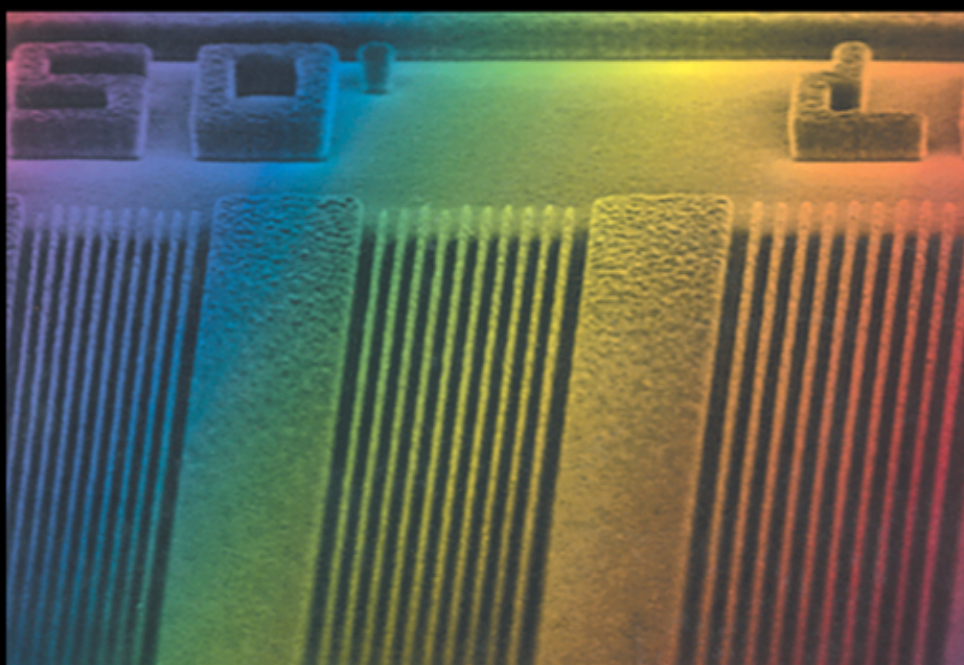


SOFT X-RAYS AND EXTREME ULTRAVIOLET RADIATION

Principles and Applications



DAVID ATTWOOD

SOFT X-RAYS AND EXTREME ULTRAVIOLET RADIATION

This self-contained, comprehensive book describes the fundamental properties of soft x-rays and extreme ultraviolet (EUV) radiation and discusses their applications in a wide variety of fields, including EUV lithography for semiconductor chip manufacture and soft x-ray biomicroscopy.

The author begins by presenting the relevant basic principles such as radiation and scattering, wave propagation, diffraction, and coherence. He then goes on to examine a broad range of phenomena and applications. Each chapter begins with a simple summary of key results and concepts, followed by an introduction with little or no mathematics so as to be accessible to the widest possible audience. This is followed by a detailed mathematical development of the theoretical structure of the subject in question. The topics covered include EUV lithography, biomicroscopy, spectromicroscopy, EUV astronomy, synchrotron radiation, and soft x-ray lasers.

The author also provides a great deal of useful reference material such as electron binding energies, characteristic emission lines, and photoabsorption cross-sections. The book will be of great interest to graduate students and researchers in engineering, physics, chemistry, and the life sciences. It will also appeal to practicing engineers involved in semiconductor fabrication and materials science.

David Attwood is the Director of the Center for X-Ray Optics at the Lawrence Berkeley National Laboratory. He is also a Professor in Residence in both the Department of Electrical Engineering and Computer Science and the Graduate Group in Applied Science and Technology at the University of California, Berkeley. He is a Fellow of the Optical Society of America and has published over 100 scientific articles.

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Principles and Applications

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UNIVERSITY OF CALIFORNIA, BERKELEY
AND
LAWRENCE BERKELEY
NATIONAL LABORATORY



CAMBRIDGE
UNIVERSITY PRESS

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS

The Edinburgh Building, Cambridge CB2 2RU, UK www.cup.cam.ac.uk
40 West 20th Street, New York, NY 10011-4211, USA www.cup.org
10 Stamford Road, Oakleigh, Melbourne 3166, Australia
Ruiz de Alarcón 13, 28014 Madrid, Spain

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First published 2000

Printed in the United States of America

Typeface Times Roman 10/12 pt. *System* L^AT_EX 2_ε [TB]

*A catalog record for this book is available from
the British Library.*

Library of Congress Cataloging-in-Publication Data

Attwood, David T.

Soft x-rays and extreme ultraviolet radiation : principles and
applications / David Attwood.

p. cm.

Includes bibliographical references.

ISBN 0-521-65214-6 (hbk.)

1. Grenz rays. 2. Ultraviolet radiation. I. Title.

QC482.G68A88 1999

539.7'222 – dc21

99-21078

CIP

ISBN 0 521 65214 6 hardback

To Professors Stanley Goldstein
and Nathan Marcuvitz

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Preface

This book is intended to provide an introduction to the physics and applications of soft x-rays and extreme ultraviolet (EUV) radiation. These short wavelengths are located within the electromagnetic spectrum between the ultraviolet, which we commonly associate with sunburn, and harder x-rays, which we often associate with medical and dental imaging. The soft x-ray/EUV region of the spectrum has been slow to develop because of the myriad atomic resonances and concomitant short absorption lengths in all materials, typically of order one micrometer or less. This spectral region, however, offers great opportunities for both science and technology. Here the wavelengths are considerably shorter than visible or ultraviolet radiation, thus permitting one to see smaller features in microscopy, and to write finer patterns in lithography. Furthermore, optical techniques such as high spatial resolution lenses and high reflectivity mirrors have been developed that enable these applications to a degree not possible at still shorter wavelengths. Photon energies in the soft x-ray/EUV spectral region are well matched to primary resonances of essentially all elements. While this leads to very short absorption lengths, typically one micrometer or less, it provides a very accurate means for elemental and chemical speciation, which is essential, for instance, in the surface and environmental sciences. Interestingly, water is relatively transparent in the spectral region below the oxygen absorption edge, providing a natural contrast mechanism for imaging carbon-containing material in the spectral window extending from 284 to 543 eV. This provides interesting new opportunities for both the life and the environmental sciences.

Exploitation of this region of the spectrum is relatively recent. Indeed the names and spectral limits of soft x-rays and extreme ultraviolet radiation are not yet uniformly accepted. We have chosen here to follow the lead of astronomers, the lithography community, and much of the synchrotron and plasma physics communities in taking extreme ultraviolet as extending from photon energies of about 30 eV to 250 eV (wavelengths from about 40 nm to 5 nm) and soft x-rays as extending from about 250 eV (just below the carbon K edge) to several thousand eV (wavelengths from 5 nm to about 0.3 nm). The overlaps with ultraviolet radiation on the low photon energy side and with x-rays on the high photon energy side of the spectrum are not well defined. For comparison, green light has a photon energy in the vicinity of 2.3 eV and a wavelength of 530 nm. Recent developments involve advances in both science and technology, moving forward in a symbiotic relationship. Of particular importance is the development of nanofabrication techniques by the electronics industry. These provide well-defined structures with feature sizes similar to the wavelengths of interest here. The development of thin film multilayer coating capabilities by the materials science community has also been of great importance.

This book is intended for use by graduate students and researchers from physics, chemistry, engineering, and the life sciences. It is an outgrowth of classes I have taught during the past 14 years at the University of California at Berkeley. Typically the students in these classes were from the Ph.D. programs in Applied Science and Technology, Electrical Engineering and Computer Science, Physics, Chemistry, Materials Science, Nuclear Engineering, and Bioengineering. In some cases there were undergraduate students. This diversity of academic backgrounds has led to a text well suited for interdisciplinary pursuits. The text is intended to be comprehensive, covering basic knowledge of electromagnetic theory, sources, optics, and applications. It is designed to bring readers from these backgrounds to a common understanding with reviews of relevant atomic physics and electromagnetic theory in the first chapters. The remaining chapters develop understanding of multilayer coated optics with applications to materials science and EUV astronomy; synchrotron and undulator radiation; laser-produced plasmas; EUV and soft-x-ray lasers; coherence at short wavelengths; zone plate lenses and other diffractive structures with applications to biomicroscopy, materials microscopy and inspection of nanostructure patterns; and, finally, a chapter on the application of EUV and soft x-ray lithography to future high-volume production of sub-100 nm feature size electronic devices.

While the book is comprehensive in nature, it is meant to be accessible to the widest possible audience. Each chapter begins with a short summary of the important points in the material, illustrations that capture the main subject matter, and a few selected equations to whet the academic appetite. Most chapters have introductory sections designed for readers new to the field that include heuristic arguments and illustrations meant to clarify basic concepts. Each chapter also contains a mathematical development of equations for graduate students and specialists with particular interest in the chapter subject matter. To follow these mathematical developments, an undergraduate training in vector calculus and Fourier transforms is required. Descriptions of current applications in the physical and life sciences are incorporated. While there is a rigorous mathematical development, it is possible to absorb important concepts in the introductory material and then skip directly to the applications. Homework problems, which may be found at the website <http://www.coe.berkeley.edu/AST/sxreuv>, are designed to strengthen understanding of the material, to familiarize the reader with units and magnitudes, and to illustrate application of various formulas to current applications.

Over 600 references are provided to serve as an entry point to current research and applications. To facilitate use as a reference work many of the more important equations are boxed. In some cases the equations are repeated in numerical form, with common units, for more convenient use in a handbook fashion. Reference appendices include tables of electron binding energies, characteristic emission lines, tables and graphs of real and imaginary scattering factors for many elements, graphs of calculated photo-absorption cross-sections, updated physical constants, and a convenient list of vector and mathematical relations. The International System of Units (SI) is also summarized, with lists of derived units and conversion factors commonly used in this field.

Berkeley, California
June 1999

Acknowledgments

It is my pleasure to acknowledge the sustained efforts, over several years, of Rudolf (Bob) Barton and Linda Geniesse. Bob typed and edited several versions of the text, carefully setting all the equations and showing great patience as I constantly revised the text and references. Linda, my wife, was responsible for all of the figures and created all of the original artwork, which I believe will benefit readers. She too showed patience far beyond reasonable expectations as we fine-tuned the artwork many times over for maximum clarity.

This book is a direct descendant of notes used at UC Berkeley in classes taught in thirteen of the past fourteen years. As such its content, method of presentation, and level of detail have been greatly influenced by Cal students. Their probing questions, discussions in class, occasional puzzled looks, contributions to homeworks, critical advice, and suggestions at semesters end have affected every paragraph of this book. I greatly appreciate their contributions. In particular I wish to acknowledge specific contributions by Kostas Adam, Junwei Bao, H. Raul Beguiristain, Kevin Bowers, Matt Brukman, Chang Chang, Gregory Denbeaux (Duke University), Eric DeVries, Daniel Finkenthal, Andrea Franke, Qian Fu, Ernie Glover, Kenneth Goldberg, Susanna Gordon, Joseph Heanue, Ronald Haff (UC Davis), John Heck, W.R. (Tony) Huff, Nasif Iskander, Ishtak Karim, Chih-wei Lai, Luke Lee, Sang Hun Lee, Yanwei Liu, Martin Magnuson (Uppsala University), Edward Moler, Vladimir Nikitin, Khanh Nguyen, Tai Nguyen, Tom Pistor, Nen-Wen Pu, Richard Schenker, Robert Socha, Regina Soufli, Alan Sullivan, Edita Tejnil, Akira Villar, Max Wei, Yan Wu, and Andrew Zenk.

The book has also benefited substantially from colleagues near and far. In preparing lectures I have sought advice and clarification from members of the Center for X-Ray Optics at Lawrence Berkeley National Laboratory. James Underwood provided original material and helpful insights on many occasions, Eric Gullikson modified many tables and graphs for use in the text, and Kwang-Je Kim, now at Argonne National Laboratory and the University of Chicago, patiently tutored me on the subject of synchrotron radiation. Werner Meyer-Ilse, Stanley Mrowka, Erik Anderson, Jeffrey Bokor (also of UC Berkeley), Patrick Naulleau, and Kenneth Goldberg each made contributions in their areas of expertise. Several of them also read particular chapters of the text and provided critical feedback. Michael Lieberman of UC Berkeley also read several early chapters and provided feedback. Portions of Chapters 2 and 6 follow lectures by Nathan Marcuvitz, then at New York University.

From a greater distance many other colleagues helped to improve the text by reading specific chapters and suggesting a wide range of improvements, corrections, and additions. For this I am grateful to Ingolf Lindau (Stanford and Lund Universities), Bernd Crasemann (University of Oregon), Joseph Nordgren (Uppsala University), David Windt (Lucent

Technologies), Claude Montcalm (LLNL), Eric Ziegler (ESRF), Alexandre Vinogradov (Lebedev Physical Institute), Albert Hofmann (CERN), R. Paul Drake (University of Michigan), R. Kauffman (LLNL), Andrei Shikanov (Lebedev Physical Institute), Luiz DaSilva (LLNL), Syzmon Suckewer (Princeton University), Jorge Rocca (Colorado State University), Emil Wolf (University of Rochester), Günter Schmahl (Göttingen University), Janos Kirz (SUNY, Stony Brook), Alexei Popov (Institut. Terr. Magn. Iono. Rad. Prop., Troitsk), Franco Cerrina (University of Wisconsin), Donald Sweeney (LLNL), Richard Stulen (Sandia), Hiroo Kinoshita (Himeji University), Victor Pol (Motorola), David Williamson (SVGL), and Frits Zernike.

Finally I am grateful to those who contributed to the atmosphere of support for research and teaching in Berkeley. These include Louis Ianiello, Iran Thomas, William Oosterhuis, and Jerry Smith at the Department of Energy's Office of Basic Energy Sciences; Howard Schlossberg at the Air Force Office of Scientific Research, who supported student research activities in our group over many years; David Patterson, who heads DARPA's Advanced Lithography Program; and the Intel, Motorola, and Advanced Micro Devices Corporations. A special note of gratitude goes to John Carruthers of Intel for his continual support of these activities and of this book in particular. Daniel Chemla is warmly acknowledged for his support and encouragement, without which it would not have been possible to maintain a vibrant research group while teaching, advising, and writing a lengthy text.

