CONTENTS

PAGE

PREFACE vii

CHAPTER I

EARLY HISTORICAL DEVELOPMENTS IN ATOMIC SPECTRA 1

1.1. Kirchhoff's Law. 1.2. A New Era. 1.3. Balmer's Law. 1.4. Rydberg's Contributions. 1.5. The Rydberg-Schuster Law. 1.6. Series Notation. 1.7. Satellites and Fine Structure. 1.8. The Lyman, Balmer, Paschen, Brackett, and Pfund Series of Hydrogen. 1.9. The Ritz Combination Principle. 1.10. The Ritz Formula. 1.11. The Hicks Formula. 1.12. Series Formulas Applied to the Alkali Metals. 1.13. Neon with 130 Series. 1.14. Normal and Abnormal Series. 1.15. Hydrogen and the Pickering Series. 1.16. Enhanced Lines.

CHAPTER II

INTRODUCTION TO THE QUANTUM THEORY AND THE BOHR ATOM 23

2.1. Planck's Simple Harmonic Oscillator. 2.2. The Bohr Atom. 2.3. Bohr's First Assumption. 2.4. Bohr's Second Assumption. 2.5. Bohr's Third Assumption. 2.6. Characteristics of the Bohr Circular Orbits. 2.7. Bohr Orbits and the Hydrogen Series. 2.8. Series of Ionized Helium, He II (He^+). 2.9. Series of Doubly Ionized Lithium, Li III (Li^{++}) and Triply Ionized Beryllium, Be IV (Be^{+++}). 2.10. Energy Level Diagrams. 2.11. Unquantized States and Continuous Spectra. 2.12. The So-called "Reduced Mass" of the Electron. 2.13. Variation of the Rydberg Constant. 2.14. Bohr's Correspondence Theorem.

CHAPTER III

SOMMERFELD'S ELLIPTIC ORBITS AND SPACE QUANTIZATION 42

3.1. Two Degrees of Freedom. 3.2. The Radial Quantum Number. 3.3. The Total Energy W. 3.4. General Characteristics of Sommerfeld's Elliptic Orbits. 3.5. Space Quantization. 3.6. Larmor's Theorem. 3.7. Magnetic Moment and the Bohr Magneton.

CHAPTER IV

QUANTUM MECHANICS AND THE SCHRÖDINGER WAVE EQUATION. 54

4.1. De Broglie's Corpuscular Wave Equation. 4.2. The Schrödinger Wave Equation. 4.3. Schrödinger's Wave Equation Applied to Hydrogen. 4.4. Eigenfunctions. 4.5. The φ Factor Φ_m of the Eigenfunction ψ. 4.6. The θ Factor $\Theta_{m,l}$ of the Eigenfunction ψ. 4.7. Correlation of $\Phi_m\Phi_m^*$ and $\Theta_{m,l}\Theta_{m,l}^*$ with the Bohr-Sommerfeld Orbits. 4.8. The Radial Factor $R_{n,l}$ of the Eigenfunction ψ. 4.9. Correlation of $R_{n,l}R_{n,l}^*$ with the Bohr-Sommerfeld Orbits. 4.10. A General Interpretation of the Eigenfunction ψ. 4.11. Useful Atomic Models. 4.12. Spherical Symmetry.

CHAPTER V

THE ALKALI METALS AND THE PERIODIC TABLE. 77

5.1. Energy Level Diagrams. 5.2. The Bohr-Stoner Scheme of the Building Up of the Elements. 5.3. The First Period. 5.4. The Second Period. 5.5.

PAGE

The Third Period. 5.6. The Fourth Period or First Long Period. 5.7. The Fifth Period or Second Long Period. 5.8. The Sixth Period or Third Long Period. 5.9. The Seventh and Last Period. 5.10. Energy Levels of the Alkali Metals. 5.11. The Effective Quantum Number and the Quantum Defect. 5.12. The Selection Principle.

CHAPTER VI

EXCITATION POTENTIALS, IONIZATION POTENTIALS, AND THE SPECTRA OF IONIZED ATOMS 92

6.1. Critical Potentials. 6.2. The Spectra of Ionized Atoms.

CHAPTER VII

PENETRATING AND NONPENETRATING ORBITS IN THE ALKALI METALS 100

7.1. The Quantum-mechanical Model of the Alkali Metals. 7.2. Penetrating and Nonpenetrating Orbits. 7.3. Nonpenetrating Orbits. 7.4. Penetrating Orbits on the Classical Model. 7.5. Quantum-mechanical Model for Penetrating Orbits.

