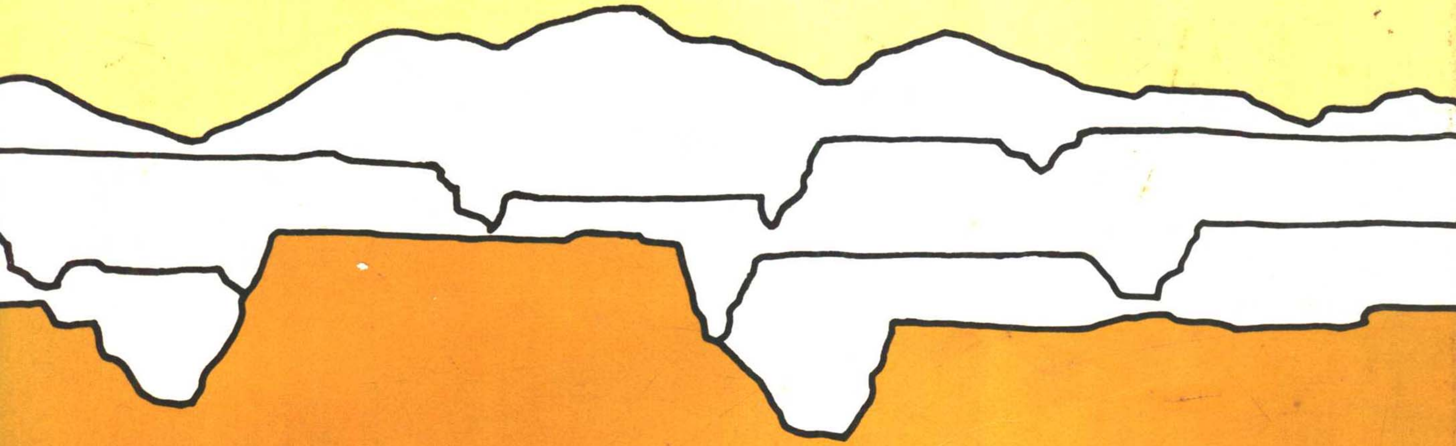
THE THEORY OF ATOMIC STRUCTURE AND SPECTRA

Robert D. Cowan



LOS ALAMOS SERIES IN BASIC AND APPLIED SCIENCES

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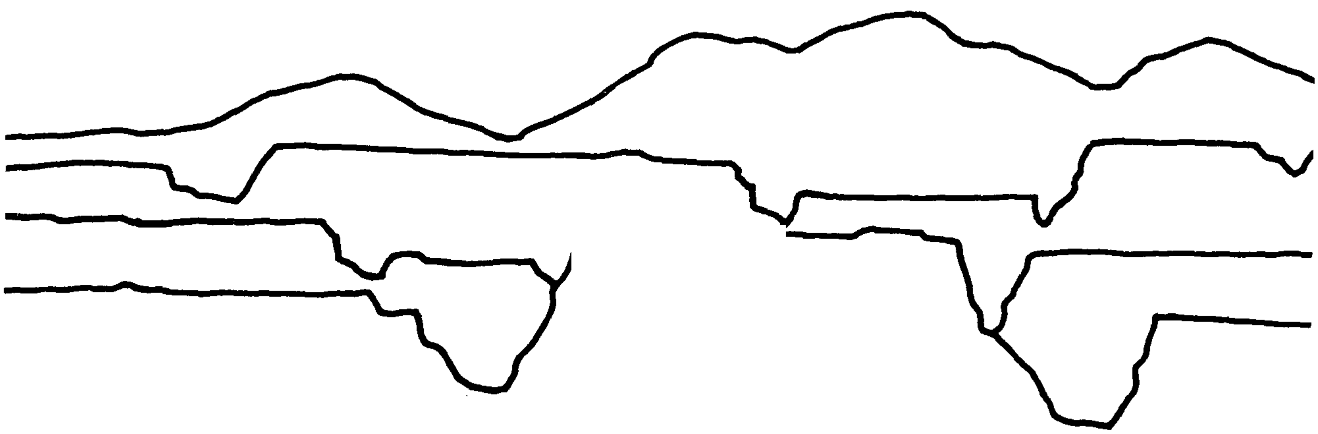

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During its cataclysmic eruptions over a million years ago, the great Jemez volcano deposited enormous quantities of ash, pumice, and other debris. Compacted to form a soft rock, and extending to depths of more than a thousand feet, this is the material of the Pajarito Plateau in north-central New Mexico. The Los Alamos Scientific Laboratory is situated here, at an elevation of 7300 feet, on the eastern edge of the Jemez range. The plateau is deeply cut by numerous canyons which create sheer walls and mesas of striking beauty. The motifs on the jacket and title page are sketches of this terrain, as viewed from the valley of the Rio Grande.