Berkeley, California
June 1999

Chapter 1

INTRODUCTION

1.1 THE SOFT X-RAY AND EXTREME ULTRAVIOLET REGIONS OF THE ELECTROMAGNETIC SPECTRUM

One of the last regions of the electromagnetic spectrum to be developed is that between ultraviolet and x-ray radiation, generally shown as a dark region in charts of the spectrum. It is a region where there are a large number of atomic resonances, leading to absorption of radiation in very short distances, typically measured in nanometers (nm) or micrometers (microns, μm), in all materials. This has historically inhibited the pursuit and exploration of the region. On the other hand, these same resonances provide mechanisms for both elemental (C, N, O, etc.) and chemical (Si, SiO_2 , TiSi_2) identification, creating opportunities for advances in both science and technology. Furthermore, because the wavelengths are relatively short, it becomes possible both to see smaller structures as in microscopy, and to write smaller patterns as in lithography. To exploit these opportunities requires advances in relevant technologies, for instance in materials science and nanofabrication. These in turn lead to new scientific understandings, perhaps through surface science, chemistry, and physics, providing feedback to the enabling technologies. Development of the extreme ultraviolet and soft x-ray spectral regions is presently in a period of rapid growth and interchange among science and technology.

Figure 1.1 shows that portion of the electromagnetic spectrum extending from the infrared to the x-ray region, with wavelengths across the top and photon energies along the bottom. Major spectral regions shown are the infrared (IR), which we associate with molecular resonances and heat; the visible region from red to violet, which we associate with color and vision; the ultraviolet (UV), which we associate with sunburn and ionizing radiation; the regions of extreme ultraviolet (EUV) and soft x-rays (SXR), which are the subject of this book; and finally hard x-rays, which we associate with medical and dental x-rays and with the scientific analysis of crystals, materials, and biological samples through the use of diffractive and other techniques.

The extreme ultraviolet is taken here as extending from photon energies of about 30 eV to about 250 eV, with corresponding wavelengths in vacuum extending from about 5 nm to 40 nm.* The soft x-ray region is taken as extending from about 250 eV (just below the carbon

*It is common to express photon energies in this spectral region in electron volts (eV) or thousands of electron volts (keV), where the photon energy is $\hbar\omega$, $\hbar$ is Planck's constant divided by 2π , and $\omega = 2\pi f$

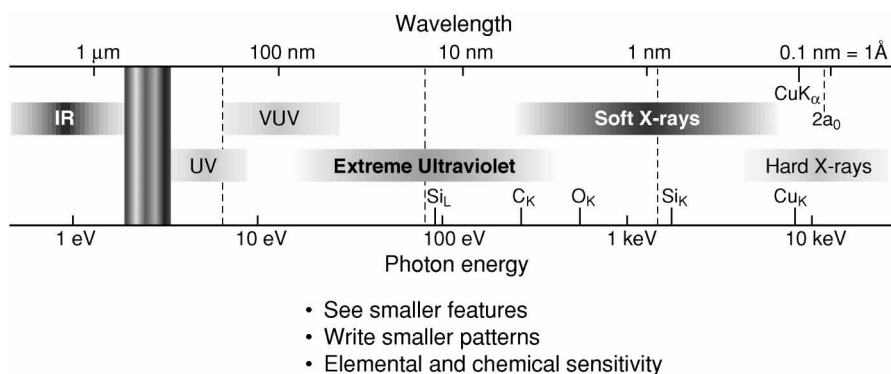


FIGURE 1.1 (see Colorplate I). The electromagnetic spectrum as it extends from the infrared (IR) to the x-ray regions. Visible light is shown with red (650 nm), green (530 nm), and blue (470 nm) wavelengths. At shorter wavelengths are ultraviolet (UV) radiation, extreme ultraviolet radiation (EUV), soft x-rays (SXR), and hard x-rays. Shown for reference are the silicon L-absorption edge at 99.2 eV (12.5 nm wavelength), the carbon K-absorption edge at 284 eV (4.37 nm), the oxygen K-absorption edge at 543 eV (2.28 nm), the silicon K-absorption edge at 1.84 keV (0.674 nm), the copper K-absorption edge at 8.98 keV (0.138 nm), the copper K_{α} -emission line at 0.154 nm or 1.54 Å (8.05 keV), and twice the Bohr radius at $2a_0 = 1.06$ Å, the diameter of the $n = 1$ orbit in Bohr's model of the hydrogen atom, but more generally a dimension within which resides most of the charge for all atoms. Vertical dashed lines correspond to the transmission limits of common window materials used to isolate vacuum. Shown are approximate transmission limits for common thicknesses of fused silica (pure SiO_2) at 200 nm, a thin film of silicon nitride (~ 100 nm thick Si_3N_4) at 15 nm, and an 8 μm thick beryllium foil at a wavelength of about 1 nm.

K-edge) to several keV, as shown in Figure 1.1. These spectral regions are characterized by the presence of the primary atomic resonances and absorption edges of most low and intermediate Z elements, where Z is the atomic number (the number of protons in the nucleus). The primary atomic absorption edges[†] for selected elements are given in Table 1.1, along with $1/e$ absorption lengths at photon energies of 100 eV and 1 keV. The K- and L-absorption edges, associated with the removal of a core electron by photoabsorption from the most tightly bound atomic states (orbitals of principal quantum numbers $n = 1$ and $n = 2$, respectively), are described later in this chapter. The K-absorption edges of carbon (C_K), oxygen, silicon, and copper are shown in Figure 1.1, as is the L-absorption edge of silicon (Si_L), just below 100 eV.

We see in Table 1.1 that many of these absorption edges lie in the combined soft-x-ray and extreme ultraviolet spectral region. What differentiates these regions from neighboring spectral regions is the high degree of absorption in all materials. At lower photon energies, in the visible and ultraviolet, and at higher photon energies, in the hard x-ray region, many materials become transparent and it is not necessary to utilize vacuum isolation techniques in general. For example, Figure 1.1 shows dashed vertical lines at the locations of common window materials that can hold vacuum over square centimeter areas while still transmitting radiation in the indicated regions. In the UV, fused silica, a form of pure SiO_2 , is transmissive to wavelengths as short as 200 nm, in millimeter thickness. For shorter wavelengths one quickly enters the vacuum ultraviolet (VUV), where air and all materials are absorbing. Shown just

is the radian frequency. Wavelengths (λ) are commonly expressed in nanometers ($1 \text{ nm} = 10^{-9} \text{ m}$) and angstroms ($1 \text{ Å} = 10^{-10} \text{ m}$). See Appendix A for the values of physical constants and conversion factors.

[†]Standard reference data for this spectral region are given in Refs. 1–4.

TABLE 1.1. K- and L₃-absorption edges for selected elements. Also given are 1/*e* absorption depths at photon energies of 100 eV and 1 keV. Energies are given to the nearest electron volt. They are measured from the vacuum level for gases (N₂, O₂), relative to the Fermi level for metals, and relative to the top of the valence band for semiconductors. Wavelengths are given to three significant figures. These K- and L-edge values can vary somewhat with the chemical environment of the atom. Values here are taken from Williams.¹ Absorption lengths are obtained from Henke, Gullikson, and Davis.³

Element	Z	K _{abs} -edge (eV)	L _{abs} -edge (eV)	λ _{K-abs} (nm)	λ _{L-abs} (nm)	l _{abs}	
						100 eV (nm)	1 keV (μm)
Be	4	112	—	11.1	—	730	9.0
C	6	284	—	4.36	—	190	2.1
N	7	410	—	3.02	—	—	—
O	8	543	—	2.28	—	—	—
H ₂ O						160	2.3
Al	13	1,560	73	0.795	17.1	34	3.1
Si	14	1,839	99	0.674	12.5	63	2.7
S	16	2,472	163	0.502	7.63	330	1.9
Ca	20	4,039	346	0.307	3.58	290	1.3
Ti	22	4,966	454	0.250	2.73	65	0.38
V	23	5,465	512	0.227	2.42	46	0.26
Cr	24	5,989	574	0.207	2.16	31	0.19
Fe	26	7,112	707	0.174	1.75	22	0.14
Ni	28	8,333	853	0.149	1.45	16	0.11
Cu	29	8,979	933	0.138	1.33	18	0.10
Se	34	12,658	1,434	0.0979	0.865	63	0.96
Mo	42	20,000	2,520	0.0620	0.492	200	0.19
Sn	50	29,200	3,929	0.0425	0.316	17	0.17
Xe	54	34,561	4,782	0.0359	0.259	—	—
W	74	69,525	10,207	0.0178	0.121	28	0.13
Au	79	80,725	11,919	0.0154	0.104	28	0.10

below 1 nm wavelength is the transmission limit of a thin ($\simeq 8 \mu\text{m}$) beryllium foil that transmits photons of energy greater than about 1.5 keV. For many years these two materials defined the limits of available window materials. More recently thin films ($\sim 100 \text{ nm}$) such as silicon nitride (stoichiometrically Si₃N₄) have extended transmissive windows to photon energies just under 100 eV, as shown in [Figure 1.1](#).

While this plenitude of atomic resonances and efficient photoabsorption has made the EUV and soft x-ray regions more difficult to access, it also provides a very sensitive tool for elemental and chemical identification, thus creating many scientific and technological opportunities. These opportunities are enhanced in this spectral region in that the wavelengths are short, but not so short as to preclude the development of high resolution optical techniques, thus permitting direct image formation and spatially resolved spectroscopies, to spatial resolutions measured in tens of nanometers. The relative transparency of water and its natural contrast with other elements further add to these opportunities, for instance for spectroscopy in the life and environmental sciences.

In the paragraphs that follow we will briefly review the basic processes of absorption, scattering, and photoemission; atomic energy levels and allowed transitions; and associated

absorption edges and characteristic emission lines. We note two interesting features associated with wavelengths in the EUV/soft-x-ray spectral region. In general the wavelengths are large compared to the Bohr radius, $\lambda \gg a_0$, where a_0 is the radius of the first ($n = 1$) stationary electron orbit in the Bohr model of hydrogen.[‡] More significantly here, the diameter $2a_0 = 1.06 \text{ \AA}$ typically encompasses most of the electronic charge in multi-electron atoms,[¶] so that to a large degree the treatment of scattering simplifies as the various electrons experience a rather uniform phase variation, an assumption that would not hold at shorter x-ray wavelengths. Furthermore, because the wavelengths are long on the atomic scale, much greater than the Compton wavelength^{4, 5} ($\lambda \gg \lambda_C = \hbar/mc = 0.0243 \text{ \AA}$), momentum transfer from the photon can be ignored during scattering, i.e., the photon momentum $\hbar k \ll \hbar k_C$, where $k = 2\pi/\lambda$ is the wavenumber, again simplifying the analysis of scattering in this spectral region.

Finally, we close this section with some numerical relationships⁷ in units⁸ convenient for work in this spectral region. Based on the dispersion relation in vacuum, $f\lambda = c$ or $\omega = kc$, where c is the velocity of light[§] in vacuum and $\omega = 2\pi f$, the product of photon energy $\hbar\omega$ and wavelength λ is given by (see Appendix A for values of physical constants)

$$\hbar\omega \cdot \lambda = hc = 1239.842 \text{ eV nm} \quad (1.1)$$

The number of photons required for one joule of energy, with wavelength given in nanometers (nm), is

$$1 \text{ joule} \Rightarrow 5.034 \times 10^{15} \lambda[\text{nm}] \text{ photons} \quad (1.2a)$$

or in terms of power

$$1 \text{ watt} \Rightarrow 5.034 \times 10^{15} \lambda[\text{nm}] \frac{\text{photons}}{\text{s}} \quad (1.2b)$$

where $1 \text{ nm} = 10 \text{ \AA}$. Thus for a wavelength $\lambda = 1 \text{ nm}$, a power of one watt corresponds to a photon flux of 5.034×10^{15} photons/s, each photon having an energy $E \simeq 1240 \text{ eV}$.

[‡]Numerically $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 0.529 \text{ \AA}$, where m is the electron rest mass, e the electron charge, ϵ_0 the permittivity of free space, and $\hbar$ Planck's constant divided by 2π . See Eisberg and Resnick, Ref. 5, for a discussion of Bohr's model of the hydrogen atom (Chapter 4) through a discussion of wave mechanics for the multi-electron atom (Chapter 10). Also see Tipler, Ref. 6, for a somewhat more introductory presentation.

[¶]In multi-electron atoms the inner shells typically have very small radii, of order a_0/Z , as they experience nearly the full Coulomb attraction of the higher- Z nucleus, with little shielding by the outer electrons. A few outer electrons typically orbit with a radius na_0 . See Eisberg and Resnick, Ref. 5.

[§]The phase velocity of EUV and soft x-ray radiation is derived from Maxwell's equations in Chapters 2 and 3, for propagation in vacuum and materials.

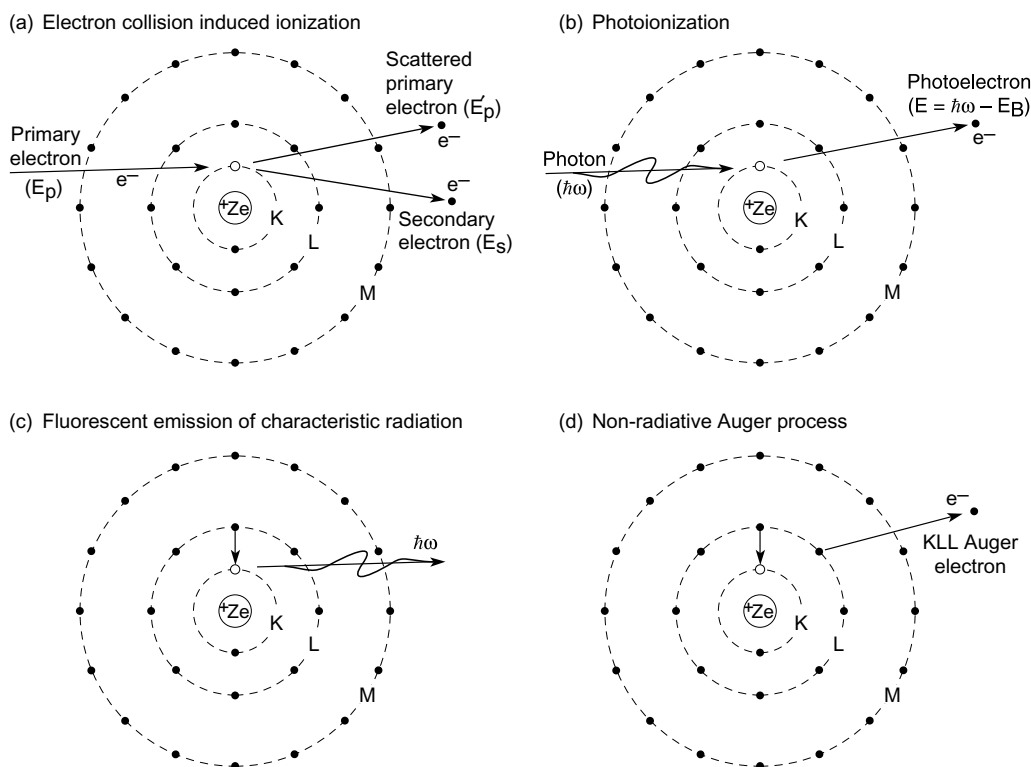


FIGURE 1.2. (a) An incident *primary electron* of sufficiently high energy E_p is scattered by an atom as it knocks free a core electron from the K-shell. The primary electron now travels in a new direction, with a reduced energy E'_p . The lost energy is used to overcome the binding energy of the previously bound electron, and to impart kinetic energy to what is now referred to as a *secondary electron*. The core vacancy (K-shell in this case) can then be filled by a higher-lying L- or M-shell electron. (b) An incident photon of sufficient energy $\hbar\omega$ is absorbed by the atom with the emission of a *photoelectron* of kinetic energy equal to the photon energy minus the binding energy. Again a vacancy is created, eventually to be filled by an outer electron. (c) An atom with a core vacancy readjusts as a higher-lying electron makes a transition to the vacancy, with the emission of a photon of characteristic energy (fluorescent radiation). (d) The atom adjusts to the core vacancy through the non-radiative Auger process in which one electron makes a transition to the core vacancy, while a second electron of characteristic energy is emitted. The second electron is not necessarily emitted from the same shell.

