

Contents

Series Preface	v
Preface	vii
Chapter 1	
Experimental Basis of Quantum Theory	1
1-1. Introductory Remarks	1
1-2. Classical Concepts of Linear Momentum, Angular Momentum, and Energy	2
1-3. Energy Levels and Photons	11
1-4. Electron Impact Experiments	13
1-5. Atomic Spectra	16
1-6. Quantization of Angular Momentum	17
1-7. Momentum of a Photon	21
1-8. Wave-Particle Duality	23
Problems	28
Chapter 2	
Vector Spaces and Linear Transformations	31
2-1. Vector Spaces	31
2-2. Linear Independence, Bases, and Dimensionality	36
2-3. Inner Product Spaces	42
2-4. Orthonormality and Complete Sets	49
2-5. Hilbert Space	61
2-6. Function Space and Generalized Fourier Series	66
2-7. Isomorphism between Hilbert Space and Function Space	69
2-8. Examples of Complete Sets of Functions	71
2-9. Extension to Continuum Functions	79
2-10. Function Minimization with Constraints	82
2-11. Linear Operators	84
2-12. Algebra of Linear Operators	87
2-13. Special Kinds of Linear Operators	91
2-14. Eigenvalues and Eigenvectors	97
Problems	98
Chapter 3	
Matrix Theory	102
3-1. Elements of Matrix Algebra	102

3-2.	Determinants	109
3-3.	Characterization of Square Matrices	117
3-4.	Matrix Inversion	121
3-5.	Matrices Having Special Properties	127
3-6.	Matrix Representations of Linear Operators and Matrix Transformations	129
3-7.	Changes of Basis and Similarity Transformations	138
3-8.	Matrix Eigenvalue Problems	147
3-9.	Infinite Matrices and Linear Transformations on Hilbert Space	167
3-10.	Dirac Notation	169
	Problems	170

Chapter 4

	Postulates of Quantum Mechanics and Initial Considerations	175
4-1.	Quantum Mechanical States and Observables	176
4-2.	Time Evolution of a Quantum State	181
4-3.	Quantum Theory of Measurement and Expectation Values	185
4-4.	Compatible Observables and Commuting Operators	192
4-5.	Constants of Motion and Transition Probabilities	198
4-6.	Different Pictures of Quantum Phenomena	204
4-7.	Hamiltonian Operator Construction: Initial Considerations	211
	Problems	216

Chapter 5

	One-Dimensional Model Problems	219
5-1.	General Comments	219
5-2.	Wavefunction Criteria and Boundary Conditions	220
5-3.	The Nondegeneracy Theorem	221
5-4.	Particle on a Ring	223
5-5.	Particle Trapped in a Box	228
5-6.	Parity of Eigenfunctions	233
5-7.	Square Well Potential	235
5-8.	Double Wells and Tunneling	241
5-9.	The Harmonic Oscillator	250
5-10.	Zero Point Energy and the Uncertainty Principle	265
	Problems	267

Chapter 6

	Angular Momentum	271
6-1.	Introduction	271
6-2.	General Angular Momentum Considerations	273
6-3.	Orbital Angular Momentum	282
6-4.	Spin Angular Momentum	288
	Problems	291

Chapter 7

The Hydrogen Atom, Rigid Rotor, and the H_2^+ Molecule	293
7-1. Separation of Motion of Center of Mass	293
7-2. Solution of Equation for Relative Electron Motion of the Hydrogen Atom and Hydrogen-Like Atoms	297
7-3. Wavefunction Shapes	303
7-4. Rigid Rotor	314
7-5. The H_2^+ Molecule Problems	317 325

Chapter 8

The Molecular Hamiltonian	327
8-1. General Principles and Discussion	327
8-2. Introduction of External Fields	328
8-3. Introduction of Relativistic Effects	333
8-4. The Born-Oppenheimer Approximation Problems	343 347

Chapter 9

Approximation Methods for Stationary States	352
9-1. The Variation Principle	352
9-2. Accuracy Considerations	355
9-3. Example: The Hydrogen Atom	357
9-4. Example: Variational Treatment of the Helium Atom	359
9-5. The Linear Variation Method	362
9-6. Example: The Hydrogen Atom Revisited	369
9-7. Lower Bounds	372
9-8. Rayleigh-Schrödinger Perturbation Theory	374
9-9. Brillouin-Wigner Perturbation Theory Problems	386 392

Chapter 10

General Considerations for Many Electron Systems	397
10-1. Early Computational Concepts and Procedures	397
10-2. Symmetry Considerations and Group Theory	402
10-3. Antisymmetry and the Pauli Exclusion Principle	429
10-4. Multielectron Systems and Slater Determinants	431
10-5. Expansion Theorem and Slater Determinant Expansions	435
10-6. Matrix Elements between Slater Determinants	437
10-7. Virial Theorem, Hypervirial Theorem, and Hellmann-Feynman Theorem	447
10-8. Scaling	453
10-9. Coupling of Angular Momenta	460
10-10. Orbital Transformations Problems	471 477

Chapter 11

**Computational Techniques for Many-Electron Systems Using
Single Configuration Wavefunctions 481**

- 11-1. Hartree–Fock Theory for Closed Shell Systems 481
- 11-2. Hall–Roothaan LCAO–MO–SCF Theory for Closed Shell Systems 498
- 11-3. Hartree–Fock Theory for Open Shell Systems 556
- Problems 573

Chapter 12

Beyond Hartree–Fock Theory 576

- 12-1. Electron Correlation: General Comments 576
- 12-2. Configuration Interaction 577
- 12-3. Specialized CI Approaches 624
- 12-4. Many-Body Perturbation Theory and Coupled Cluster Theory 648
- Problems 653

Appendix 1 657**References 659****Index 677**