

Contents

PREFACE

v

| | |
|--|---------------|
| Chapter 1. The Hydrogen Molecular Ion | 1 |
| 1-1. Energy Levels and Wave Functions for H_2^+ | 1 |
| 1-2. The Born-Oppenheimer Approximation and the Separation of Nuclear and Electronic Motion | 9 |
| 1-3. The Vibrations and Rotations of Diatomic Molecules | 14 |
| 1-4. The Morse Curve | 17 |
| 1-5. General Nature of the Energy Levels of Diatomic Molecules | 19 |
| Chapter 2. LCAO and Variation Methods, and the Virial Theorem, for H_2^+ | 22 |
| 2-1. Introduction | 22 |
| 2-2. The Overlap Charge | 23 |
| 2-3. Calculation of the Energy | 25 |
| 2-4. The Variation Method and the Virial Theorem | 29 |
| 2-5. Kinetic and Potential Energies in Diatomic Molecules | 34 |
| 2-6. Feynman's Theorem and the Bond between Atoms | 39 |
| Chapter 3. The Heitler-London Method for the Hydrogen Molecule | 41 |
| 3-1. The Many-electron Problem in Quantum Mechanics | 41 |
| 3-2. The Heitler-London Method for Hydrogen—General Formulation | 45 |
| 3-3. The Heitler-London Method for Hydrogen—Detailed Calculation | 49 |
| 3-4. Improvements of the Heitler-London Method | 54 |
| Chapter 4. The Molecular-orbital Method for Hydrogen, and Its Extensions | 60 |
| 4-1. Molecular Orbitals and Self-consistent Fields | 60 |

| | |
|--|---------|
| 4-2. Configurations Formed from 1s Hydrogen Orbitals | 62 |
| 4-3. The Secular Problem Using the Molecular-orbital Method | 66 |
| 4-4. Variation Method for the Molecular-orbital Calculation | 70 |
| 4-5. The Coulson-Fischer Method, and Orthogonalized Atomic Orbitals | 71 |
| 4-6. The James-Coolidge Calculation for the Hydrogen Molecule | 74 |
| 4-7. Extended Configuration Interaction in the Hydrogen Molecule | 76 |
| 4-8. Details of Configuration-interaction Calculations in Hydrogen | 80 |
| Chapter 5. The Method of Molecular Orbitals | 85 |
| 5-1. The Historical Development of Molecular Theory | 85 |
| 5-2. The Hartree-Fock Equations and the Molecular-orbital Method | 92 |
| 5-3. Roothaan's Method for the Hartree-Fock Problem | 97 |
| Chapter 6. Homonuclear Diatomic Molecules | 102 |
| 6-1. Introduction | 102 |
| 6-2. One-electron Energies of Homonuclear Diatomic Molecules | 103 |
| 6-3. Molecular Orbitals and Their Bonding Properties | 109 |
| 6-4. The Repulsion of Two Helium Atoms | 111 |
| 6-5. The Oxygen Molecule | 117 |
| 6-6. Linear Polyatomic Molecules: The CO ₂ Molecule | 127 |
| Chapter 7. Heteronuclear Diatomic Molecules | 131 |
| 7-1. One-electron Energies and Dipole Moments of Heteronuclear Diatomic Molecules | 131 |
| 7-2. The Molecular-orbital Method for the Lithium Hydride Molecule | 136 |
| 7-3. The Heitler-London Method for the LiH Molecule | 142 |
| Chapter 8. Group Theory and the Symmetry of Wave Functions | 151 |
| 8-1. Group Theory and Atomic Structure | 151 |
| 8-2. The Groups C_{N_v} and D_{N_h} as Examples of Finite Groups | 157 |
| 8-3. The Conditions for Formation of a Group | 162 |
| 8-4. Irreducible Representations and Basis Functions | 164 |
| 8-5. Basis Functions for the Irreducible Representations of the Groups C_{N_v} and C_N | 167 |
| 8-6. Relation of the Group C_{N_v} to the Problem of Cylindrical Symmetry | 169 |

