

Chapter 1

**The Schrödinger Equation 1**

- 1.1 Quantum Chemistry 1
- 1.2 Historical Background of Quantum Mechanics 2
- 1.3 The Uncertainty Principle 6
- 1.4 The Time-Dependent Schrödinger Equation 7
- 1.5 The Time-Independent Schrödinger Equation 11
- 1.6 Probability 14
- 1.7 Complex Numbers 16
- 1.8 Units 17
- 1.9 Calculus 18
- Summary 18*
- Problems 19*

Chapter 2

**The Particle in a Box 21**

- 2.1 Differential Equations 21
- 2.2 Particle in a One-Dimensional Box 22
- 2.3 The Free Particle in One Dimension 28
- 2.4 Particle in a Rectangular Well 28
- 2.5 Tunneling 30
- Summary 31*
- Problems 31*

Chapter 3

**Operators 34**

- 3.1 Operators 34
- 3.2 Eigenfunctions and Eigenvalues 38
- 3.3 Operators and Quantum Mechanics 39
- 3.4 The Three-Dimensional, Many-Particle Schrödinger Equation 44
- 3.5 The Particle in a Three-Dimensional Box 47
- 3.6 Degeneracy 50
- 3.7 Average Values 51
- 3.8 Requirements for an Acceptable Wave Function 54
- Summary 55*
- Problems 56*

**Chapter 4 The Harmonic Oscillator 60**

- 4.1 Power-Series Solution of Differential Equations 60
- 4.2 The One-Dimensional Harmonic Oscillator 62
- 4.3 Vibration of Diatomic Molecules 71
- 4.4 Numerical Solution of the One-Dimensional Time-Independent Schrödinger Equation 74
- Summary* 84
- Problems* 84

**Chapter 5 Angular Momentum 90**

- 5.1 Simultaneous Specification of Several Properties 90
- 5.2 Vectors 94
- 5.3 Angular Momentum of a One-Particle System 99
- 5.4 The Ladder-Operator Method for Angular Momentum 110
- Summary* 114
- Problems* 115

**Chapter 6 The Hydrogen Atom 118**

- 6.1 The One-Particle Central-Force Problem 118
- 6.2 Noninteracting Particles and Separation of Variables 120
- 6.3 Reduction of the Two-Particle Problem to Two One-Particle Problems 121
- 6.4 The Two-Particle Rigid Rotor 124
- 6.5 The Hydrogen Atom 128
- 6.6 The Bound-State Hydrogen-Atom Wave Functions 135
- 6.7 Hydrogenlike Orbitals 143
- 6.8 The Zeeman Effect 147
- 6.9 Numerical Solution of the Radial Schrödinger Equation 149
- Summary* 150
- Problems* 151

**Chapter 7 Theorems of Quantum Mechanics 155**

- 7.1 Notation 155
- 7.2 Hermitian Operators 156
- 7.3 Expansion in Terms of Eigenfunctions 161
- 7.4 Eigenfunctions of Commuting Operators 167
- 7.5 Parity 170
- 7.6 Measurement and the Superposition of States 172
- 7.7 Position Eigenfunctions 177
- 7.8 The Postulates of Quantum Mechanics 180
- 7.9 Measurement and the Interpretation of Quantum Mechanics 184
- 7.10 Matrices 187
- Summary* 191
- Problems* 191

## Chapter 8

**The Variation Method 197**

- 8.1 The Variation Theorem 197
- 8.2 Extension of the Variation Method 201
- 8.3 Determinants 202
- 8.4 Simultaneous Linear Equations 205
- 8.5 Linear Variation Functions 209
- 8.6 Matrices, Eigenvalues, and Eigenvectors 215
- Summary* 223
- Problems* 223

## Chapter 9

**Perturbation Theory 232**

- 9.1 Perturbation Theory 232
- 9.2 Nondegenerate Perturbation Theory 233
- 9.3 Perturbation Treatment of the Helium-Atom Ground State 238
- 9.4 Variation Treatments of the Ground State of Helium 242
- 9.5 Perturbation Theory for a Degenerate Energy Level 245
- 9.6 Simplification of the Secular Equation 248
- 9.7 Perturbation Treatment of the First Excited States of Helium 250
- 9.8 Time-Dependent Perturbation Theory 256
- 9.9 Interaction of Radiation and Matter 258
- Summary* 260
- Problems* 261

## Chapter 10

**Electron Spin and the Spin–Statistics Theorem 265**

- 10.1 Electron Spin 265
- 10.2 Spin and the Hydrogen Atom 268
- 10.3 The Spin–Statistics Theorem 268
- 10.4 The Helium Atom 271
- 10.5 The Pauli Exclusion Principle 273
- 10.6 Slater Determinants 277
- 10.7 Perturbation Treatment of the Lithium Ground State 278
- 10.8 Variation Treatments of the Lithium Ground State 279
- 10.9 Spin Magnetic Moment 280
- 10.10 Ladder Operators for Electron Spin 283
- Summary* 285
- Problems* 285