1.2 BASIC ABSORPTION AND EMISSION PROCESSES

In this section we briefly review the basic processes through which radiation interacts with matter. In Figure 1.2 we show simplified models of the atom, with point electrons in orbit around a nucleus of positive charge $+Ze$. In x-ray notation the electron orbits are labeled K, L, and M, corresponding to principal quantum numbers $n = 1, 2$, and 3 , respectively. A more accurate model of the atom is discussed in the next section, but that shown in Figure 1.2 suffices for these introductory comments.

Shown in Figure 1.2(a) is a primary electron incident on a multi-electron atom, with sufficient energy to remove a core electron in a close encounter. Common nomenclature refers to the incident electron as a *primary* electron, shown as *scattered* (redirected) off at some new

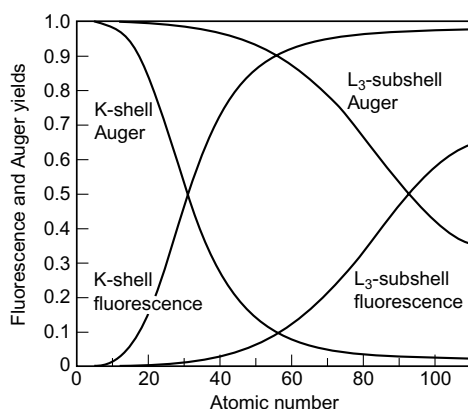


FIGURE 1.3. Fluorescence and Auger yields for the K-shell and the L_3 -subshell as a function of atomic number Z . The Auger yields include all non-radiative contributions. (Following M. Krause,⁹ Oak Ridge National Laboratory.)

angle, and in this case with reduced energy (E'_p), where the lost energy is used to overcome the binding energy needed to remove the core electron, now free and referred to as a *secondary* electron, and to supply kinetic energy to the electron (E_s). The core vacancy can then be filled by an electron from a higher-lying orbit, pulled by the strong nuclear potential, with the emission of a photon of characteristic energy equal to the difference between the two shells. In Figure 1.2(b), a related process, photoionization, is shown in which a photon of sufficient energy is absorbed by the atom, transferring the energy to an emitted *photoelectron* with a kinetic energy equal to that of the incident photon, minus the binding energy of an electron in the particular shell. As an L-shell electron is bound to the atom with less energy than a K-shell electron, it will emerge with greater kinetic energy. Electron binding energies for hydrogen through uranium are given in Appendix B, Table B.1.

In both of these ionization processes [(a) and (b)] the atom is left with a core vacancy. The atom can rearrange itself for minimal total energy by the transition of a higher-lying electron, pulled by the strong nuclear potential, to the vacancy by one of two competing processes.

In (c) the atom is shown rearranging in a process of fluorescence, in which the electron transition is accompanied by the emission of a photon of characteristic energy equal to the difference between that of the initial and final atomic states. Characteristic emission energies are given in Appendix B, Table B.2. In a competing effect (d) the atom rearranges through the emission of a second *Auger* (pronounced *ō - 'zhā*), electron, again of characteristic energy. The emitted Auger electron is labeled with three capital letters, the first representing the shell of the original vacancy, the second representing the shell from which the vacancy is filled, and the third representing the shell from which the Auger electron is ejected. In the competition between fluorescent emission and the Auger process, the probability tends to favor fluorescence for high Z atoms, as shown in Figure 1.3, and the Auger process for low Z atoms.⁹ Auger electron energies¹⁰ for lithium through uranium are given in Appendix B, Table B.3. As the Auger electrons have a fixed characteristic energy, they are used extensively for elemental characterization in surface and interface analysis.

The study of atoms, molecules, and surfaces by the measurement of photoelectron kinetic energies, as a function of incident photon energy, is known as photoemission spectroscopy. This process is widely used for the elemental identification and analysis of chemical bonding for atoms at or near surfaces. As generally employed, photons of fixed energy illuminate a surface or thin film, providing the necessary energy to lift bound electrons into the continuum, as shown in Figure 1.4. With well-known electron binding energies (Appendix B, Table B.1) the observed kinetic energies can be used to identify the elements present. As the binding energies of core electrons are affected by the orbital parameters of the outer electrons (chemical

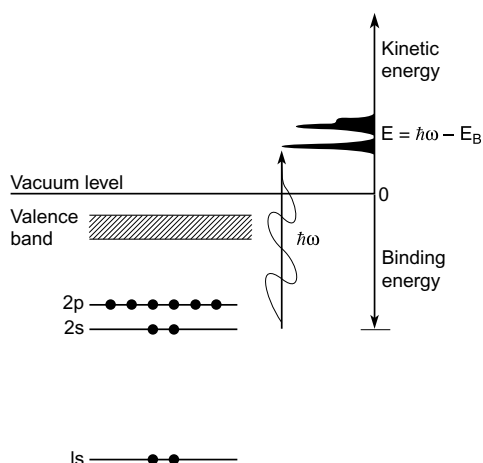


FIGURE 1.4. The process of photoemission in which an absorbed photon transfers its energy to a bound electron near the material–vacuum interface, resulting in a transition to a free electron state in the continuum with kinetic energy (E) equal to that of the incident photon ($\hbar\omega$) minus the binding energy (E_B).

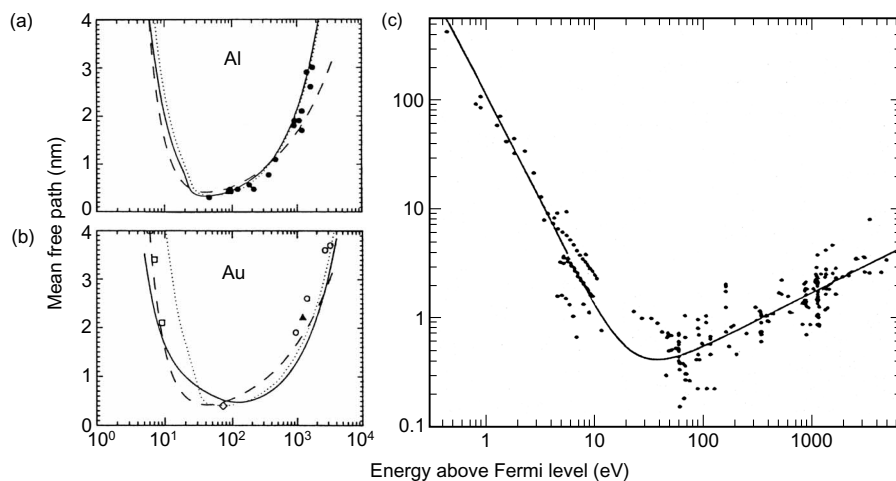


FIGURE 1.5. Electron mean free path, as a function of electron energy, for (a) aluminum, (b) gold, and (c) a combination of many materials. The data in (a) and (b) is from Penn,¹⁸ while that in (c) is from Seah and Dench.¹⁹ The various curves reflect efforts to develop a universal model that describes inelastic scattering of electrons in a solid.

bonding in molecules, valence and conduction bonds in solids), photoemission also provides a powerful tool for the study of chemical states.^{11–17} As L-shell energies are more sensitive to the bonding of outer electrons than are the energies of the more tightly bound and shielded K-shell electrons, the L-shell electrons are more commonly used in photoemission studies.

If the emitted photoelectron travels any distance in a material, it is likely to lose energy quickly through interactions with other electrons (individual collisions or collective motion). Figure 1.5 shows typical electron range data, as a function of electron energy, in aluminum and gold,¹⁸ as well as a *universal curve* for many materials.^{19, 20} With incident photon energies characteristic of the EUV/soft-x-ray spectral region, it is clear that photoelectron ranges will be extremely short, of order 1 nm, so that these techniques are clearly limited to surface science.

When observing the emission spectrum from a solid material bombarded by electrons it is typical to observe both characteristic line emission and continuum emission. This latter

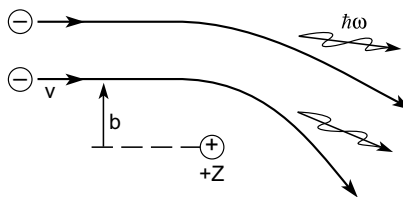


FIGURE 1.6. Bremsstrahlung radiation occurs predominantly when an incident electron is accelerated as it passes a nucleus, causing it to radiate. A broad continuum of radiation results when a large number of electrons interact randomly with nuclei at various distances of closest approach, b , resulting in wide variations in experienced acceleration and collision time.

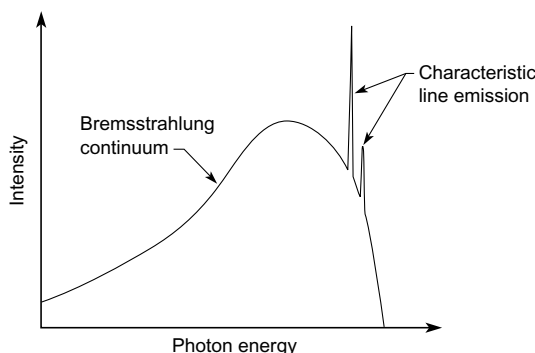


FIGURE 1.7. Continuum radiation and narrow line emission from a solid target with incident electrons, as might be observed from the anode of an electrical discharge tube.

process is called *bremstrahlung*, from the German word for “braking radiation.” Figure 1.6 shows a simple diagram of the process, in which electrons of a given velocity v , or energy E , approach an electron or nucleus at various distances of closest approach, b (the *impact parameter*), experiencing a wide range of accelerations (depending on the closeness of the interaction) and thus emitting photons across a wide range of energies. With a large number of incident electrons and a wide variety of impact parameters, a rather broad continuum of radiation is produced. Where photoemission occurs due to direct impact with bound electrons, as described earlier in Figure 1.2(a), characteristic line emission is also observed. Both phenomena are illustrated, as they might typically be observed,²¹ in Figure 1.7. The nature and nomenclature of the characteristic line emissions are discussed in the following section.

Historically, the process of photoabsorption [Figure 1.2(b)] has been observed macroscopically by passing radiation through thin foils and observing the resultant decrease in intensity as a function of thickness.²² As shown in Figure 1.8, one observes that with incremental increases in thickness, Δx , there is an incremental decrease in transmitted intensity I , relative to the incident intensity I_0 , such that

$$\frac{\Delta I}{I_0} = -\rho\mu \Delta x$$

where ρ is the mass density and μ is an energy- and material-dependent absorption coefficient. Writing this in the differential limit ($\Delta x \rightarrow dx$, $\Delta I \rightarrow dI$), the equation integrates to a

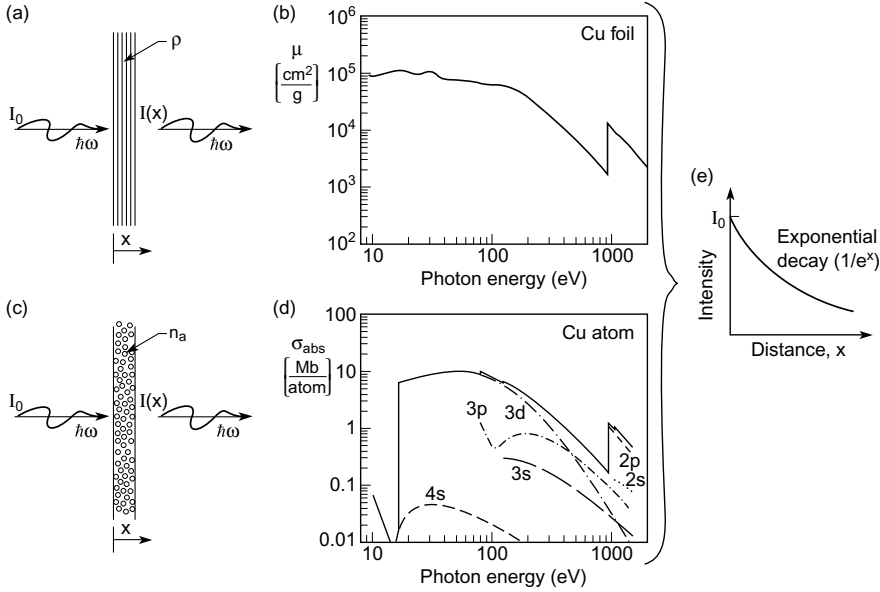


FIGURE 1.8. (a) Photoabsorption as observed with thin foils of increasing thickness x at fixed photon energy, with (b) an example of the (mass) absorption coefficient μ for copper (from Henke, Gullikson, and Davis³). The same process is described on an atomic level in (c), with the photoabsorption cross-section (photoionization) for a copper atom in (d) (from Yeh and Lindau⁴). Exponential attenuation of the radiation is shown in (e). Differences observed in comparing (b) and (d) are due to solid state effects in metallic copper foils, most noticeably for copper in the absence of the atomic 3d edge just above 10 eV photon energy.

logarithmic dependence $\ln(I/I_0) = -\rho\mu x$, or in exponential form

$$\frac{I}{I_0} = e^{-\rho\mu x} \quad (1.3a)$$

where $\mu = \mu(E, Z)$, $E = \hbar\omega$ is the photon energy, Z represents the elemental dependence, and μ has the somewhat unfortunate, but historical, name *mass absorption coefficient*. Standard values of μ are given in Appendix C for representative materials. This same expression can be written in terms of an atomic density n_a and a cross-section for photoabsorption, σ_{abs} , as

$$\frac{I}{I_0} = e^{-n_a\sigma_{\text{abs}}x} \quad (1.3b)$$

where σ_{abs} depends on both element (Z) and photon energy. Curves of σ_{abs} , also referred to as the photoionization cross-section, are given in Appendix C for representative elements, and more completely in Ref. 4. The development of Eqs. (1.3a) and (1.3b), which represent macroscopic and microscopic descriptions of the same process, is given in [Chapter 3](#),

Section 3.2, where it is shown that $\mu = \sigma_{\text{abs}}/Am_u$, where A is the number of atomic mass units and m_u is an atomic mass unit (approximately the mass of a proton or neutron), as given in Appendix A. There are some differences in the two sets of data, as the thin foil absorption coefficients μ are experimentally derived and thus involve atoms in a particular solid material or molecular form. The cross-sections σ_{abs} are calculated for single isolated atoms. The latter have the benefit that they include separately identifiable contributions of the various atomic subshells,⁴ as seen here in Figure 1.8(d).

