Contents

Foreword *xix*
Preface *xxiii*
Editors' Note *xxvii*

Part I Fundamental Principles *1*

1 The Principle of Wave–Particle Duality: An Overview *3*
1.1 Introduction *3*
1.2 The Principle of Wave–Particle Duality of Light *4*
1.2.1 The Photoelectric Effect *4*
1.2.2 The Compton Effect *7*
1.2.3 A Note on Units *10*
1.3 The Principle of Wave–Particle Duality of Matter *11*
1.3.1 From Frequency Quantization in Classical Waves to Energy Quantization in Matter Waves: The Most Important General Consequence of Wave–Particle Duality of Matter *12*
1.3.2 The Problem of Atomic Stability under Collisions *13*
1.3.3 The Problem of Energy Scales: Why Are Atomic Energies on the Order of eV, While Nuclear Energies Are on the Order of MeV? *15*
1.3.4 The Stability of Atoms and Molecules Against External Electromagnetic Radiation *17*
1.3.5 The Problem of Length Scales: Why Are Atomic Sizes on the Order of Angstroms, While Nuclear Sizes Are on the Order of Fermis? *19*
1.3.6 The Stability of Atoms Against Their Own Radiation: Probabilistic Interpretation of Matter Waves *21*
1.3.7 How Do Atoms Radiate after All? Quantum Jumps from Higher to Lower Energy States and Atomic Spectra *22*
1.3.8 Quantized Energies and Atomic Spectra: The Case of Hydrogen *25*
1.3.9 Correct and Incorrect Pictures for the Motion of Electrons in Atoms: Revisiting the Case of Hydrogen *25*
1.3.10 The Fine Structure Constant and Numerical Calculations in Bohr's Theory *29*

1.3.11 Numerical Calculations with Matter Waves: Practical Formulas and Physical Applications *31*
1.3.12 A Direct Confirmation of the Existence of Matter Waves: The Davisson–Germer Experiment *33*
1.3.13 The Double-Slit Experiment: Collapse of the Wavefunction Upon Measurement *34*
1.4 Dimensional Analysis and Quantum Physics *41*
1.4.1 The Fundamental Theorem and a Simple Application *41*
1.4.2 Blackbody Radiation Using Dimensional Analysis *44*
1.4.3 The Hydrogen Atom Using Dimensional Analysis *47*

2 The Schrödinger Equation and Its Statistical Interpretation *53*
2.1 Introduction *53*
2.2 The Schrödinger Equation *53*
2.2.1 The Schrödinger Equation for Free Particles *54*
2.2.2 The Schrödinger Equation in an External Potential *57*
2.2.3 Mathematical Intermission I: Linear Operators *58*
2.3 Statistical Interpretation of Quantum Mechanics *60*
2.3.1 The "Particle–Wave" Contradiction in Classical Mechanics *60*
2.3.2 Statistical Interpretation *61*
2.3.3 Why Did We Choose $P(x) = |\psi(x)|^2$ as the Probability Density? *62*
2.3.4 Mathematical Intermission II: Basic Statistical Concepts *63*
2.3.4.1 Mean Value *63*
2.3.4.2 Standard Deviation (or Uncertainty) *65*
2.3.5 Position Measurements: Mean Value and Uncertainty *67*
2.4 Further Development of the Statistical Interpretation: The Mean-Value Formula *71*
2.4.1 The General Formula for the Mean Value *71*
2.4.2 The General Formula for Uncertainty *73*
2.5 Time Evolution of Wavefunctions and Superposition States *77*
2.5.1 Setting the Stage *77*
2.5.2 Solving the Schrödinger Equation. Separation of Variables *78*
2.5.3 The Time-Independent Schrödinger Equation as an Eigenvalue Equation: Zero-Uncertainty States and Superposition States *81*
2.5.4 Energy Quantization for Confined Motion: A Fundamental General Consequence of Schrödinger's Equation *85*
2.5.5 The Role of Measurement in Quantum Mechanics: Collapse of the Wavefunction Upon Measurement *86*
2.5.6 Measurable Consequences of Time Evolution: Stationary and Nonstationary States *91*
2.6 Self-Consistency of the Statistical Interpretation and the Mathematical Structure of Quantum Mechanics *95*
2.6.1 Hermitian Operators *95*
2.6.2 Conservation of Probability *98*
2.6.3 Inner Product and Orthogonality *99*
2.6.4 Matrix Representation of Quantum Mechanical Operators *101*
2.7 Summary: Quantum Mechanics in a Nutshell *103*

