orbitals in a spherically symmetric potential can

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be written as the product of radial functions $R_{nl}(r)$, which depend on the potential, and universal angular functions that have the same form for all central (spherically symmetric) potentials. The detailed shapes and scales of the functions $R_{nl}(r)$ differ as a function of atomic number, but they have certain general properties and shapes. The spherical harmonics $Y_{lm}(\theta, \phi)$ are complex functions of the angular spherical coordinates θ and ϕ, and they are natural forms in which to express the angular part of the wavefunction. They are simultaneously eigenfunctions of the operators for the squared angular momentum $\hat{L}^2$ (with eigenvalue $l(l+1)\hbar^2$) and the z component of the angular momentum $\hat{L}_z$ (with eigenvalue $m\hbar$). In this case the orbital is written $\Psi_{nlm} \propto R_{nl}(r)Y_{lm}(\theta, \phi)$. They can also be expressed in other forms, such as the real-valued s, p, d orbitals familiar from basic chemistry; the converse is evidently true also.

The quantum numbers n, l, m are integers with $n \geq 1$, $l < n$, and $-l \leq m \leq l$. The principal quantum number n is one greater than the number of "nodes" (zeros) of the radial wavefunction. For example, in the $n = 1$ shell, there are no radial nodes; the $n = 2$ shell has one radial node. The reason this is significant is that the more nodes there are, the more rapidly in r the wavefunction must oscillate. The average kinetic energy is related to the mean square slope of the wavefunction, so more nodes translates to a higher kinetic energy. Similar trends apply to the shape of the angular functions, so that larger l implies a greater number of nodes in the angular part of the wavefunction, and usually a larger energy.

Solving for the hydrogenic wavefunctions is one thing – exactly solving the complete many-electron wavefunction of a heavy atom is quite another. Fortunately, mean-field methods, in particular "self-consistent field" (SCF) methods, are sufficiently accurate for our present purposes.[1] These allow us to approximate the potential energy experienced by an electron in an atom as due to the attraction of the nucleus of charge Z, the repulsion of the other $\approx Z - 1$ electrons, and quantum statistical effects owing to the Pauli Exclusion Principle and collective motions of the electrons which introduce a contribution (called the "exchange correlation potential" (static case) or "self-energy" (dynamic case)) to the effective one-electron potential. This allows us to approximate the many-electron problem as a one-electron (or at least one quasiparticle) problem.

Since we may approximate the many-electron atom problem as that of a single electron in an effective central potential, the orbitals have the same product form familiar from the hydrogen atom, $\Psi_{nlm} \propto R_{nl}(r)Y_{lm}(\theta, \phi)$.

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[1] It must be mentioned however that multielectron excitations do play an important role in the quantitative theory of XAFS.