While Figure 1.8(b) and (d) are macroscopic and microscopic manifestations of the same physical processes, some differences are notable. At low photon energies solid state effects in the metallic copper foil [Figure 1.8(b)] are important, and as a result the sharp 3d edge of the isolated copper atom [Figure 1.8(d)] just above 10 eV is not observed. Such data are of great interest to atomic and solid state researchers. Examples of the measured and calculated curves are given in Appendix C. A variety of techniques are employed to study atomic positions within solids and on surfaces, based on details of the absorption and emission processes in the presence of near-neighbor atoms. Examples of the literature are given in Refs. 11–17.

1.3 ATOMIC ENERGY LEVELS AND ALLOWED TRANSITIONS

The modern understanding of atomic energy levels, and allowed transitions between these levels, began with the Bohr–Rutherford model of the atom^{5,6} consisting of a small positive nucleus of charge $+Ze$, surrounded by electrons of charge $-e$ orbiting at relatively large radii, of order 1 Å. Based on Rutherford’s experiments (1911) with the scattering of α -particles,^{||} which demonstrated the existence of a very small nucleus of positive charge, Planck’s concept (1900) of radiation from quantized oscillators, and extensive spectroscopic data showing that atoms emit characteristic narrow lines with frequencies (or wavelengths) in specific numerical sequences, Bohr (1913) proposed the first partially successful quantum model of the atom. By equating the Coulomb force due to the positive nucleus, $Ze^2/4\pi\epsilon_0 r^2$, to the centripetal force mv^2/r for quantized circular orbits of angular momentum $mvr = n\hbar$ ($n = 1, 2, 3, \dots$), Bohr found stationary electron orbits, for the single electron atom, of energy E_n and radius r_n , where

$$E_n = -\frac{mZ^2e^4}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^2} \quad (1.4)$$

and

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{mZe^2} \cdot n^2 \quad (1.5)$$

where e and m are the electron charge and mass, respectively, Ze is the nuclear charge, ϵ_0 is the permittivity of free space, and $\hbar$ is Planck’s constant divided by 2π .

^{||}The α -particle derives its name from early studies of the radioactive decay of heavy elements. It consists of two protons and two neutrons, but no electrons, and thus is essentially a bare helium nucleus, ${}^4\text{He}$. As a radioactive decay product it is typically emitted with an energy of 5–9 MeV (Ref. 4). The other particles observed through trajectory variations in a magnetic field were β -particles (electrons, opposite curvature of trajectory to α -particles) and γ -rays (photons, no deflection).

The Bohr model, despite continuous acceleration of the electron, permits radiation only when the electron makes a transition from one stationary state (n_i) to another (n_f), with characteristic energies

$$\hbar\omega = E_i - E_f = \frac{mZ^2e^4}{32\pi^2\epsilon_0^2\hbar^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (1.6)$$

– characteristic in that there is a Z^2 dependence specific to the particular element radiating, and because of the numerical sequence involving the possible combinations of n_i and n_f . The constant $me^4/32\pi^2\epsilon_0^2\hbar^2 = hcR_\infty = 13.606$ eV, known historically as the Rydberg constant from earlier studies of hydrogen spectra, gives the ionization potential** of the ground state ($n_i = 1$, $n_f = \infty$) of the hydrogen atom ($Z = 1$). The value of the first Bohr radius of the hydrogen atom, $r_1 \equiv a_0$, is a common scale of atomic radii; from Eq. (1.5)

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \text{ \AA} \quad (1.7)$$

In terms of the Rydberg constant and first Bohr radius, the characteristic emission lines of a single electron atom of nuclear charge Z are

$$\hbar\omega = (13.606 \text{ eV})Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (1.8)$$

and the radii are

$$r_n = \frac{a_0 n^2}{Z} \quad (1.9)$$

A great success of the Bohr model was its ability to accurately match the well-known optical spectra of hydrogen, known as the Balmer series (1885), corresponding to $n_f = 2$ and $n_i = 3, 4, 5, \dots$, and also to give an accurate theoretical value for the experimentally known (1890) Rydberg constant. This was soon extended to the then unknown Lyman series, largely in the ultraviolet, with $n_f = 1$, $n_i = 2, 3, 4, \dots$; the Paschen series with $n_f = 3$, $n_i = 4, 5, 6, \dots$; the Brackett and Pfund series with $n_f = 4$ and $n = 5$, respectively, both in the infrared. Sommerfeld (1916) extended the success of the Bohr atom by introducing elliptical orbits and a second, azimuthal quantum number characterizing the ellipticity of the orbits. Additionally, taking account of the relativistic nature of the electron motion ($v/c \sim 10^{-2}$ in the hydrogen atom), Sommerfeld showed that quantized elliptical orbits introduce energetic fine structure in the spectra, as was observed experimentally.

**The energy required to remove an electron from an atom.

These successes, however, raised questions about the model and the very nature of the physics. Among the specifics, not all predicted emission lines were observed, suggesting that among the possible quantum states, only some transitions were permitted. Indeed, the model said nothing regarding transition rates or line intensities. More generally, the model was perplexing in that it was based on continuous electron acceleration within the permitted orbits, but without radiation and thus loss of energy – clearly in conflict with classical radiation physics. Collectively, elements contributing to the above model are now known as “the old quantum theory.” Following a decade of intense creativity,^{††} in the period from 1925 to 1930, Schrödinger, Heisenberg, Dirac and others developed a new quantum theory based on wave mechanics, in which the particles are described in terms of a probabilistic wave function $\Psi(\mathbf{r}, t)$. In combination with the introduction of electron spin, the new quantum mechanics provides a procedure for accurately predicting and matching experimental observations regarding properties of the atoms.

The quantum mechanical description^{5, 6, 23–26} of a particle’s motion is in terms of a wave function $\Psi(\mathbf{r}, t)$, which obeys Schrödinger’s wave equation

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}, t) + V(\mathbf{r}, t)\Psi(\mathbf{r}, t) = i\hbar\frac{\partial\Psi(\mathbf{r}, t)}{\partial t} \quad (1.10)$$

where m is the particle mass, $V(\mathbf{r})$ is the potential energy, and ∇ is the vector gradient. Particle energy and momentum are associated with the operators

$$E \rightarrow i\hbar\frac{\partial}{\partial t} \quad (1.11)$$

and

$$\mathbf{p} \rightarrow -i\hbar\nabla \quad (1.12)$$

respectively. In wave mechanics, the probability of finding a particle within coordinates $d\mathbf{r}$ is

$$P(\mathbf{r}, t)d\mathbf{r} = \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\mathbf{r} \quad (1.13)$$

where Ψ^* is the complex conjugate of Ψ , and $d\mathbf{r}$ is shorthand notation for the scalar volume around the position $\mathbf{r}$, for instance $d\mathbf{r} = dx dy dz$ in rectangular coordinates. The function $\Psi(\mathbf{r}, t)$ is normalized to unity, so that

$$\iiint_{\text{all space}} |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1 \quad (1.14)$$

Furthermore, expectation values for quantities such as the position vector, energy, and momentum are given by integrals of the following form: For the expectation value of vector position,

$$\bar{\mathbf{r}} = \iiint \mathbf{r}P(\mathbf{r}, t)d\mathbf{r} = \iiint \Psi^*(\mathbf{r}, t)\mathbf{r}\Psi(\mathbf{r}, t)d\mathbf{r} \quad (1.15)$$

which is a probabilistic average position where the particle can be expected to be found at a

^{††}For a review see the texts by Tipler (Ref. 6) and by Eisberg and Resnick (Ref. 5), for example.

time t . For the expectation value of energy,

$$\bar{E} = \iiint \Psi^*(\mathbf{r}, t) E \Psi(\mathbf{r}, t) d\mathbf{r} = i\hbar \iiint \Psi^*(\mathbf{r}, t) \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} d\mathbf{r} \quad (1.16)$$

and for the expectation value of momentum,

$$\bar{\mathbf{p}} = \iiint \Psi^*(\mathbf{r}, t) \mathbf{p}(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\mathbf{r} = -i\hbar \iiint \Psi^*(\mathbf{r}, t) \nabla \Psi(\mathbf{r}, t) d\mathbf{r} \quad (1.17)$$

where Eqs. (1.11) and (1.12) have been used.

Solution of Schrödinger's equation for the one-electron atom assumes a time dependence

$$\Psi(\mathbf{r}, t) = \Psi(\mathbf{r}) e^{-iEt/\hbar} \quad (1.18)$$

in a Coulomb potential

$$V(\mathbf{r}) = \frac{-Ze^2}{4\pi\epsilon_0 r} \quad (1.19)$$

with separable functions in spherical coordinates

$$\Psi(\mathbf{r}) = \Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (1.20)$$

where θ is measured from the z -axis. Requiring that these functions be finite, continuous, singlevalued and normalizable introduces three quantum numbers, n , l , and m_l , one for each coordinate. For negative energy these correspond to bound electrons in orbits of discrete, quantized energy. For positive energy the states are continuous and the electron is free. Here n is the principal quantum number, associated with the radial coordinate, and having allowed integer values $n = 1, 2, 3, \dots$. The orbital quantum number l associated with the θ -coordinate is related to the angular momentum by $L = \sqrt{l(l+1)}\hbar$, and is constrained to the integer values $l = 0, 1, 2, \dots, n-1$. The magnetic quantum number m_l , associated with continuity of the wave function in the angle ϕ , is related to the z -component of angular momentum by $L_z = m_l\hbar$, and is constrained to the integer values $m_l = -l, -l+1, \dots, 0, 1, \dots, l$.

The quantum mechanical description is completed with the introduction of a fourth quantum number, m_s , associated with the intrinsic electron angular momentum or spin, s . With s having a value of $\frac{1}{2}$, the quantum number m_s can have values of $\pm\frac{1}{2}$. This admits the Pauli exclusion principle, that no two electrons can have an identical set of quantum numbers. Electron spin additionally allows a spin-orbit coupling that energetically matches the fine structure observed in emission lines.

The enumerated constraints on allowable quantum numbers n , l , m_l , and m_s , along with the exclusion principle, dictate limits on the number of electrons in each shell. For instance, the first shell, with $n = 1$, can hold only two electrons, with quantum numbers $l = 0$, $m_l = 0$, $m_s = \pm\frac{1}{2}$. The second shell, with $n = 2$, can hold eight electrons, two in the $l = 0$ subshell, and six in the $l = 1$ subshell, with $m_l = 0, \pm 1$ and $m_s = \pm\frac{1}{2}$. The third shell, with $n = 3$, can hold 18, with quantum number combinations $l = 0$, $m_l = 0$, $m_s = \pm\frac{1}{2}$; $l = 1$, $m_l = 0, \pm 1$, and $m_s = \pm\frac{1}{2}$; and $l = 2$, $m_l = 0, \pm 1, \pm 2$, and $m_s = \pm\frac{1}{2}$; etc. In spectroscopic notation the electron configuration according to n and l , for an atom such as argon ($Z = 18$), would be written as $1s^2 2s^2 2p^6 3s^2 3p^6$, where s refers to an $l = 0$ subshell and p refers to $l = 1$ (d refers to $l = 2$, f refers to $l = 3$, etc.), and where the historical use of s predates the later use of s for spin.

With the constraints on the quantum numbers n , l , m_l , the Schrödinger equation provides a set of wavefunctions, Ψ_{n,l,m_l} , with which to describe the atom. For instance, the probability

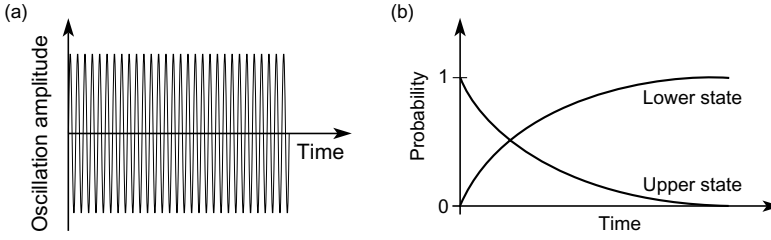


FIGURE 1.9. (a) Radiative decay from an upper state Ψ_i to a lower state Ψ_f involves a mixed atomic state in which the atom oscillates between the two at a frequency $\omega_{if} = (E_i - E_f)/\hbar$, (b) with the probability of finding the atom in the upper state slowly decaying to zero in a transition lifetime equal to many millions of cycles. (Following Liboff³¹.)

of finding an electron within coordinates $d\mathbf{r}$ at a vector position $\mathbf{r}$, in a state described by Ψ_{n,l,m_l} , is given by Eq. (1.13) to be $|\Psi_{n,l,m_l}|^2 d\mathbf{r}$. The expectation value of vector coordinates for this particular state (“orbit”) of the atom is given by Eq. (1.15) to be

$$\bar{\mathbf{r}}_{n,l,m_l} = \iiint \Psi_{n,l,m_l}^* \mathbf{r} \Psi_{n,l,m_l} d\mathbf{r}$$

That is, the coordinates are only known probabilistically, in contrast with the Bohr model, where there were well-defined orbital coordinates. Interestingly, for the hydrogen atom, the expectation values of energy are equal to those of the Bohr atom [Eq. (1.4)], with a correction due to spin–orbit coupling. The explicit coordinate dependence of the hydrogen atom wavefunctions, and their energies including spin–orbit fine structure, are described in the literature.^{5, 27, 28}

The probability of a transition between two stationary states of the atom, which we abbreviate here as Ψ_i and Ψ_f for initial and final states, is proportional to the square of the quantum mechanical dipole matrix element^{29–31}

$$-e\bar{\mathbf{r}}_{if} = -e \int \Psi_i^* \mathbf{r} \Psi_f d\mathbf{r} \quad (1.21)$$

During a transition from the higher energy stationary state Ψ_i to the lower energy stationary state Ψ_f , the average position of the electron oscillates between the two states at a frequency equal to the difference in energies $\omega_{if} = (E_i - E_f)/\hbar$, as shown in Figure 1.9. Quantum mechanically the atom is in a mixed state in which the probability of finding the atom in the upper state gradually diminishes from unity to zero, while the probability of finding it in the lower state increases during this same transition period, or *lifetime*, from zero to unity. During the transition period the electron typically executes millions of oscillations. This provides a quantum mechanical description of the spontaneous emission of radiation that occurs after an atom is excited to a higher energy level by photoabsorption (the inverse process) or collision with an electron. The line width of the resultant emission depends on the time duration (lifetime) of the transition, as the latter affects the number of oscillations corresponding to the emitted photon or wavetrain. The longer the wavetrain, the better defined the wavelength and hence the narrower the line width.