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Preface

During the past half century an enormous amount of effort has been expended on the important task of deriving energy levels of atoms and ions from their observed optical spectra. An equally enormous amount of work remains to be done, particularly on the very complex rare-earth (lanthanide and actinide) spectra, and on highly ionized atoms, where serious experimental difficulties exist. In addition, much of the older work on relatively simple spectra needs to be redone because of errors arising from the inadequate experimental apparatus and theoretical knowledge available at that time.

Essential both to persons doing basic research of this type and to those interested in astrophysical, plasma-physics, and other applications of spectroscopy is an adequate knowledge of the theory of atomic structure and spectra, and the ability to use modern electronic computers for the calculation of energy levels and wavefunctions. The basic theoretical principles were established within a decade after the invention of quantum mechanics, and were well summarized in the classic book by Condon and Shortley in 1935; mathematical techniques adequate to apply the theory to the complex atomic systems of current interest became available within another decade, as a result of the work of Racah and others. In spite of the thirty-odd years that have passed since, and the appearance during that time of several books dealing with the theory of atomic spectra, many aspects of the theory and its application remain widely scattered in the literature.

The present book is an outgrowth of theoretical work in which I have been engaged at the Los Alamos Scientific Laboratory over the past two decades; the topics emphasized most strongly are those that I have had occasion to investigate myself, and many of the illustrative examples are drawn from this work. However, I have tried to present a coherent and reasonably complete treatment of the Slater-Condon theory, in a form adapted particularly to the use of digital computers as an aid to the interpretation of observed complex spectra. For this purpose, calculations—though generally very involved and lengthy—usually need give results of only moderate accuracy. Consequently, there is no mention in this book of the highly accurate calculational methods that are available for helium and other systems containing only a very few electrons. The hydrogen-atom problem is discussed only in the detail required as a basis for the treatment of many-electron atoms; there is no discussion of the Lamb shift and similar fine points. There is also no consideration of accurate methods of calculating correlation energies in many-electron systems.

Early drafts of the book were prepared in connection with courses in atomic structure that I taught at Purdue University in the spring of 1971 and at the Los Alamos Graduate Center of the University of New Mexico in the spring of 1972. These drafts have been considerably expanded, and the present version contains far more material than can comfortably be included in a typical one-semester, three-hour course, even though several tedious mathematical derivations have been omitted, and other detailed and expendable sections have been indicated by asterisks. The text can be further shortened by omission of various obvious topics in Chapters 17-21, depending on the particular interests of the user. For those who wish to truncate the book even further, or who may wish to skim through portions of the book in a preliminary fashion in order to obtain a relatively brief overview of the subject, two outlines are suggested—one for those whose interest lies in the mathematical theory and numerical calculations, and one for those interested primarily in the qualitative features of atomic structure:

Theory	**Common**	**Qualitative**
	Secs. 1-1 to 1-8	
	1-11 to 1-12	
	2-1 to 2-3	
	2-5	
	2-7 to 2-14	
	3-1 to 3-7	
	4-1 to 4-12	
Secs. 4-21 to 4-23		Secs. 4-13 to 4-19
5-1 to 5-3		
	Appendix E	
	Secs. 7-1 to 7-2	
	7-7	
	7-14 to 7-15	
	8-1	
Appendix F		
		Secs. 8-6
Secs. 12-1 to 12-6		10-6 to 10-9
13-1		12-7 to 12-9
	14-1 to 14-10	
16-1 to 16-4		14-12

Finally, for anyone wishing a super-short outline of the Slater-Condon method of calculating energy levels and spectra, with only references to the pertinent equations, I suggest Secs. 4-1 to 4-6, 4-23, 7-1, 7-2, 7-7, 7-14, 7-15, 8-1, 16-1, and 16-2. Even those working their way through the book in detail may find it helpful, after finishing Chapter 4, to skim through Appendix F in order to obtain an outline of the general mathematical method, and to refer to this appendix occasionally by way of review while wading through Chapters 9-11. This appendix also contains a summary of the basic equations of Racah algebra for convenient reference in connection with Chapters 12-15, or independent evaluations of other matrix elements.