3 The Uncertainty Principle *107*
3.1 Introduction *107*
3.2 The Position–Momentum Uncertainty Principle *108*
3.2.1 Mathematical Explanation of the Principle *108*
3.2.2 Physical Explanation of the Principle *109*
3.2.3 Quantum Resistance to Confinement. A Fundamental Consequence of the Position–Momentum Uncertainty Principle *112*
3.3 The Time–Energy Uncertainty Principle *114*
3.4 The Uncertainty Principle in the Classical Limit *118*
3.5 General Investigation of the Uncertainty Principle *119*
3.5.1 Compatible and Incompatible Physical Quantities and the Generalized Uncertainty Relation *119*
3.5.2 Angular Momentum: A Different Kind of Vector *122*

Part II Simple Quantum Systems *127*

4 Square Potentials. I: Discrete Spectrum—Bound States *129*
4.1 Introduction *129*
4.2 Particle in a One-Dimensional Box: The Infinite Potential Well *132*
4.2.1 Solution of the Schrödinger Equation *132*
4.2.2 Discussion of the Results *134*
4.2.2.1 Dimensional Analysis of the Formula $E_n = (\hbar^2\pi^2/2mL^2)n^2$. Do We Need an Exact Solution to Predict the Energy Dependence on $\hbar$, m, and L? *135*
4.2.2.2 Dependence of the Ground-State Energy on $\hbar$, m, and L : The Classical Limit *136*
4.2.2.3 The Limit of Large Quantum Numbers and Quantum Discontinuities *137*
4.2.2.4 The Classical Limit of the Position Probability Density *138*
4.2.2.5 Eigenfunction Features: Mirror Symmetry and the Node Theorem *139*
4.2.2.6 Numerical Calculations in Practical Units *139*
4.3 The Square Potential Well *140*
4.3.1 Solution of the Schrödinger Equation *140*
4.3.2 Discussion of the Results *143*
4.3.2.1 Penetration into Classically Forbidden Regions *143*
4.3.2.2 Penetration in the Classical Limit *144*
4.3.2.3 The Physics and "Numerics" of the Parameter λ *145*

5 Square Potentials. II: Continuous Spectrum—Scattering States *149*
5.1 Introduction *149*
5.2 The Square Potential Step: Reflection and Transmission *150*
5.2.1 Solution of the Schrödinger Equation and Calculation of the Reflection Coefficient *150*
5.2.2 Discussion of the Results *153*

5.2.2.1 The Phenomenon of Classically Forbidden Reflection *153*
5.2.2.2 Transmission Coefficient in the "Classical Limit" of High Energies *154*
5.2.2.3 The Reflection Coefficient Depends neither on Planck's Constant nor on the Mass of the Particle: Analysis of a Paradox *154*
5.2.2.4 An Argument from Dimensional Analysis *155*
5.3 Rectangular Potential Barrier: Tunneling Effect *156*
5.3.1 Solution of the Schrödinger Equation *156*
5.3.2 Discussion of the Results *158*
5.3.2.1 Crossing a Classically Forbidden Region: The Tunneling Effect *158*
5.3.2.2 Exponential Sensitivity of the Tunneling Effect to the Energy of the Particle *159*
5.3.2.3 A Simple Approximate Expression for the Transmission Coefficient *160*
5.3.2.4 Exponential Sensitivity of the Tunneling Effect to the Mass of the Particle *162*
5.3.2.5 A Practical Formula for T *163*