The transition probability depends on the integral matrix element given by Eq. (1.21). The integral has a classical counterpart²³ in the current density $\mathbf{J} = -en\mathbf{v}$, whose time derivative is used to calculate radiation in Maxwell’s equations, a subject we return to in Chapter 2. Here the particle *density* is given by $\Psi^*\Psi$, the charge density by $-e\Psi^*\Psi$, and the velocity $\mathbf{v}$ by $d\mathbf{r}/dt \rightarrow -i\omega_{if}\mathbf{r}$, so that a time derivative of the classical current is analogous to that of the

quantum mechanical *dipole moment* as given in Eq. (1.21). Transitions from an initial state Ψ_i to a final state Ψ_f occur quantum mechanically when the two wave functions yield a finite oscillation amplitude $\bar{\mathbf{r}}(t)$ as given by the matrix element in Eq. (1.21). If the wavefunctions Ψ_i, Ψ_f are such that the integral is zero, there is no oscillation leading to a transition, and the transition is said to be *not allowed*. Examining the integral, one notes that $\mathbf{r}$ is an odd function of the coordinates (replacing r by $-r$ changes the sign of the integrand), requiring that the initial and final wavefunctions be of opposite parity (one even, one odd in the coordinates of integration) for a non-zero integral. The parity of the wavefunctions is found to alternate with increasing quantum number l , leading to *selection rules* for allowed transitions in the hydrogen or single electron atom^{5, 6, 23–31}:

$$\Delta l = \pm 1 \quad (1.22)$$

Furthermore, the total angular momentum quantum number, j , determined by the vector sum of orbital and spin angular momentum, must satisfy

$$\Delta j = 0, \pm 1 \quad (1.23)$$

where j can take the values $l + s$, $l - s$, or s when $l = 0$. The special case of a transition between $j = 0$ states is not allowed. Note that in order to conserve angular momentum in the allowed transitions, the emitted photon must carry away a quantum ($\hbar$) of angular momentum.^{5, 29} These allowed transitions lead to the strong characteristic spectral emission lines observed experimentally. Furthermore, the atomic transition probabilities^{23, 29, 30} between any two states can be computed on the basis of matrix elements of the form given in Eq. (1.21).

Selection rules for transitions involving multi-electron atoms follow similar rules when the quantum numbers are assigned to a core level vacancy, as occurs in the photoemission process described earlier in Figure 1.2. Figures 1.10 and 1.11 illustrate the energy levels and several prominent transitions for the multi-electron atom. Figure 1.10 introduces the x-ray nomenclature²² wherein the $n = 1$ state is referred to as the K-shell, $n = 2$ as the L-shell, $n = 3$ as the M-shell, etc. Emission lines terminating in the ground state ($n = 1$) are referred to as K-shell emissions, shown here as K_α, K_β , etc. The energy required to lift a K-shell electron to a free state of zero binding energy is referred to as the K-absorption edge $E_{K,abs}$. Excess energy beyond this value goes to kinetic energy of the liberated electron. Similar notation is shown for the L-shell emissions.

Figure 1.10 is useful for an introduction. It is simplified, however, in that it does not show shell substructure, and that it implies a systematic labeling of sequential emission lines within a given series by ordered Greek subscripts α, β , etc. In fact the lines have historical designations of limited value today. Figure 1.11 shows a more accurate version²⁸ of the energy levels and some well-known transitions (on a logarithmic scale) for the copper atom ($Z = 29$). Values of the quantum numbers n, l , and total angular momentum j are given for each subshell, along with the subshell designations and spectroscopic notation. Specific values of the various energy levels and a few well-known transition energies are given for the specific example of a copper atom. Note the substantial energy fine structure due to spin-orbit coupling in the various angular momentum states.^{5, 27, 28} Note also that the 29 copper electrons are written in spectroscopic notation as $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$, thus consisting of closed K-, L-, and M-shells, plus a single valance or conduction electron. Tabulated values of binding energies¹ and prominent emission lines² for elements through uranium ($Z = 92$) are given in Appendix B.

Of great interest to us in later chapters is the spatial distribution of charge in multi-electron atoms, as we will be calculating the scattering of electromagnetic radiation and are interested in the appropriateness of assuming that the wavelength λ is large compared to atomic

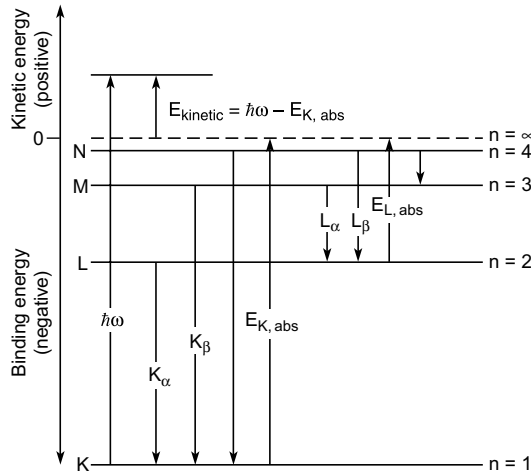


FIGURE 1.10. Energy levels for a multi-electron atom, showing the K-shell ($n = 1$), L-shell ($n = 2$), M-shell ($n = 3$), and N-shell ($n = 4$), with transitions that provide characteristic narrow line emission at well-defined photon energies. Examples shown include K_α ($n = 2$ to $n = 1$), K_β ($n = 3$ to $n = 1$), L_α ($n = 3$ to $n = 2$), etc. Also shown are the absorption edge energies, such as $E_{K,abs}$, the energy required to take an electron from the K-shell ($n = 1$) to the continuum limit ($n = \infty$). For an incident photon of energy $\hbar\omega > E_{K,abs}$, a K-shell electron can be lifted beyond the continuum limit to a state of positive kinetic energy, as shown. An L-shell electron would acquire a greater kinetic energy. The binding energies are not drawn to scale. Subscript labeling of the emission lines is less systematic than implied here, as discussed in the text. (Following Compton and Allison.²²)

radii for extreme ultraviolet and soft x-ray radiation. Toward that end, the probabilistic radial charge distribution density for filled quantum states of the argon atom ($1s^2 2s^2 2p^6 3s^2 3p^6$) is shown in Figure 1.12. Due to the strong nuclear attraction ($Z = 18$), the K-shell electrons ($1s$; $n = 1$, $l = 0$) are pulled into a region of small radius, with highest probable radial coordinate much smaller than the hydrogenic Bohr radius a_0 . The 2s and 2p L-shells ($n = 2$, $l = 0$ and $n = 2$, $l = 1$, respectively) have their charge distribution largely within a radius less than a_0 , while only the M-shell 3s and 3p have significant probability of being located in the radial interval from a_0 to $3a_0$. Thus in EUV and soft-x-ray scattering calculations, with wavelengths of order 1 nm or longer (about $20a_0$), a reasonable approximation is that all electrons see approximately the same phase and scatter collectively (in phase) in all directions. This approximation cannot be made for shorter x-ray wavelengths where $\lambda \sim a_0$, at least not for the outer valence levels. Note that the valence electrons at radii beyond a_0 are those responsible for chemical bonding, and to first order set the apparent size of an atom, as in a molecule, crystal, or other solid.³² This compact binding of the inner electrons explains the relatively small variation of volume occupied by atoms of widely different atomic number (Z) in solids and molecules: in the higher Z elements the additional electrons are largely confined to tight orbits nearer to the highly charged nucleus, with outer *valence* electrons having radial charge distributions, or equivalent mean radii, not too different from their lower Z cousins. For instance, in diamond the carbon atoms are separated by only 1.5 Å. For comparison, the hydrogen $n = 1$ mean diameter ($2a_0$) is 1.1 Å. For the face-centered cubic silicon crystal ($Z = 14$), adjacent silicon nuclei are separated by about 2.4 Å, and for common salt (NaCl) the separation distance between closest Na and Cl nuclei is about 2.8 Å.^{27, 32} Indeed, for gold ($Z = 79$) with an atomic mass of 197 and a mass density of 19.3 g/cm³, the atom to

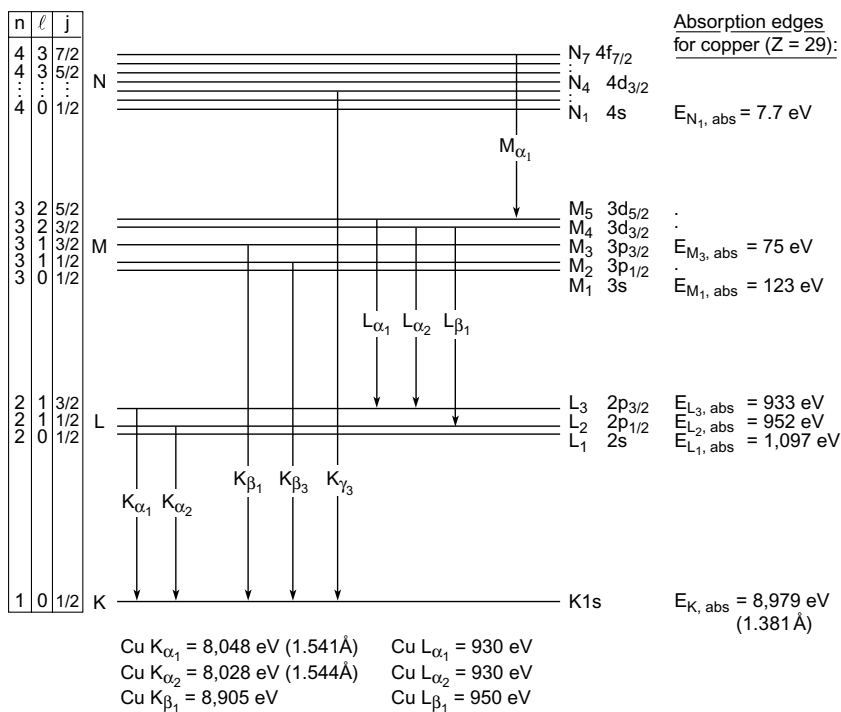


FIGURE 1.11. Energy level diagram for copper ($Z = 29$) showing transitions allowed by the selection rules $\Delta l = \pm 1$ and $\Delta j = 0, \pm 1$, where n is the principal quantum number, l is the quantum number for orbital angular momentum, and j is the quantum number for total angular momentum (orbital plus spin). In x-ray notation the K-shell corresponds to $n = 1$, the L-shell to $n = 2$, etc. Absorption edge nomenclature is shown to the right. Following spectroscopic notation, angular momentum quantum numbers $l = 0, 1, 2, 3$ are represented by the letters s, p, d, and f, respectively. Sample energies (and wavelengths) are shown for various absorption edges and allowed transitions. Note that the energy levels are not to scale, but are approximately logarithmic.

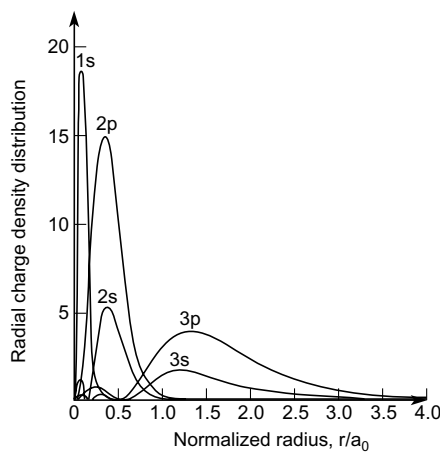
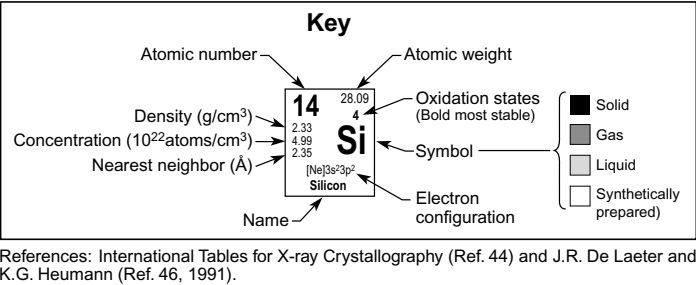


FIGURE 1.12. The probabilistic radial distribution of charge density in the argon atom, in units of electrons per unit radius ($e/\text{\AA}$), as a function of normalized radius r/a_0 , where a_0 is the Bohr radius as given in Eq. (7). This is essentially the probability of finding an electron in the region between two concentric spheres of radius r and $r + \Delta r$. Probabilities are shown for the 1s K-shell ($n = 1, l = 0$), the 2s and 2p L-shells ($n = 2, l = 0$ and $n = 2, l = 1$), and the 3s and 3p M-shells. Note that much of the electronic charge is pulled close to the high Z nucleus. (From *Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles*, 2nd ed., by R. Eisberg and R. Resnick⁵; reprinted by permission of John Wiley & Sons, Inc.)

TABLE 1.2. Key to the periodic table of the elements. See back inside cover of book for full periodic table.



atom separation is only 2.9 Å. There is strikingly little difference in the separation distances between gold, or other high Z atoms, and low Z atoms in their natural states.

A periodic table of the elements, including atomic number, atomic mass, common mass density, atomic separation distance, and spectroscopic notation of electron structure, can be found on the inside of the back cover. The key to the periodic table of the elements is given in Table 1.2. The atomic density is obtained from the relation $n_a = \rho N_A/A$, where ρ is the mass density, N_A is Avogadro’s number (see Appendix A), and A is the atomic weight of the atom, as given in the periodic chart, expressed in atomic mass units (amu).