Particularly for those interested in the theoretical details, it is assumed that readers have a good working knowledge of elementary quantum mechanics, through the hydrogen atom and first-order perturbation theory, and some familiarity with matrix theory (eigenvalues and eigenvectors, and orthogonal transformations). Some previous acquaintance with the qualitative elements of atomic spectra and structure (the vector model of the atom and the Zeeman effect) would be helpful, but should not be essential; persons having a strong background in this subject can omit or skim through much of the first four chapters. Although an extensive knowledge of group theory can be used to greatly shorten some otherwise tedious derivations, and can lead to a deeper understanding of many aspects of the theory, I have preferred to follow the approach of Condon and Shortley, and base the discussion of wavefunction symmetries on more physical angular-momentum arguments. An effort has been made to present all material in the most elementary and unsophisticated manner possible consistent with the aim of being able to treat atoms of arbitrary complexity. The use of coupled wavefunctions, 3n-j symbols, and Racah algebra is unavoidable; however, these topics are discussed thoroughly from an elementary point of view, and no previous acquaintance with them should be necessary. Wherever feasible, I have included sample numerical calculations to illustrate how the theory is applied in practice, and have included comparisons of theoretical results with experimental data to show the degree of accuracy that can be expected of the theory. The limited number of homework problems included are mainly intended for this same purpose.

Phase and normalization conventions in atomic structure theory are far from standardized, forming repeated pitfalls for the unwary. I have chosen to employ the conventions of Condon and Shortley, except to use LS coupling ($\mathbf{L} + \mathbf{S} = \mathbf{J}$) instead of SL coupling ($\mathbf{S} + \mathbf{L} = \mathbf{J}$). The latter is more commonly used, and is more in line with the standard Russell-Saunders LS-coupling [sic!] level notation $^{2S+1}L_J$, but the former fits in better with the progression of couplings LS $\rightarrow$ LK $\rightarrow$ jK $\rightarrow$ jj. In any event, the difference between LS and SL is only a phase factor $(-1)^{L+S-J}$ in each wavefunction. I have tried at all appropriate points in the text to call attention to the most common phase and normalization differences in the literature.

It is no exaggeration to say that this book would never have been written without the inspiration and encouragement of K. L. Andrew. Many of the topics included are ones that I have investigated jointly with him and his students—especially D. C. Griffin—and his laboratory has provided much of the experimental data against which theoretical methods have been tested. N. J. Peacock was responsible for my initial interest in the calculation of atomic spectra by *ab initio* methods (as opposed to least-squares fitting of experimental energy levels). For suggestions, data, and general encouragement, I am greatly indebted also to J. Blaise, P. G. Burkhalter, C. Corliss, H. M. Crosswhite, G. A. Doschek, B. Edlén, J. O. Ekberg, B. C. Fawcett, U. Feldman, M. Fred, J. E. Hansen, W. F. Huebner, R. C. Isler, V. Kaufman, N. H. Magee, Jr., J. B. Mann, W. C. Martin, A. L. Merts, L.

Minnhagen, L. J. Radziemski, Jr., J. Reader, W. D. Robb, D. W. Steinhaus, J. Sugar, L. Å. Svensson, S. von Goeler, K. G. Widing, W. L. Wiese, and many others—especially M. Wilson, who read preliminary drafts of the entire manuscript, catching innumerable errors, and offering many suggestions for improvement.

My deep thanks are due to Martha Wooten and Christella Secker, who typed a long and difficult manuscript, and to members of the LASL photocomposition group who converted it beautifully to type—particularly to Katherine Valdez, head compositor and layout artist, and to Mary Louise Garcia and Samia L. Davis, compositors. The University of California Press editorial and production staffs headed by Grant Barnes and Chet Grycz were always friendly and helpful. And finally, I am much indebted to my wife, Dot, who sympathetically endured countless evenings and weekends alone, and also helped with proofreading and matters of grammar and style.