6 The Harmonic Oscillator *167*
6.1 Introduction *167*
6.2 Solution of the Schrödinger Equation *169*
6.3 Discussion of the Results *177*
6.3.1 Shape of Wavefunctions. Mirror Symmetry and the Node Theorem *178*
6.3.2 Shape of Eigenfunctions for Large n: The Classical Limit *179*
6.3.3 The Extreme Anticlassical Limit of the Ground State *180*
6.3.4 Penetration into Classically Forbidden Regions: What Fraction of Its "Lifetime" Does the Particle "Spend" in the Classically Forbidden Region? *181*
6.3.5 A Quantum Oscillator Never Rests: Zero-Point Energy *182*
6.3.6 Equidistant Eigenvalues and Emission of Radiation from a Quantum Harmonic Oscillator *184*
6.4 A Plausible Question: Can We Use the Polynomial Method to Solve Potentials Other than the Harmonic Oscillator? *187*

7 The Polynomial Method: Systematic Theory and Applications *191*
7.1 Introduction: The Power-Series Method *191*
7.2 Sufficient Conditions for the Existence of Polynomial Solutions: Bidimensional Equations *194*
7.3 The Polynomial Method in Action: Exact Solution of the Kratzer and Morse Potentials *197*
7.4 Mathematical Afterword *202*

8 The Hydrogen Atom. I: Spherically Symmetric Solutions *207*
8.1 Introduction *207*

8.2 Solving the Schrödinger Equation for the Spherically Symmetric Eigenfunctions *209*
8.2.1 A Final Comment: The System of Atomic Units *216*
8.3 Discussion of the Results *217*
8.3.1 Checking the Classical Limit $\hbar \to 0$ or $m \to \infty$ for the Ground State of the Hydrogen Atom *217*
8.3.2 Energy Quantization and Atomic Stability *217*
8.3.3 The Size of the Atom and the Uncertainty Principle: The Mystery of Atomic Stability from Another Perspective *218*
8.3.4 Atomic Incompressibility and the Uncertainty Principle *221*
8.3.5 More on the Ground State of the Atom. Mean and Most Probable Distance of the Electron from the Nucleus *221*
8.3.6 Revisiting the Notion of "Atomic Radius": How Probable is It to Find the Electron Within the "Volume" that the Atom Supposedly Occupies? *222*
8.3.7 An Apparent Paradox: After All, Where Is It Most Likely to Find the Electron? Near the Nucleus or One Bohr Radius Away from It? *223*
8.3.8 What Fraction of Its Time Does the Electron Spend in the Classically Forbidden Region of the Atom? *223*
8.3.9 Is the Bohr Theory for the Hydrogen Atom Really Wrong? Comparison with Quantum Mechanics *225*
8.4 What Is the Electron Doing in the Hydrogen Atom after All? A First Discussion on the Basic Questions of Quantum Mechanics *226*

9 The Hydrogen Atom. II: Solutions with Angular Dependence *231*
9.1 Introduction *231*
9.2 The Schrödinger Equation in an Arbitrary Central Potential: Separation of Variables *232*
9.2.1 Separation of Radial from Angular Variables *232*
9.2.2 The Radial Schrödinger Equation: Physical Interpretation of the Centrifugal Term and Connection to the Angular Equation *235*
9.2.3 Solution of the Angular Equation: Eigenvalues and Eigenfunctions of Angular Momentum *237*
9.2.3.1 Solving the Equation for Φ *238*
9.2.3.2 Solving the Equation for Θ *239*
9.2.4 Summary of Results for an Arbitrary Central Potential *243*
9.3 The Hydrogen Atom *246*
9.3.1 Solution of the Radial Equation for the Coulomb Potential *246*
9.3.2 Explicit Construction of the First Few Eigenfunctions *249*
9.3.2.1 $n = 1$: The Ground State *250*
9.3.2.2 $n = 2$: The First Excited States *250*
9.3.3 Discussion of the Results *254*
9.3.3.1 The Energy-Level Diagram *254*
9.3.3.2 Degeneracy of the Energy Spectrum for a Coulomb Potential: Rotational and Accidental Degeneracy *255*
9.3.3.3 Removal of Rotational and Hydrogenic Degeneracy *257*