1.4 SCATTERING, DIFFRACTION, AND REFRACTION OF ELECTROMAGNETIC RADIATION

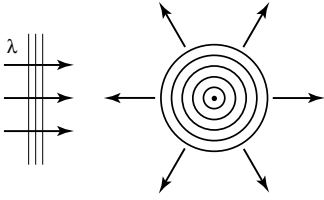
This text assumes a familiarity with Maxwell’s equations, which describe the propagation of electromagnetic radiation. A wide range of literature is available that discusses the development of these equations.^{33–38} In Chapters 2, 3, 4, 8, and 9 we will consider various aspects of wave propagation, scattering, diffraction, and refraction of radiation, with particular emphasis on application to the soft x-ray and extreme ultraviolet regions of the spectrum. In general we will use these words in the following senses.

Scattering is a process by which incident radiation^{‡‡} is redirected over a very wide angular pattern, perhaps even 4π sr, generally by disordered systems or rough surfaces, as shown in Figure 1.13(a) and (b). The angular pattern of scattering is related to the spatial periodicities of the scattering object through the Fourier transform of their charge density correlation function. A point particle, for example, scatters radiation equally in all directions. The subject of scattering from free and bound electrons is discussed in Chapter 2. The term “scattering” is used in the same sense when discussing particles, as when high energy electrons are scattered by individual nuclei.

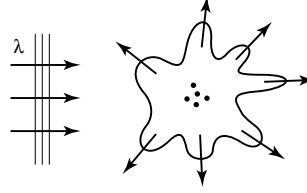
Diffraction is generally used to describe the process whereby incident radiation is redirected into relatively well-defined directions by ordered arrays of scatterers. The diffraction patterns result from positive interference in certain directions. Examples include the diffraction of x-rays by a crystal in which the position of the atoms, in a periodic array, provide well-defined planes from which the radiation appears to reflect at well-defined angles, as

^{‡‡}In this section we use “incident radiation” to mean nearly monochromatic radiation propagating in a well-defined direction.

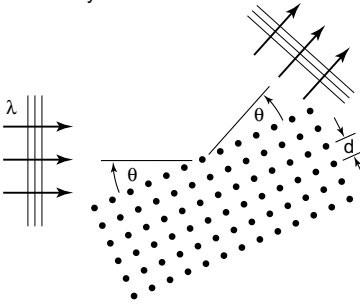
(a) Isotropic scattering from a point object



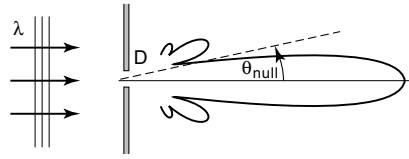
(b) Non-isotropic scattering from a partially ordered system



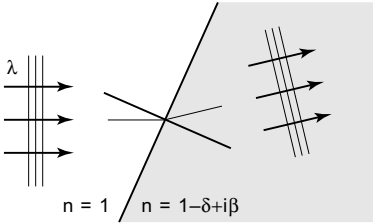
(c) Diffraction by an ordered array of atoms, as in a crystal



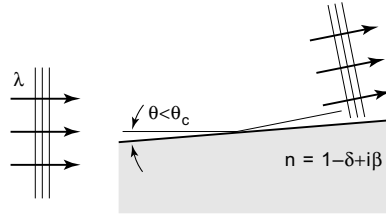
(d) Diffraction from a well-defined geometric structure, such as a pinhole



(e) Refraction at an interface



(f) Total external reflection

**FIGURE 1.13.** Scattering, diffraction, and refraction of electromagnetic radiation.

described by Bragg's law (1913) [see [Chapter 4](#)].^{22, 27, 28, 32, 41, 42}

$$m\lambda = 2d \sin \theta$$

(1.24)

where d is the spatial periodicity, λ is the wavelength, m is an integer, and θ is measured from the reflecting plane, as shown in [Figure 1.13\(c\)](#). In fact, the atomic positions in a crystal always describe many such planes, so that diffraction (positive interference) occurs in several directions. While the diffraction of x-rays by crystals is not discussed further in this text, diffraction from one-dimensional ordered systems, known in the EUV and soft-x-ray community as multilayer mirrors, is described in [Chapter 4](#). These structures may be amorphous or partially ordered within the individual layers but well ordered in the stack direction, leading to very strong positive interference in directions described by the Bragg condition, Eq. (24). This leads to very high reflectance for appropriate choices of material, wavelength (photon energy), and angle. Readers interested in the important subject of x-ray diffraction by crystals are referred to Refs. 27, 28, 32, and 41–43.

“Diffraction” is also used to describe the situation in which incident radiation is redirected in some well-defined pattern, as when visible light or shorter wavelength radiation is diffracted by a small circular aperture (a pinhole), causing a divergence of the radiation with bright and dark angular interference rings, as shown in [Figure 1.13\(d\)](#). This is known as an Airy pattern (1835); the first dark null in the diffraction pattern occurs at a half angle (see [Chapter 9, Section 9.3](#))

$$\theta_{\text{null}} = \frac{1.22\lambda}{d} \quad (1.25)$$

where θ is measured from the axis of symmetry through the center of the pinhole, and d is the pinhole diameter. Similar characteristic angular patterns occur when radiation is diffracted from other well-defined objects, such as a knife edge or a sphere.

Finally, *refraction* is the turning of radiation at an interface of materials of dissimilar refractive index n , generally written in the EUV/soft x-ray region as^{††}

$$n = 1 - \delta + i\beta \quad (1.26)$$

where in this spectral region both δ and β are generally small compared to unity, as is discussed in [Chapter 3](#). Refractive turning at an interface occurs as the incident wave excites radiation among atoms at the surface of the second material. This launches a new wave through interference of radiation from the various atoms, in a manner that ensures continuity of the field quantities at the boundary. The process is sketched in [Figure 1.13\(e\)](#). Finally, [Figure 1.13\(f\)](#) shows an example of reflection peculiar to this spectral region. With a refractive index less than unity it is possible to have *total external reflection* in which most of the incident energy is redirected by the surface. There is little absorption even in the case of an otherwise absorptive material ($\beta \leq \delta$). Total external reflection occurs as long as the glancing angle of incidence θ is less than a critical angle $\theta_c \simeq \sqrt{2\delta}$, as described²² first by Compton in 1922. This subject is described further in [Chapter 3](#).

The development of electromagnetic theory with special emphasis on the application to EUV and soft x-ray wavelengths, based on Maxwell’s equations, begins in [Chapter 2](#). The wave equation in vacuum is obtained, Poynting’s theorem and expressions for radiated power are developed, and scattering cross-sections are introduced. The cross-sections for scattering

^{††}The choice of $\pm i\beta$ in [Eq. \(1.26\)](#) depends on the mathematical form by which waves are represented, and must be consistent with wave decay in the presence of absorption. Early x-ray workers such as Compton²² employed a plane wave representation equivalent to $\exp[i(\omega t - kr)]$, where ω is the radian frequency, $k = 2\pi/\lambda$, and the refractive index n is defined by the dispersion relation $\omega = kc/n$, or equivalently $f\lambda = c/n$. Written in this form, n has a *negative* imaginary component in the presence of absorption; thus for x-rays $n = 1 - \delta - i\beta$. This form continues to dominate common usage in the x-ray community. However, in the broader community of modern electrodynamics and optical sciences (Sommerfeld,³⁹ Born and Wolf,³⁷ Fowles,⁴⁰ Jackson,³⁶ and Spiller⁴⁵) plane wave representations are more commonly written in the form $\exp[-i(\omega t - kr)]$, where the imaginary component of refractive index is *positive* in the presence of absorption, as in [Eq. \(1.26\)](#). For this text the more modern approach has been adopted; however, its adaptation to the older one should cause the reader little inconvenience. Algebraic demonstration of the above is given in [Chapter 3, Section 3.2](#).

of radiation by free and bound electrons are obtained. These results are extended to scattering by multi-electron atoms and to atomic scattering factors, within certain approximations generally applicable in the EUV and soft x-ray regions of the spectrum.

In [Chapter 3](#) Maxwell's equations are applied to the propagation of short wavelength radiation in a medium of uniform density, developing expressions for the complex refractive index, phase variation, and attenuation. Also discussed are reflection and refraction at arbitrary angle of incidence, total external reflectance and normal incidence reflection as special cases, Brewster's angle, and topics such as the Kramers–Kronig relations among the real and imaginary parts of the atomic scattering factors.

In [Chapter 4](#) the subject of multilayer interference coatings is discussed, with applications to a variety of activities, including multilayer curved mirrors for focusing EUV, soft x-ray, and x-ray radiation. The applications discussed in [Chapter 4](#) include photoemission microscopy, polarization control, astronomy, plasma diagnostics, and industrial lithography.

In [Chapters 8 and 9](#) the topics of coherence and diffraction are discussed. In [Chapter 9](#) the use of Fresnel zone plates as diffractive lenses is discussed, with application to soft x-ray microscopy at high spatial resolution – well beyond that of visible light microscopy – in the physical and life sciences.

REFERENCES

1. A compilation by G.P. Williams of Brookhaven National Laboratory, "Electron Binding Energies," in *X-Ray Data Booklet* (Lawrence Berkeley National Laboratory Pub-490 Rev.2, 1999), based largely on values given by J.A. Bearden and A.F. Barr, "Reevaluation of X-Ray Atomic Energy Levels," *Rev. Mod. Phys.* 39, 125 (1967); M. Cardona and L. Ley, Editors, *Photoemission in Solids I: General Principles* (Springer, Berlin, 1978); and J.C. Fuggle and N. Mårtensson, "Core-Level Binding Energies in Metals," *J. Electron. Spectrosc. Relat. Phenom.* 21, 275 (1980).
2. A compilation by J.B. Kortright, "Characteristic X-Ray Energies," in *X-Ray Data Booklet* (Lawrence Berkeley National Laboratory Pub. 490 Rev. 2, 1999), based on values given by J.A. Bearden, "X-Ray Wavelengths," *Rev. Mod. Phys.* 39, 78 (1967).
3. B.L. Henke, E.M. Gullikson, and J.C. Davis, "X-Ray Interactions: Photoabsorption, Scattering, Transmission, and Reflection at $E = 50\text{--}30,000$ eV, $Z = 1\text{--}92$," *Atomic Data and Nucl. Data Tables* 54, 181 (1993). Current updates maintained by E.M. Gullikson at <http://www-cxro.lbl.gov/>
4. J.-J. Yeh and I. Lindau, "Atomic Subshell Photoionization Cross Sections and Asymmetry Parameters: $1 \leq Z \leq 103$," *Atomic Data and Nucl. Data Tables* 32, 1–155 (1985); J.-J. Yeh, *Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters* (Gordon and Breach, Langhorne, PA, 1993); I. Lindau, "Photoemission Cross Sections," [Chapter 1](#), p. 3, in *Synchrotron Radiation Research: Advances in Surface and Interface Science*, Vol. 2 (Plenum, New York, 1992), R.Z. Bachrach, Editor.
5. R. Eisberg and R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles* (Wiley, New York, 1985), Second Edition.
6. P.A. Tipler, *Modern Physics* (Worth, New York, 1978).
7. Numerical values of fundamental physical constants are obtained from E.R. Cohen and B.N. Taylor, "The Fundamental Physical Constants," *Phys. Today*, p. BG9 (August 1995).
8. Use of metric units (SI) follows R.A. Nelson, "Guide for Metric Practice," *Phys. Today*, p. BG15 (August 1995).
9. M.O. Krause, "Atomic Radiative and Radiationless Yields for K and L Shells," *J. Phys. Chem. Ref. Data* 8, 307 (1979); M.O. Krause and J.H. Oliver, "Natural Widths of Atomic K and L Levels, K_{α} X-Ray Lines and Several KLL Auger Lines," *J. Phys. Chem. Ref. Data* 8, 329 (1979); M.O. Krause, "Average L-Shell Fluorescence, Auger, and Electron Yields," *Phys. Rev. A* 22, 1958 (1980).
10. J.F. Moulder, W.F. Stickle, P.E. Sobol, and K.D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy* (Physical Electronics, Eden Prairie, MN, 1995).

11. D.E. Eastman and F.J. Himpsel, "Ultraviolet Radiation – An Incisive and Versatile Tool," *Physics Today*, p. 64 (May 1981).
12. C.S. Fadley, "Basic Concepts of X-Ray Photoelectron Spectroscopy," pp. 1–156 in *Electron Spectroscopy, Theory, Techniques and Applications* (Pergamon Press, Oxford, 1978), C.R. Brundle and A.D. Baker, Editors; C.S. Fadley et al., "Surface, Interface and Nanostructure Characterization with Photoelectron Diffraction and Photoelectron and X-ray Holography," *J. Surface Anal.* 3, 334 (1997); C.S. Fadley and P.M. Len, "Holography with X-rays," *Nature* 380, 27 (1996); A. Kay, E. Arenholz, S. Mun, F.J. Garcia de Abajo, C.S. Fadley, R. Denecke, Z. Hussain, and M.A. Van Hove, "Multi-atom Resonant Photoemission: A Method for Determining Near-Neighbor Atomic Identities and Bonding," *Science* 281, 679 (1998); G. Faigel and M. Tegze, "X-ray Holography," *Rep. Progr. Phys.* 62, 355 (1999).
13. P.Y. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties* (Springer, Berlin, 1996), [Chapter 8](#), "Photoelectron Spectroscopy."
14. S. Hüfner, *Photoelectron Spectroscopy: Principles and Application* (Springer, Berlin, 1996).
15. V. Schmidt, *Electron Spectroscopy of Atoms Using Synchrotron Radiation* (Cambridge Univ. Press, 1997).
16. W. Eberhardt, Editor, *Applications of Synchrotron Radiation: High Resolution Studies of Molecular Adsorbates on Surfaces* (Springer-Verlag, Berlin, 1995).
17. C.R. Brundle, C.A. Evans, and S. Wilson, *Encyclopedia of Materials Characterization* (Butterworth-Heinemann, London, 1992); J. Stöhr, *NEXAFS Spectroscopy* (Springer-Verlag, Berlin, 1992).
18. D.R. Penn, "Electron Mean-Free-Path Calculations Using a Model Dielectric Function," *Phys. Rev. B* 35, 482 (1987).
19. M.P. Seah and W.A. Dench, "Quantitative Electron Spectroscopy of Surfaces: A Standard Data Base for Electron Inelastic Mean Free Paths in Solids," *Surface and Interface Anal.* 1, 2 (1979).
20. C.J. Powell, "Attenuation Lengths of Low-Energy Electrons in Solids," *Surface Sci.* 44, 29 (1974); C.J. Powell and M.P. Seah, "Precision, Accuracy, and Uncertainty in Quantitative Surface Analysis by Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy," *J. Vac. Sci. Technol. A* 8, 735 (March/April 1990).
21. For example, see data for Mo ($Z = 42$) in the *Handbuch der Physik: Röntgenstrahlen*, Encyclopedia of Physics: X-Rays, Vol. XXX, (Springer-Verlag, Berlin, 1957), S. Flügge, Editor, pp. 10, 338.
22. A.H. Compton and S.K. Allison, *X-Rays in Theory and Experiment* (Van Nostrand, New York, 1935), Second Edition.
23. L.I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968), Third Edition.
24. A. Messiah, *Quantum Mechanics* (Wiley, New York, 1961).
25. J.L. Powell and B. Crasemann, *Quantum Mechanics* (Addison-Wesley, Reading, MA, 1961).
26. D.I. Blokhintsev, *Principles of Quantum Mechanics* (Allyn and Bacon, Boston, 1964).
27. R.B. Leighton, *Principles of Modern Physics* (McGraw-Hill, New York, 1959).
28. F.K. Richtmyer, E.H. Kennard, and T. Lauritsen, *Introduction to Modern Physics* (McGraw-Hill, New York, 1955).
29. A. Corney, *Atomic and Laser Spectroscopy* (Clarendon, Oxford, 1977).
30. R. Loudon, *The Quantum Theory of Light* (Clarendon Press, Oxford, 1983), Second Edition.
31. R.L. Liboff, *Introductory Quantum Mechanics* (Addison-Wesley, Reading, MA, 1998), Third Edition, Section 10.7.
32. C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976), Fifth Edition.
33. G.S. Smith, *Classical Electromagnetic Radiation* (Cambridge Univ. Press, 1997).
34. J.A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941).
35. S. Ramo, J. Whinnery, and T. Van Duzer, *Fields and Waves in Communications Electronics* (Wiley, New York, 1984).
36. J.D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1998), Third Edition.
37. M. Born and E. Wolf, *Principles of Optics* (Cambridge Univ. Press, New York, 1999), Seventh Edition.
38. E. Hecht, *Optics* (Addison-Wesley, Reading, MA, 1998), Third Edition.