Robert D. Cowan
Los Alamos, New Mexico, March 1981

Contents

*The starred sections may be skipped with little loss of continuity.

1

EXPERIMENTAL BACKGROUND AND BASIC CONCEPTS

Spectroscopic studies of the light emitted or absorbed by atoms and ions date from the early nineteenth century. From these studies, it gradually became clear that the particular wavelengths of light associated with atoms of a given element are characteristic of that element, and that spectral information must therefore provide clues to the internal structure of the atom. During the last quarter of the century, important regularities were discovered among the wavelengths of hydrogen and other comparatively simple spectra. However, efforts to interpret these regularities by means of classical models of the atom all ended—despite some apparent initial successes—in dismal failure. The first real success appeared only in 1913 with Bohr's theory of the hydrogen atom. Progress in the understanding of multi-electron atoms had to await the invention of quantum mechanics a decade later, but thereafter was extremely rapid.

It is not necessary for our purposes to describe the slow and painful pre-quantum-mechanical steps that led to our present understanding of the relationship between atomic structure and atomic spectra. The interested reader may find brief outlines in the introductory chapters of the books by Sawyer[1] and by White;[2] a more detailed account of the earlier phases has been given by McGucken.[3] English translations of some important early research papers are included in Hindmarsh's source book.[4]

There is likewise no need here to include an extensive description of spectroscopic apparatus and techniques; these are discussed in detail by Sawyer[1] and by Harrison, et al.,[5] though their books are somewhat obsolescent.

[1]Ralph A. Sawyer, *Experimental Spectroscopy* (Dover Publications, New York, 1963), 3rd ed. (For convenience of later reference, Sawyer's text and other major items are listed in a bibliography at the end of this book.)

[2]Harvey E. White, *Introduction to Atomic Spectra* (McGraw-Hill, New York, 1934).

[3]William McGucken, *Nineteenth-Century Spectroscopy; Development of the Understanding of Spectra, 1802-1897* (The Johns Hopkins Press, Baltimore, 1969).

[4]W. R. Hindmarsh, *Atomic Spectra* (Pergamon, Oxford, 1967).

[5]George R. Harrison, Richard C. Lord, and John R. Loofbourow, *Practical Spectroscopy* (Prentice-Hall, Englewood Cliffs, N. J., 1948). See also additional references listed in Sec. 1 of the bibliography.

It is anticipated that most readers of the present book will have some familiarity with the qualitative aspects of spectra and atomic structure, as presented in the recent books by Woodgate[6] and Kuhn,[7] or in the older but still useful texts of White[2] and Herzberg.[8] Nonetheless, it is deemed appropriate in this chapter to review some of the basic facts and terminology of spectroscopy and atomic structure, as a background for the more highly theoretical material to follow. Numerous references to recent spectroscopic techniques and observations are included to supplement the older works cited above.

1-1. LINE SPECTRA

Information concerning the electronic structure of an isolated atom (or ion[9]) can be inferred from a variety of different types of experimental information—for example, data on elastic and inelastic scattering of electrons, ions, or x-rays by the atom, and data on the energies of photoelectrons ejected from the atom. By far the most important source of high-accuracy information, however, comes from the spectroscopic study of light radiated by, or absorbed by, the atom.

The spectrum of the light radiated by atoms in an appropriate light source may be examined with the aid of a simple prism spectrograph as illustrated in Fig. 1-1. Light from the source is focused on a narrow entrance slit that is oriented parallel to the dispersing faces of the prism. The light passing through the slit is dispersed according to wavelength in passing through the prism. For each wavelength of light present, a camera lens forms an image of the slit on a photographic plate; the various images for the different wavelengths are displaced from one another in a direction perpendicular to the length of each slit image. If the source is such (for example, an incandescent solid) as to radiate light of all wavelengths, the spectrographic plate records a continuous succession of overlapping slit images, and the spectrum is correspondingly known as a continuous spectrum. However, if the light from the source is radiated by a collection of isolated atoms, it is found to consist of a greater or smaller number of isolated wavelengths: if a very narrow spectrograph slit is used, the spectrum appears on the photographic plate as a set of isolated parallel lines. Such spectra are accordingly referred to as line spectra, to distinguish them from the continuous spectra of solids and the "band" spectra of molecules; examples of all three types of spectra are shown in Fig. 1-2.