9.3.3.4 The Ground State is Always Nondegenerate and Has the Full Symmetry of the Problem *257*
9.3.3.5 Spectroscopic Notation for Atomic States *258*
9.3.3.6 The "Concept" of the Orbital: *s* and *p* Orbitals *258*
9.3.3.7 Quantum Angular Momentum: A Rather Strange Vector *261*
9.3.3.8 Allowed and Forbidden Transitions in the Hydrogen Atom: Conservation of Angular Momentum and Selection Rules *263*

10 Atoms in a Magnetic Field and the Emergence of Spin *267*
10.1 Introduction *267*
10.2 Atomic Electrons as Microscopic Magnets: Magnetic Moment and Angular Momentum *270*
10.3 The Zeeman Effect and the Evidence for the Existence of Spin *274*
10.4 The Stern–Gerlach Experiment: Unequivocal Experimental Confirmation of the Existence of Spin *278*
10.4.1 Preliminary Investigation: A Plausible Theoretical Description of Spin *278*
10.4.2 The Experiment and Its Results *280*
10.5 What is Spin? *284*
10.5.1 Spin is No Self-Rotation *284*
10.5.2 How is Spin Described Quantum Mechanically? *285*
10.5.3 What Spin Really Is *291*
10.6 Time Evolution of Spin in a Magnetic Field *292*
10.7 Total Angular Momentum of Atoms: Addition of Angular Momenta *295*
10.7.1 The Eigenvalues *295*
10.7.2 The Eigenfunctions *300*

11 Identical Particles and the Pauli Principle *305*
11.1 Introduction *305*
11.2 The Principle of Indistinguishability of Identical Particles in Quantum Mechanics *305*
11.3 Indistinguishability of Identical Particles and the Pauli Principle *306*
11.4 The Role of Spin: Complete Formulation of the Pauli Principle *307*
11.5 The Pauli Exclusion Principle *310*
11.6 Which Particles Are Fermions and Which Are Bosons *314*
11.7 Exchange Degeneracy: The Problem and Its Solution *317*

Part III Quantum Mechanics in Action: The Structure of Matter *321*

12 Atoms: The Periodic Table of the Elements *323*
12.1 Introduction *323*
12.2 Arrangement of Energy Levels in Many-Electron Atoms: The Screening Effect *324*

12.3 Quantum Mechanical Explanation of the Periodic Table: The "Small Periodic Table" *327*
12.3.1 Populating the Energy Levels: The Shell Model *328*
12.3.2 An Interesting "Detail": The Pauli Principle and Atomic Magnetism *329*
12.3.3 Quantum Mechanical Explanation of Valence and Directionality of Chemical Bonds *331*
12.3.4 Quantum Mechanical Explanation of Chemical Periodicity: The Third Row of the Periodic Table *332*
12.3.5 Ionization Energy and Its Role in Chemical Behavior *334*
12.3.6 Examples *338*
12.4 Approximate Calculations in Atoms: Perturbation Theory and the Variational Method *341*
12.4.1 Perturbation Theory *342*
12.4.2 Variational Method *346*

13 Molecules. I: Elementary Theory of the Chemical Bond *351*
13.1 Introduction *351*
13.2 The Double-Well Model of Chemical Bonding *352*
13.2.1 The Symmetric Double Well *352*
13.2.2 The Asymmetric Double Well *356*
13.3 Examples of Simple Molecules *360*
13.3.1 The Hydrogen Molecule H_2 *360*
13.3.2 The Helium "Molecule" He_2 *363*
13.3.3 The Lithium Molecule Li_2 *364*
13.3.4 The Oxygen Molecule O_2 *364*
13.3.5 The Nitrogen Molecule N_2 *366*
13.3.6 The Water Molecule H_2O *367*
13.3.7 Hydrogen Bonds: From the Water Molecule to Biomolecules *370*
13.3.8 The Ammonia Molecule NH_3 *373*
13.4 Molecular Spectra *377*
13.4.1 Rotational Spectrum *378*
13.4.2 Vibrational Spectrum *382*
13.4.3 The Vibrational–Rotational Spectrum *385*