| | |
|--|----------------|
| Chapter 9. Bloch's Method for the Construction of Symmetry Orbitals | 172 |
| 9-1. Introduction | 172 |
| 9-2. Bloch's Method for Constructing Symmetry Orbitals | 173 |
| 9-3. Matrix Elements of One-electron Symmetric Operators with Respect to Bloch Functions | 176 |
| 9-4. Energy Bands and the Theory of Solids | 181 |
| 9-5. Orthogonalized Atomic Orbitals, or Wannier Functions | 184 |
| Chapter 10. The Ammonia Molecule | 188 |
| 10-1. Experimental Methods of Studying Molecular Configurations | 188 |
| 10-2. Molecular Orbitals for the Ammonia Molecule | 189 |
| 10-3. Directed Orbitals and Covalent Binding in Polyatomic Molecules | 193 |
| 10-4. The Valence-bond Function | 196 |
| 10-5. The Formula of Hurley, Lennard-Jones, and Pople for the Extended Valence-bond Method | 198 |
| 10-6. Construction of the Orbitals A_i and B_i | 202 |
| 10-7. Configuration Interaction in Ammonia | 207 |
| Chapter 11. The Methane and Water Molecules | 209 |
| 11-1. Molecular and Equivalent Orbitals for Methane | 209 |
| 11-2. Configuration Interaction in Methane—General Discussion | 213 |
| 11-3. Configuration Interaction in Methane—Analogy to Neon | 215 |
| 11-4. The Water Molecule | 221 |
| Chapter 12. The Ethylene and Benzene Molecules | 227 |
| 12-1. The Ethylene Molecule | 227 |
| 12-2. The Benzene Molecule | 232 |
| 12-3. The Method of Alternant Molecular Orbitals for Benzene | 240 |
| 12-4. Excited Energy Levels in Benzene | 246 |
| Appendix 1. The H_2^+ Problem | 247 |
| Appendix 2. The Born-Oppenheimer Theorem and Feynman's Theorem | 252 |
| Appendix 3. The Virial Theorem | 254 |
| Appendix 4. The Hartree-Fock Method | 256 |

| | | |
|---------------------|--|------------|
| Appendix 5. | The Variation Principle for Nonorthogonal Basis Functions | 261 |
| Appendix 6. | Two-center Integrals | 263 |
| | Generalization of Results for Two-center Integrals | 274 |
| Appendix 7. | Roothaan's Method | 277 |
| Appendix 8. | Determinantal Functions Formed from Linear Combinations of Orbitals | 283 |
| Appendix 9. | Matrix Elements of the Hamiltonian and Other Operators for Determinantal Functions Composed of Nonorthogonal Orbitals | 285 |
| Appendix 10. | The Repulsion of Two Helium Atoms | 290 |
| Appendix 11. | Configuration Interaction in the Oxygen Molecule | 294 |
| A11-1. | Tabulation of Multiplets Involved in the Configuration Interaction | 294 |
| A11-2. | Method of Finding Multiplets in the Molecular-orbital Scheme | 294 |
| A11-3. | Multiplets in the Oxygen Configuration Interaction, Atomic-orbital Basis | 302 |
| A11-4. | Method of Finding Multiplets in the Atomic-orbital Scheme | 304 |
| Appendix 12. | The Group Theory | 315 |
| A12-1. | Introduction: The Group C_{3v} | 315 |
| A12-2. | General Properties of Representations | 318 |
| A12-3. | The Regular Representation and Projection Operators | 323 |
| A12-4. | Irreducible Representations and Schrödinger's Equation | 333 |
| A12-5. | The Two-dimensional Rotation and Reflection Groups | 336 |
| A12-6. | The Three-dimensional Rotation and Reflection Groups | 340 |
| A12-7. | The Tetrahedral and Cubic Point Groups | 346 |
| A12-8. | The Splitting of Atomic Energy Levels in Cubic or Tetrahedral Fields | 363 |
| Appendix 13. | Multiplet Structure and Configuration Interaction in the Ring of Six Hydrogen Atoms | 367 |
| A13-1. | Introduction | 367 |
| A13-2. | The Molecular-orbital Approach for Multiplets in the Ring of Hydrogen Atoms | 372 |
| A13-3. | The Atomic-orbital Approach for the H_6 Molecule | 381 |
| A13-4. | General Discussion of the Problem of H_6 | 388 |

CONTENTS

xv

| | | |
|--------------|---|-----|
| Appendix 14. | The Method of Hurley, Lennard-Jones, and Pople | 390 |
| Appendix 15. | Three- and Four-center Integrals | 397 |
| BIBLIOGRAPHY | | 401 |
| INDEX | | 481 |