## Chapter 11

**Many-Electron Atoms 289**

- 11.1 The Hartree–Fock Self-Consistent-Field Method 289
- 11.2 Orbitals and the Periodic Table 295
- 11.3 Electron Correlation 298
- 11.4 Addition of Angular Momenta 300

11.5 Angular Momentum in Many-Electron Atoms	305
11.6 Spin–Orbit Interaction	316
11.7 The Atomic Hamiltonian	318
11.8 The Condon–Slater Rules	320
<i>Summary</i>	323
<i>Problems</i>	324

## Chapter 12

**Molecular Symmetry 328**

12.1 Symmetry Elements and Operations	328
12.2 Symmetry Point Groups	335
<i>Summary</i>	341
<i>Problems</i>	342

## Chapter 13

**Electronic Structure of Diatomic Molecules 344**

13.1 The Born–Oppenheimer Approximation	344
13.2 Nuclear Motion in Diatomic Molecules	347
13.3 Atomic Units	352
13.4 The Hydrogen Molecule Ion	353
13.5 Approximate Treatments of the $H_2^+$ Ground Electronic State	357
13.6 Molecular Orbitals for $H_2^+$ Excited States	365
13.7 MO Configurations of Homonuclear Diatomic Molecules	369
13.8 Electronic Terms of Diatomic Molecules	375
13.9 The Hydrogen Molecule	379
13.10 The Valence-Bond Treatment of $H_2$	382
13.11 Comparison of the MO and VB Theories	384
13.12 MO and VB Wave Functions for Homonuclear Diatomic Molecules	386
13.13 Excited States of $H_2$	389
13.14 SCF Wave Functions for Diatomic Molecules	390
13.15 MO Treatment of Heteronuclear Diatomic Molecules	393
13.16 VB Treatment of Heteronuclear Diatomic Molecules	396
13.17 The Valence-Electron Approximation	396
<i>Summary</i>	397
<i>Problems</i>	398

## Chapter 14

**Theorems of Molecular Quantum Mechanics 402**

14.1 Electron Probability Density	402
14.2 Dipole Moments	404
14.3 The Hartree–Fock Method for Molecules	407
14.4 The Virial Theorem	416
14.5 The Virial Theorem and Chemical Bonding	422
14.6 The Hellmann–Feynman Theorem	426
14.7 The Electrostatic Theorem	429
<i>Summary</i>	432
<i>Problems</i>	433

## Chapter 15

**Molecular Electronic Structure 436**

- 15.1 Ab Initio, Density-Functional, Semiempirical, and Molecular-Mechanics Methods 436
- 15.2 Electronic Terms of Polyatomic Molecules 437
- 15.3 The SCF MO Treatment of Polyatomic Molecules 440
- 15.4 Basis Functions 442
- 15.5 The SCF MO Treatment of H<sub>2</sub>O 449
- 15.6 Population Analysis and Bond Orders 456
- 15.7 The Molecular Electrostatic Potential, Molecular Surfaces, and Atomic Charges 460
- 15.8 Localized MOs 464
- 15.9 The SCF MO Treatment of Methane, Ethane, and Ethylene 470
- 15.10 Molecular Geometry 480
- 15.11 Conformational Searching 490
- 15.12 Molecular Vibrational Frequencies 496
- 15.13 Thermodynamic Properties 498
- 15.14 Ab Initio Quantum Chemistry Programs 500
- 15.15 Performing Ab Initio Calculations 501
- 15.16 Speeding Up Hartree–Fock Calculations 507
- 15.17 Solvent Effects 510
- Problems 518*

## Chapter 16

**Electron-Correlation Methods 525**

- 16.1 Correlation Energy 525
- 16.2 Configuration Interaction 528
- 16.3 Møller–Plesset (MP) Perturbation Theory 539
- 16.4 The Coupled-Cluster Method 546
- 16.5 Density-Functional Theory 552
- 16.6 Composite Methods for Energy Calculations 572
- 16.7 The Diffusion Quantum Monte Carlo Method 575
- 16.8 Noncovalent Interactions 576
- 16.9 NMR Shielding Constants 578
- 16.10 Fragmentation Methods 580
- 16.11 Relativistic Effects 581
- 16.12 Valence-Bond Treatment of Polyatomic Molecules 582
- 16.13 The GVB, VBSCF, and BOVB Methods 589
- 16.14 Chemical Reactions 591
- Problems 595*

## Chapter 17

**Semiempirical and Molecular-Mechanics Treatments of Molecules 600**

- 17.1 Semiempirical MO Treatments of Planar Conjugated Molecules 600
- 17.2 The Hückel MO Method 601
- 17.3 The Pariser–Parr–Pople Method 619
- 17.4 General Semiempirical MO and DFT Methods 621

17.5 The Molecular-Mechanics Method	634
17.6 Empirical and Semiempirical Treatments of Solvent Effects	648
17.7 Chemical Reactions	652
17.8 The Future of Quantum Chemistry	655
<i>Problems</i>	656

**Appendix** 661

**Bibliography** 665

**Answers to Selected Problems** 667

**Index** 679