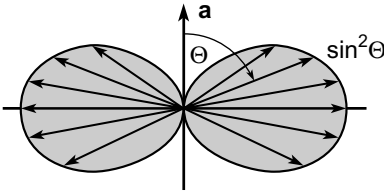
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39. A. Sommerfeld, *Optics* (Academic Press, New York, 1964); A. Sommerfeld, *Electrodynamics* (Academic Press, New York, 1964).
 40. G.R. Fowles, *Introduction to Modern Optics* (Dover, New York, 1975), Second Edition.
 41. R.W. James, *The Optical Principles of the Diffraction of X-Rays* (Ox Bow Press, Woodbridge, CT., 1982).
 42. J. Helliwell, *Macromolecular Crystallography with Synchrotron Radiation* (Cambridge Univ. Press, New York, 1992); S.W. Lovesey and S.P. Collins, *X-ray Scattering and Absorption by Magnetic Materials* (Oxford Univ. Press, 1996); J.R. Helliwell and P.M. Rentzepis, Editors, *Time-Resolved Diffraction* (Oxford Univ. Press, 1997).
 43. B.D. Cullity, *Elements of X-Ray Diffraction* (Addison-Wesley, Reading, MA, 1978), Second Edition.
 44. *International Tables for X-Ray Crystallography, Vol. III*, International Union of Crystallography (Reidel, London, 1983), C.H. MacGillavry, G.D. Rieck, and K. Lonsdale, Editors.
 45. E. Spiller, *Soft X-Ray Optics* (SPIE, Bellingham, WA, 1994).
 46. J.R. DeLaeter and K.G. Heumann, "Atomic Weights of the Elements 1989," *J. Phys. Chem. Ref. Data* 20, 1313 (1991).

HOMEWORK PROBLEMS

Homework problems for each chapter will be found at the website:

<http://www.coe.berkeley.edu/AST/sxreuv>

RADIATION AND SCATTERING AT EUV AND SOFT X-RAY WAVELENGTHS



$$\frac{dP}{d\Omega} = \frac{e^2 |\mathbf{a}|^2 \sin^2 \Theta}{16\pi^2 \epsilon_0 c^3} \quad (2.34)$$

$$r_e = \frac{e^2}{4\pi \epsilon_0 m c^2} \quad (2.44)$$

$$\sigma_e = \frac{8\pi}{3} r_e^2 \quad (2.45)$$

$$\sigma = \frac{8\pi}{3} r_e^2 \frac{\omega^4}{(\omega^2 - \omega_s^2)^2 + (\gamma\omega)^2} \quad (2.51)$$

$$f(\Delta\mathbf{k}, \omega) = \sum_{s=1}^Z \frac{\omega^2 e^{-i\Delta\mathbf{k} \cdot \Delta\mathbf{r}_s}}{\omega^2 - \omega_s^2 + i\gamma\omega} \quad (2.66)$$

$$f^0(\omega) = \sum_{s=1}^Z \frac{\omega^2}{\omega^2 - \omega_s^2 + i\gamma\omega} \quad (2.72)$$

In this chapter basics of electromagnetic theory are reviewed. Beginning with Maxwell's equations, the wave equation is developed and used to solve several problems of interest at short wavelengths. Poynting's theorem regarding the flow of electromagnetic energy is used to solve the power radiated by an accelerated electron. The concept of a scattering cross-section is introduced and applied to the scattering of radiation by free and bound electrons. A semiclassical model is used in the latter case. Scattering by a multi-electron atom is described in terms of a complex atomic scattering factor. Tabulated scattering factors, which are available in the literature for use in special circumstances, are described.

2.1 MAXWELL'S EQUATIONS AND THE WAVE EQUATION

In this chapter we will consider radiation and scattering by accelerated charges. We will use these results to study scattering cross-sections and interesting phenomena at visible, EUV, and

soft x-ray wavelengths. In later chapters we will examine their relation to the refractive index (propagation effects) and the properties of undulator radiation.

Our study begins with *Maxwell's equations*,^{1–5} written in a form appropriate to the use of MKS units:*

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} \quad (\text{Ampere's law}) \quad (2.1)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (\text{Faraday's law}) \quad (2.2)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2.3)$$

$$\nabla \cdot \mathbf{D} = \rho \quad (\text{Coulomb's law}) \quad (2.4)$$

where $\mathbf{E}$ is the electric field vector, $\mathbf{H}$ is the magnetic field vector, $\mathbf{D}$ is the electric displacement, $\mathbf{B}$ is the magnetic density or magnetic induction, $\mathbf{J}$ is the current density, ρ is the charge density, ϵ_0 is the permittivity (dielectric constant) of free space, and μ_0 is the magnetic permeability. If the above are considered to describe fields in free space (vacuum), the constitutive relations take the form

$$\mathbf{D} = \epsilon_0 \mathbf{E} \quad (2.5)$$

$$\mathbf{B} = \mu_0 \mathbf{H} \quad (2.6)$$

where now the charge density ρ and current density $\mathbf{J}$ must be described in a self-consistent manner, i.e., where the fields affect the particles and the particles contribute to the fields. Note that, as is common in the literature, we have used ρ for both charge and mass density (Chapter 1). The reader will recognize the difference by the context.

As described by James Maxwell in 1865, these equations can be combined to form a vector wave equation describing the propagation of electromagnetic waves, as later demonstrated by Heinrich Hertz in 1888. The mathematical description covers electromagnetic phenomena extending from very long wavelengths, to radiowaves, microwaves, infrared, visible, ultraviolet, and x-rays and beyond. The *vector wave equation* can be obtained from Maxwell's equations by taking $\nabla \times$ [Eq. (2.2)] and using the vector identity[†] $\nabla \times \nabla \times \mathbf{A} = \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$ to obtain

$$\nabla \times (\nabla \times \mathbf{E}) = \nabla \times \left(-\frac{\partial \mathbf{B}}{\partial t} \right)$$

$$\nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\mu_0 \frac{\partial}{\partial t} (\nabla \times \mathbf{H})$$

*See Appendix A, Units and Physical Constants.

†See Appendix D, Mathematical and Vector Relations.

$$\begin{aligned}\nabla \left(\frac{\rho}{\epsilon_0} \right) - \nabla^2 \mathbf{E} &= -\mu_0 \frac{\partial}{\partial t} \left(\frac{\partial D}{\partial t} + \mathbf{J} \right) \\ \nabla \left(\frac{\rho}{\epsilon_0} \right) - \nabla^2 \mathbf{E} &= -\epsilon_0 \mu_0 \frac{\partial}{\partial t} \left(\frac{\partial \mathbf{E}}{\partial t} + \frac{\mathbf{J}}{\epsilon_0} \right)\end{aligned}$$

Rearranging terms, we obtain

$$\epsilon_0 \mu_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} - \nabla^2 \mathbf{E} = -\mu_0 \frac{\partial \mathbf{J}}{\partial t} - \frac{1}{\epsilon_0} \nabla \rho$$

which when properly grouped is recognized as the vector wave equation:

$$\left(\frac{\partial^2}{\partial t^2} - c^2 \nabla^2 \right) \mathbf{E}(\mathbf{r}, t) = -\frac{1}{\epsilon_0} \left[\frac{\partial \mathbf{J}(\mathbf{r}, t)}{\partial t} + c^2 \nabla \rho(\mathbf{r}, t) \right] \quad (2.7)$$

where

$$c \equiv \frac{1}{\sqrt{\epsilon_0 \mu_0}} \quad (2.8)$$

is identified as the phase velocity of an electromagnetic wave in vacuum, often referred to as the “speed of light in vacuum.” Note that this is an inhomogeneous partial differential equation. The driving terms on the right-hand side of the equation can be linear or non-linear, leading to a wealth of interesting phenomena.

The wave equation (2.7) will serve as our point of departure in considering radiation, scattering, and refractive index in situations including free and bound electrons, single atoms, and various distributions of atoms. In this chapter we will treat the scattering of x-rays by individual electrons and atoms through appropriate representations of the induced source terms on the right side of the wave equation. We will obtain several interesting results, including expressions for the well-known Thomson and Rayleigh scattering cross-sections for free and bound electrons, as well as atomic scattering cross-sections for multi-electron atoms. We will employ very simple models of the atom, but will observe that the basic results are identical in form to those obtained with more sophisticated quantum mechanical models. In [Chapter 3](#) we will treat wave propagation phenomena in relatively uniform media containing many atoms. There we will find it convenient to bring the uniformly distributed source terms to the left side of the wave equation, where the combined terms will lead to a modified phase velocity and thus the introduction of a refractive index. This will lead to several practical results, including equations governing the total external reflection of x-rays. We will also discuss how refractive indices and complex scattering cross-sections are determined and tabulated in practice.

Before proceeding to these topics, we note that an expression for conservation of charge, the so-called equation of charge continuity, is easily developed and will be useful later. This follows by taking $\nabla \cdot$ [Eq. (2.1)] and noting the vector identity $\nabla \cdot \nabla \times \mathbf{A} \equiv 0$. We have

$$\nabla \cdot \nabla \times \mathbf{H} = \frac{\partial}{\partial t} \nabla \cdot \mathbf{D} + \nabla \cdot \mathbf{J}$$

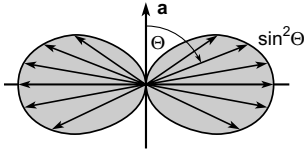


FIGURE 2.1. As observed at a great distance, fields radiated by an accelerated charge propagate over a broad angular range, but not in the direction of acceleration.

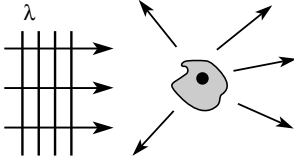


FIGURE 2.2. Irregularly shaped objects and isolated charges, including free electrons and electrons bound to isolated atoms, scatter radiation in many directions.

where the left hand side is identically 0, and on the right-hand side $\nabla \cdot \mathbf{D} = \rho$. This gives the equation for conservation of charge:

$$\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = 0 \quad (2.9)$$

What we would like to accomplish in this chapter is a solution to Eq. (2.7) for $\mathbf{E}(\mathbf{r}, t)$ in the presence of source terms – for instance, radiated fields due to accelerated free and bound electrons (Figure 2.1), or the *scattered* fields caused by such oscillating charges in the presence of incident (x-ray) radiation. The latter is a process whereby well-directed energy, propagating in a given direction, is widely redirected by non-uniformly distributed charges or by irregularly shaped objects (Figure 2.2).

One can write the current density $\mathbf{J}(\mathbf{r}, t)$ as

$$\mathbf{J}(\mathbf{r}, t) = qn(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t) \quad (2.10)$$

a product of charge density and velocity, both as functions of space and time. Note that the product nv raises the possibility of non-linear terms entering via particle motions into the otherwise linear electromagnetic fields. This interesting phenomenon, which we touch on in later chapters, occurs in media (plasmas, fluids, solids) in which both n and $\mathbf{v}$ vary, giving rise to beat frequencies, sum and difference frequencies, and such phenomena as harmonic generation. In this chapter we concern ourselves with isolated charges, both free and bound, for which Eq. (2.10) can be written in a somewhat different form convenient to this simple case. We will consider this shortly.

2.2 CALCULATING SCATTERED FIELDS

First we outline the approach to be taken in solving the wave equation (2.7) for $\mathbf{E}(\mathbf{r}, t)$ in the presence of a source term. Then we calculate the radiated power and its angular dependence. Treating the bracketed quantity on the left side of Eq. (2.7) as an operator, we can imagine solving for $\mathbf{E}(\mathbf{r}, t)$ in terms of arbitrary sources, with a formal solution of the form

$$\mathbf{E}(\mathbf{r}, t) = \int_{\text{volume}} [\text{Green's function}][\text{source terms}] d\mathbf{r} \quad (2.11)$$

where the field $\mathbf{E}$ is described mathematically in terms of the response to a distribution of sources – embodied in the so-called *Green's function* – integrated over the full volume.

This is not convenient to do with Eq. (2.7) in the form of a vector partial differential equation. But it can be accomplished^{6,7} without too much difficulty by introducing space-time transformations of $\mathbf{E}(\mathbf{r}, t)$ that algebraize the partial differential operators, ∇ and $\partial/\partial t$. Working then with transform amplitudes $\mathbf{E}(\mathbf{k}, \omega)$, abbreviated $\mathbf{E}_{k\omega}$, the differential operators become algebraic multipliers, the inversions required in Eq. (2.11) become simple, and the integration proceeds using standard techniques. Note that the vector field transform amplitudes $\mathbf{E}_{k\omega}$ are a generalization of the Fourier coefficients utilized in one dimensional (scalar) problems. Using this technique to solve for $\mathbf{E}(\mathbf{r}, t)$, the remaining fields, including $\mathbf{H}(\mathbf{r}, t)$ etc., can be determined from transforms of Eqs. (2.1)–(2.6).