CHAPTER VIII

DOUBLET FINE STRUCTURE AND THE SPINNING ELECTRON 114

8.1. Observed Doublet Fine Structure in the Alkali Metals and the Boron Group of Elements. 8.2. Selection Rules for Doublets. 8.3. Intensity Rules for Fine-structure Doublets. 8.4. The Spinning Electron and the Vector Model. 8.5. The Normal Order of Fine-structure Doublets. 8.6. Electron Spin-orbit Interaction. 8.7. Spin-orbit Interaction for Nonpenetrating Orbits. 8.8. Spin-orbit Interaction for Penetrating Orbits.

CHAPTER IX

HYDROGEN FINE STRUCTURE AND THE DIRAC ELECTRON 132

9.1. Sommerfeld Relativity Correction. 9.2. Fine Structure and the Spinning Electron. 9.3. Observed Hydrogen Fine Structure. 9.4. Fine Structure of the Ionized Helium Line $\lambda 4686$. 9.5. The Dirac Electron and the Hydrogen Atom. 9.6. The Angular Distribution of the Probability Density P_θ. 9.7. The Radial Distribution of the Probability Density P_r. 9.8. The Probability Density Distribution $\psi\psi^*$. 9.9. The Sommerfeld Formula from Dirac's Theory.

CHAPTER X

THE ZEEMAN EFFECT AND THE PASCHEN-BACK EFFECT 149

10.1. Early Discoveries and Developments. 10.2 The Vector Model of a One-electron System in a Weak Magnetic Field. 10.3. The Magnetic Moment of a Bound Electron. 10.4. Magnetic Interaction Energy. 10.5 Selection Rules. 10.6. Intensity Rules. 10.7. The Paschen-Back Effect. 10.8. Paschen-Back Effect of a Principal-series Doublet. 10.9. Selection Rules for the Paschen-Back Effect. 10.10. The Zeeman Effect, and Paschen-Back Effect, of Hydrogen. 10.11. A Quantum-mechanical Model of the Atom in a Strong Magnetic Field.

CHAPTER XI

SINGLET AND TRIPLET SERIES OF TWO-VALENCE-ELECTRON SYSTEMS. 171

11.1. General Series Relations. 11.2. Triplet Fine Structure. 11.3. The Quantum Numbers n and l of Both Valence Electrons. 11.4. Penetrating and Nonpenetrating Electrons for Two-electron Systems. 11.5. The Excitation of Both Valence Electrons.

PAGE

CHAPTER XII

THE ATOM MODEL FOR TWO VALENCE ELECTRONS 184

12.1. *ll*-coupling. 12.2. Spin-spin-, or *ss*-coupling. 12.3. *LS*-, or Russell-Saunders Coupling. 12.4. The Pauli Exclusion Principle. 12.5. Triplet Multiplets in Ionized Scandium, Sc II. 12.6. Coupling Schemes for Two Electrons. 12.7. Γ Factors for *LS*-coupling. 12.8. The Landé Interval Rule. 12.9. *jj*-coupling. 12.10. *jj*-coupling in the Carbon Group of Elements. 12.11. Term Series and Limits in Two-electron Systems. 12.12. The Great Calcium Triad. 12.13. The Branching Rule. 12.14. Selection Rules. 12.15. Intensity Relations. 12.16. Relative Intensities of Related Multiplets. 12.17. Helium and Helium-like Atoms. 12.18. Quantum mechanical Model of Helium. 12.19. Fine Structure of Helium-like Atoms.

CHAPTER XIII

ZEEMAN EFFECT, PASCHEN-BACK EFFECT, AND THE PAULI EXCLUSION PRINCIPLE, FOR TWO ELECTRONS 215

13.1. The Magnetic Moment of the Atom. 13.2. The Zeeman Effect. 13.3. Intensity Rules for the Zeeman Effect. 13.4. The Calculation of Zeeman Patterns. 13.5. *LS*- and *jj*-coupling and the *g* Sum Rule. 13.6. Paschen-Back Effect. 13.7. *LS*-coupling and the Paschen-Back Effect. 13.8. *jj*-coupling and the Paschen-Back Effect. 13.9. Complete Paschen-Back Effect. 13.10 Breit's Scheme for the Derivation of Spectral Terms from Magnetic Quantum Numbers. 13.11. The Pauli Exclusion Principle. 13.12. Pauli's *g* Permanence Rule. 13.13. Pauli's *g* Sum Rule for All Field Strengths. 13.14. Landé's Γ Permanence Rule. 13.15. Goudsmit's Γ Sum Rule. 13.16. The Γ Permanence and Γ Sum Rules Applied to Two Equivalent Electrons.