Evidently, the line-image form of the observed spectra of atoms is a characteristic of the shape of the entrance slit of the spectrograph. For modern research work, the prism spectrograph has been almost entirely replaced by spectrographs using a diffraction grating[10]

[6]G. K. Woodgate, *Elementary Atomic Structure* (McGraw-Hill, London, 1970).

[7]H. G. Kuhn, *Atomic Spectra* (Longmans, Green, London, 1969), 2nd ed.

[8]Gerhard Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1944), 2nd ed.

[9]For brevity, the unqualified term "atom" will generally be used to mean either a neutral atom (a nucleus of charge +Ze surrounded by a number of electrons N equal to Z), or a positively or negatively charged ion ($N < Z$ or $N > Z$, respectively).

[10]The term "diffraction grating" is a universally used misnomer for what should more appropriately be called an interference grating.

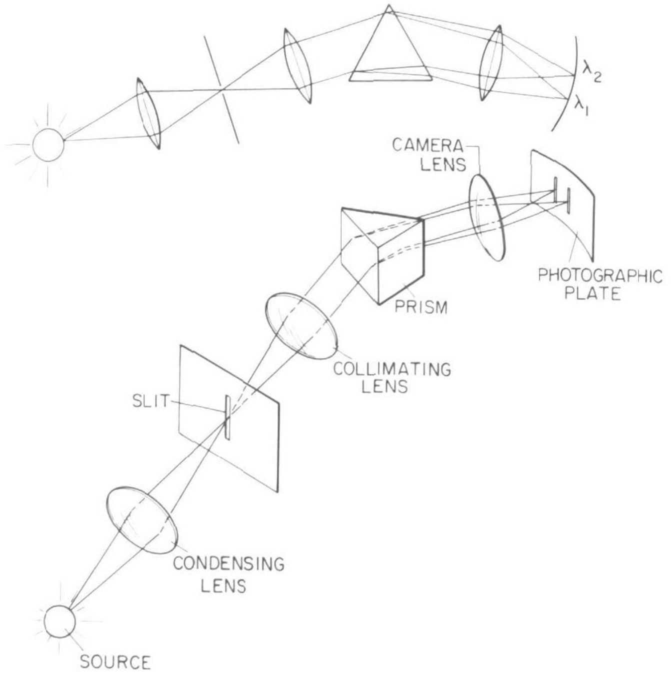

Fig. 1-1. Simple prism spectrograph, showing the separation of two spectrum lines. Top, plan; bottom, perspective view.

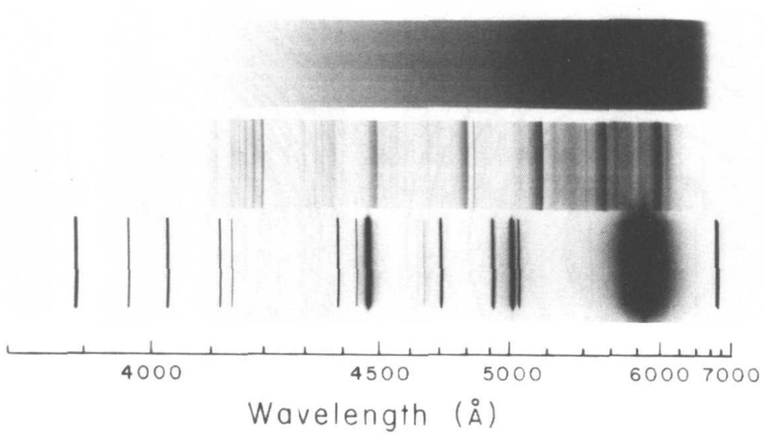

Fig. 1-2. Typical emission spectra, taken with a low-dispersion prism spectrograph. Top: Continuous spectrum of an incandescent filament. Middle: Band spectrum of the CO molecule. Bottom: The line spectrum of the neutral helium atom in a Geissler discharge. (Photographic negatives, courtesy of K. L. Andrew.)