In order to simplify both the space (∇) and time ($\partial/\partial t$) operators, we introduce the *Fourier–Laplace transform*

$$\mathbf{E}(\mathbf{r}, t) = \int_{\mathbf{k}} \int_{\omega} \mathbf{E}_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4} \quad (2.12a)$$

and its inverse

$$\mathbf{E}_{k\omega} = \int_{\mathbf{r}} \int_t \mathbf{E}(\mathbf{r}, t) e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} d\mathbf{r} dt \quad (2.12b)$$

where the symbols $d\mathbf{k}$ and $d\mathbf{r}$ are shorthand notation for scalar volume elements. These abbreviations correspond in rectangular coordinates to $d\mathbf{r} = dx dy dz$ and $d\mathbf{k} = dk_x dk_y dk_z$. We also understand that the Fourier–Laplace amplitudes $\mathbf{E}_{k\omega}$ are shorthand notation for $\mathbf{E}(\mathbf{k}, \omega)$, as they are vector field amplitudes and are functions of the wave vector $\mathbf{k}$ and frequency ω . We assume that the frequency has a small imaginary component such that the amplitude $\mathbf{E}_{k\omega}$, defined by the integral in Eq. (2.12b), is finite for real fields $\mathbf{E}(\mathbf{r}, t)$. Thus with $\omega = \omega_r + i\omega_i$, where ω_i is small but positive, the integrand in Eq. (2.12b) goes to zero as $t \rightarrow \infty$.

Representing all field quantities in a similar manner, i.e.,

$$\mathbf{J}(\mathbf{r}, t) = \int_{\mathbf{k}} \int_{\omega} \mathbf{J}_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4} \quad (2.13a)$$

$$\mathbf{J}_{k\omega} = \int_{\mathbf{r}} \int_t \mathbf{J}(\mathbf{r}, t) e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} d\mathbf{r} dt \quad (2.13b)$$

$$\rho(\mathbf{r}, t) = \int_{\mathbf{k}} \int_{\omega} \rho_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4} \quad (2.14a)$$

$$\rho_{k\omega} = \int_{\mathbf{r}} \int_t \rho(\mathbf{r}, t) e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} d\mathbf{r} dt \quad (2.14b)$$

etc., we can appreciate the algebraized nature of the operators. For instance, if we consider the time derivative, $\partial/\partial t$, acting on $\rho(\mathbf{r}, t)$, we have

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \frac{\partial}{\partial t} \int_{\mathbf{k}} \int_{\omega} [\rho_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})}] \frac{d\omega d\mathbf{k}}{(2\pi)^4}$$

Note that $\partial/\partial t$ passes through the integrals (to first order, $\mathbf{k}$ and ω are not functions of time). Since $\rho_{k\omega}$ is also not a function of time (to first order), the time derivative acts only on the

exponent, giving

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \int_{\mathbf{k}} \int_{\omega} (-i\omega) \rho_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4}$$

Thus the time differential operator $\partial/\partial t$ results in an algebraic multiplier $(-i\omega)$ when acting on $\rho(\mathbf{r}, t)$, i.e., when operating in $\mathbf{k}, \omega$ -space. Similarly the gradient operator, taken component by component in some coordinate space, becomes

$$\nabla \rho(\mathbf{r}, t) = \nabla \int_{\mathbf{k}} \int_{\omega} [\rho_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})}] \frac{d\omega d\mathbf{k}}{(2\pi)^4}$$

Although the algebraization may be evident to the reader at this point, it is easily illustrated by introducing rectangular coordinates, such that the $\mathbf{k} \cdot \mathbf{r}$ term in the exponent becomes $k_x x + k_y y + k_z z$, the gradient becomes $\nabla = \mathbf{x}_0 \partial/\partial x + \mathbf{y}_0 \partial/\partial y + \mathbf{z}_0 \partial/\partial z$, and $\mathbf{k} = \mathbf{x}_0 k_x + \mathbf{y}_0 k_y + \mathbf{z}_0 k_z$, where $\mathbf{x}_0, \mathbf{y}_0, \mathbf{z}_0$ are unit vectors. Since the components $\partial/\partial x, \partial/\partial y, \partial/\partial z$ act only on the exponent, the expression for $\nabla \rho(\mathbf{r}, t)$ becomes

$$\nabla \rho(\mathbf{r}, t) = \int_{\mathbf{k}} \int_{\omega} (i\mathbf{x}_0 k_x + i\mathbf{y}_0 k_y + i\mathbf{z}_0 k_z) [\rho_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})}] \frac{d\omega d\mathbf{k}}{(2\pi)^4}$$

or

$$\nabla \rho(\mathbf{r}, t) = \int_{\mathbf{k}} \int_{\omega} i\mathbf{k} \rho_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4}$$

so that the ∇ operator is replaced by a multiplicative factor $i\mathbf{k}$ in $\mathbf{k}, \omega$ -space. Finally, if we consider the operator $\nabla^2 \equiv \nabla \cdot \nabla = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$, we can readily demonstrate that

$$\nabla^2 \mathbf{E}(\mathbf{r}, t) = \int_{\mathbf{k}} \int_{\omega} (i\mathbf{k})^2 \mathbf{E}_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4}$$

where now it can be seen that $\nabla^2 = \nabla \cdot \nabla$ algebraizes to $i\mathbf{k} \cdot i\mathbf{k} = -k^2$ in $\mathbf{k}, \omega$ -space.

The vector wave equation (2.7) can now be algebraized itself into a very convenient form in terms of the Fourier–Laplace amplitudes:

$$\begin{aligned} & \int_{\mathbf{k}} \int_{\omega} (-i\omega)^2 \mathbf{E}_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4} - c^2 \int_{\mathbf{k}} \int_{\omega} (-k^2) \mathbf{E}_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4} \\ &= -\frac{1}{\epsilon_0} \left[\int_{\mathbf{k}} \int_{\omega} (-i\omega) \mathbf{J}_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4} + c^2 \int_{\mathbf{k}} \int_{\omega} i\mathbf{k} \rho_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4} \right] \end{aligned}$$

where we note that every term includes the same $\mathbf{k}, \omega$ -integration, which can therefore be removed, and further, that each term contains an exponential factor $-i(\omega t - \mathbf{k} \cdot \mathbf{r})$, which can also be removed, leaving

$$(-i\omega)^2 \mathbf{E}_{k\omega} - c^2 (-k^2) \mathbf{E}_{k\omega} = -\frac{1}{\epsilon_0} [(-i\omega) \mathbf{J}_{k\omega} + c^2 (i\mathbf{k}) \rho_{k\omega}]$$

In operator form, the wave equation in $\mathbf{k}, \omega$ -space is

$$(\omega^2 - k^2 c^2) \mathbf{E}_{k\omega} = \frac{1}{\epsilon_0} [(-i\omega) \mathbf{J}_{k\omega} + i c^2 \mathbf{k} \rho_{k\omega}] \quad (2.15)$$

which, if inverted, can be solved for $\mathbf{E}_{k\omega}$:

$$\mathbf{E}_{k\omega} = \frac{(-i\omega)\mathbf{J}_{k\omega} + ic^2\mathbf{k}\rho_{k\omega}}{\epsilon_0(\omega^2 - k^2c^2)} \quad (2.16)$$

This shows the source terms in the numerator, and poles at $\omega = \pm kc$ representing the system response in terms of incoming and outgoing waves. Our task now is to set models for the sources in a given problem, $\mathbf{J}(\mathbf{r}, t)$ and $\rho(\mathbf{r}, t)$, obtain their transforms $\mathbf{J}_{k\omega}$ and $\rho_{k\omega}$, determine a solution for $\mathbf{E}_{k\omega}$ from Eq. (2.16), and then return to the inverse transform [Eq. (6.12a)] to calculate the radiated field $\mathbf{E}(\mathbf{r}, t)$ through the required $d\omega d\mathbf{k}$ integrations [Eq. (6.12a)].

Making the same substitutions as above in the equation for charge conservation [Eq. (2.9)],

$$\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = 0$$

permits similar simplification of it. Upon use of similar transforms and operations this becomes

$$i\mathbf{k} \cdot \mathbf{J}_{k\omega} - i\omega\rho_{k\omega} = 0$$

so that

$$\rho_{k\omega} = \frac{\mathbf{k} \cdot \mathbf{J}_{k\omega}}{\omega}$$

Thus the expression for the radiated fields $\mathbf{E}_{k\omega}$ [Eq. (16)] can be written as

$$\mathbf{E}_{k\omega} = -\frac{i\omega}{\epsilon_0} \left[\frac{\mathbf{J}_{k\omega} - (c^2/\omega^2)\mathbf{k}(\mathbf{k} \cdot \mathbf{J}_{k\omega})}{\omega^2 - k^2c^2} \right]$$

or

$$\mathbf{E}_{k\omega} = -\frac{i\omega}{\epsilon_0} \left[\frac{\mathbf{J}_{k\omega} - \mathbf{k}_0(\mathbf{k}_0 \cdot \mathbf{J}_{k\omega})}{\omega^2 - k^2c^2} \right] \quad (2.17)$$

Here we have written the wave propagation vector as $\mathbf{k} = k\mathbf{k}_0$. The unit vector $\mathbf{k}_0$ is in the propagation direction, and $k = 2\pi/\lambda$ is the scalar wavenumber. The equation $\omega = kc$ (equivalent to $f\lambda = c$) is most readily appreciated from Eq. (2.17) as the required condition for finite field amplitude $\mathbf{E}_{k,\omega}$ even in the absence of sources. In other words, $\omega = kc$ satisfies the homogeneous (vacuum) case where the right-hand side of Eq. (2.15) is zero. These are the so-called resonances or natural modes of the system. The condition $\omega = kc$ is often referred to as a dispersion relation; we will discuss it further in Chapter 3.

We can simplify Eq. (2.17) for $\mathbf{E}_{k\omega}$ by introducing a coordinate system oriented around the wave propagation direction $\mathbf{k}_0$, as shown in Figure 2.3. For instance, we can decompose the vector $\mathbf{J}_{k\omega}$ into components along and transverse to the propagation direction $\mathbf{k}_0$:

$$\mathbf{J}_{k\omega} = \mathbf{J}_{T_{k\omega}} + J_{L_{k\omega}}\mathbf{k}_0$$

If we do so, it is evident that with $\mathbf{k} = k\mathbf{k}_0$ the numerator in the bracketed factor in Eq. (2.17) becomes

$$\mathbf{J}_{k\omega} - \underbrace{\mathbf{k}_0(\mathbf{k}_0 \cdot \mathbf{J}_{k\omega})}_{\mathbf{k}_0 \text{ portion}} = \mathbf{J}_{T_{k\omega}}$$

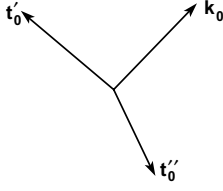


FIGURE 2.3. (a) A vector coordinate system useful for decomposing vector fields into components parallel and transverse to the wave propagation direction. Polar coordinates in this k -space are k, θ, ϕ , where θ is the polar angle measured from $\mathbf{k}_0$ and ϕ lies in the transverse plane (t'_0, t''_0). The unit vectors are related by $\mathbf{k}_0 \times \mathbf{t}'_0 = \mathbf{t}''_0$.

where $\mathbf{J}_{T_{k\omega}}$ is the component of the vector $\mathbf{J}_{k\omega}$ *transverse* to $\mathbf{k}_0$. Note that $\mathbf{k}_0 \cdot \mathbf{J}_{k\omega}$ is the scalar component of $\mathbf{J}_{k\omega}$ in the $\mathbf{k}_0$ -direction, and thus $\mathbf{k}_0(\mathbf{k}_0 \cdot \mathbf{J}_{k\omega})$ is the vector component of $\mathbf{J}_{k\omega}$ in the $\mathbf{k}_0$ -direction, i.e., the longitudinal vector component. Thus, when it is subtracted from $\mathbf{J}_{k,\omega}$, only the transverse vector portion remains. The solution for $\mathbf{E}_{k\omega}$, Eq. (2.17), then becomes

$$\mathbf{E}_{k\omega} = \frac{-i\omega}{\epsilon_0} \cdot \frac{\mathbf{J}_{T_{k\omega}}}{\omega^2 - k^2 c^2} \quad (2.18)$$

Having a formal solution (2.18) to $\mathbf{E}_{k\omega}$ in terms of the source, we can now return to the Fourier–Laplace transform relations, specifically Eq. (2.12a), to find the space and time dependent field $\mathbf{E}(\mathbf{r}, t)$:

$$\mathbf{E}(\mathbf{r}, t) = \int_{\mathbf{k}} \int_{\omega} \mathbf{E}_{k\omega} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \frac{d\omega d\mathbf{k}}{(2\pi)^4}$$

With Eq. (2.18) we can express the radiated electric field $\mathbf{E}(\mathbf{r}, t)$ in terms of the transverse component of current density as

$$\mathbf{E}(\mathbf{r}, t) = \int_{\mathbf{k}} \int_{\omega} \left(-\frac{i\omega}{\epsilon_0} \right) \frac{\mathbf{J}_{T_{k\omega}} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})}}{(\omega^2 - k^2 c^2)} \frac{d\omega d\mathbf{k}}{(2\pi)^4} \quad (2.19)$$

which is the form of a Green’s function integration, albeit in k, ω -space. The question now is: what is $\mathbf{J}_{T_{k\omega}}$? This will depend on the specific problem of interest.

Let us start by considering a *point radiator* that is small compared to the radiating wavelength, and could be an oscillating free or bound electron. If this radiating particle is sufficiently small, we can represent its density $n(\mathbf{r})$ as a Dirac delta function[‡] such that the current density, $\mathbf{J}(\mathbf{r}, t)$ [Eq. (2.10)], given by

$$\mathbf{J}(\mathbf{r}, t) = qn(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)$$

can be written for an electron as

$$\mathbf{J}(\mathbf{r}, t) = -e\delta(\mathbf{r})\mathbf{v}(t) \quad (2.20)$$

In rectangular coordinates $\delta(\mathbf{r})$ is shorthand notation for the product $\delta(x)\delta(y)\delta(z)$, where the delta function has the properties

$$\delta(x) = \begin{cases} 0 & \text{for } x \neq 0 \\ \infty & \text{for } x = 0 \end{cases}$$

[‡]See Appendix D.