CHAPTER XIV

COMPLEX SPECTRA 248

14.1. The Displacement Law. 14.2. Alternation Law of Multiplicities. 14.3. The Vector Model for Three or More Valence Electrons. 14.4. Terms Arising from Three or More Equivalent Electrons. 14.5. The Landé Interval Rule. 14.6. Inverted Terms. 14.7. Hund's Rule. 14.8. The Nitrogen Atom. 14.9. The Scandium Atom. 14.10. The Oxygen Atom. 14.11. The Titanium Atom. 14.12. The Manganese Atom. 14.13. The Rare-gas Atoms, Neon, Argon, Krypton, and Xenon. 14.14. The Normal States of the Elements in the First and Second Long Periods. 14.15. Houston's Treatment of One *s* Electron and One Arbitrary Electron. 14.16. Slater's Multiplet Relations. 14.17. Multiplet Relations of Goudsmit and Inglis. 14.18. Relative Intensities of Multiplet Lines.

CHAPTER XV

THE ZEEMAN EFFECT AND MAGNETIC QUANTUM NUMBERS IN COMPLEX SPECTRA 286

15.1. Magnetic Energy and the Landé *g* Factor. 15.2. The Calculation of Zeeman Patterns. 15.3. Intensity Rules and Zeeman Patterns for Quartets, Quintets, and Sextets. 15.4. Paschen-Back Effect in Complex Spectra. 15.5. Derivation of Spectral Terms by Use of Magnetic Quantum Numbers. 15.6. Equivalent Electrons and the Pauli Exclusion Principle.

CHAPTER XVI

X-RAY SPECTRA 299

16.1. The Nature of X-rays. 16.2. X-ray Emission Spectra and the Moseley Law. 16.3. Absorption Spectra. 16.4. Energy Levels. 16.5. Selection

PAGE

and Intensity Rules. 16.6. Fine Structure of X-rays. 16.7. Spin-relativity Doublets (Regular Doublets). 16.8. The Regular-doublet Law. 16.9. Screening Doublets and the Irregular-doublet Law. 16.10. A Predicted Structure in X-rays. 16.11. X-ray Satellites. 16.12. Explanation of X-ray Absorption Spectra.

CHAPTER XVII

ISOELECTRONIC SEQUENCES 331

17.1. Isoelectronic Sequences of Atoms Containing One Valence Electron. 17.2. Optical Doublets and the Irregular-doublet Law. 17.3. Optical Doublets and the Regular-doublet Law. 17.4. Isoelectronic Sequences of Atoms Containing Two Valence Electrons. 17.5. Isoelectronic Sequences Containing Three or More Valence Electrons. 17.6. The Irregular-doublet Law in Complex Spectra. 17.7. Energy Relations for the Same Atom in Different Stages of Ionization. 17.8. Centroid Diagrams.

CHAPTER XVIII

HYPERFINE STRUCTURE 352

18.1. Introduction. 18.2. Hyperfine Structure and the Landé Interval Rule. 18.3. Nuclear Interaction with One Valence Electron. 18.4. Nuclear Interaction with a Penetrating Electron. 18.5. Classical Explanation of Normal and Inverted *Hfs*. 18.6. Hyperfine Structure in Atoms with Two or more Valence Electrons. 18.7. Hyperfine Structure in Complex Spectra. 18.8. Nuclear g_I Factors. 18.9. Zeeman Effect in Hyperfine Structure. 18.10. Back-Goudsmit Effect in Hyperfine Structure. 18.11. Isotope Structure. 18.12. Isotope Structure and Hyperfine Structure Combined.

CHAPTER XIX

SERIES PERTURBATIONS AND AUTOIONIZATION 386

19.1. Observed Abnormal Series. 19.2. Energy Level Perturbations. 19.3. The Nature of and Conditions for Term Perturbations. 19.4. The Anomalous Diffuse Series of Calcium. 19.5. The Anomalous Principal Series in Copper. 19.6. The Inverted Alkali Doublets. 19.7. Autoionization. 19.8. Autoionization in Copper. 19.9. Autoionization in Calcium, Strontium, and Barium. 19.10. Hyperfine-structure Term Perturbations.

CHAPTER XX

THE STARK EFFECT 401

20.1. Discovery of the Stark Effect. 20.2. The Stark Effect of Hydrogen. 20.3. Early Orbital Model of Hydrogen in an Electric Field. 20.4. Weak-field Stark Effect in Hydrogen. 20.5. Strong-field Stark Effect in Hydrogen. 20.6. Second-order Stark Effect in Hydrogen. 20.7 Stark Effect for More than One Electron. 20.8. The Stark Effect in Helium.

CHAPTER XXI

THE BREADTH OF SPECTRUM LINES 418

21.1. The Doppler Effect. 21.2. Natural Breadths from Classical Theory. 21.3. Natural Breadths and the Quantum Mechanics. 21.4. Observed Natural Breadths and Doppler Broadening. 21.5. Collision Damping. 21.6. Asymmetry and Pressure Shift. 21.7 Stark Broadening.

APPENDIX 437

INDEX 443