14 Molecules. II: The Chemistry of Carbon *393*
14.1 Introduction *393*
14.2 Hybridization: The First Basic Deviation from the Elementary Theory of the Chemical Bond *393*
14.2.1 The CH_4 Molecule According to the Elementary Theory: An Erroneous Prediction *393*
14.2.2 Hybridized Orbitals and the CH_4 Molecule *395*
14.2.3 Total and Partial Hybridization *401*
14.2.4 The Need for Partial Hybridization: The Molecules C_2H_4, C_2H_2, and C_2H_6 *404*
14.2.5 Application of Hybridization Theory to Conjugated Hydrocarbons *408*

14.2.6 Energy Balance of Hybridization and Application to Inorganic Molecules *409*
14.3 Delocalization: The Second Basic Deviation from the Elementary Theory of the Chemical Bond *414*
14.3.1 A Closer Look at the Benzene Molecule *414*
14.3.2 An Elementary Theory of Delocalization: The Free-Electron Model *417*
14.3.3 LCAO Theory for Conjugated Hydrocarbons. I: Cyclic Chains *418*
14.3.4 LCAO Theory for Conjugated Hydrocarbons. II: Linear Chains *424*
14.3.5 Delocalization on Carbon Chains: General Remarks *427*
14.3.6 Delocalization in Two-dimensional Arrays of *p* Orbitals: Graphene and Fullerenes *429*

15 Solids: Conductors, Semiconductors, Insulators *439*
15.1 Introduction *439*
15.2 Periodicity and Band Structure *439*
15.3 Band Structure and the "Mystery of Conductivity." Conductors, Semiconductors, Insulators *441*
15.3.1 Failure of the Classical Theory *441*
15.3.2 The Quantum Explanation *443*
15.4 Crystal Momentum, Effective Mass, and Electron Mobility *447*
15.5 Fermi Energy and Density of States *453*
15.5.1 Fermi Energy in the Free-Electron Model *453*
15.5.2 Density of States in the Free-Electron Model *457*
15.5.3 Discussion of the Results: Sharing of Available Space by the Particles of a Fermi Gas *460*
15.5.4 A Classic Application: The "Anomaly" of the Electronic Specific Heat of Metals *463*

16 Matter and Light: The Interaction of Atoms with Electromagnetic Radiation *469*
16.1 Introduction *469*
16.2 The Four Fundamental Processes: Resonance, Scattering, Ionization, and Spontaneous Emission *471*
16.3 Quantitative Description of the Fundamental Processes: Transition Rate, Effective Cross Section, Mean Free Path *473*
16.3.1 Transition Rate: The Fundamental Concept *473*
16.3.2 Effective Cross Section and Mean Free Path *475*
16.3.3 Scattering Cross Section: An Instructive Example *476*
16.4 Matter and Light in Resonance. I: Theory *478*
16.4.1 Calculation of the Effective Cross Section: Fermi's Rule *478*
16.4.2 Discussion of the Result: Order-of-Magnitude Estimates and Selection Rules *481*
16.4.3 Selection Rules: Allowed and Forbidden Transitions *483*
16.5 Matter and Light in Resonance. II: The Laser *487*
16.5.1 The Operation Principle: Population Inversion and the Threshold Condition *487*

16.5.2 Main Properties of Laser Light *491*
16.5.2.1 Phase Coherence *491*
16.5.2.2 Directionality *491*
16.5.2.3 Intensity *491*
16.5.2.4 Monochromaticity *492*
16.6 Spontaneous Emission *494*
16.7 Theory of Time-dependent Perturbations: Fermi's Rule *499*
16.7.1 Approximate Calculation of Transition Probabilities $P_{n\to m}(t)$ for an Arbitrary "Transient" Perturbation $V(t)$ *499*
16.7.2 The Atom Under the Influence of a Sinusoidal Perturbation: Fermi's Rule for Resonance Transitions *503*
16.8 The Light Itself: Polarized Photons and Their Quantum Mechanical Description *511*
16.8.1 States of Linear and Circular Polarization for Photons *511*
16.8.2 Linear and Circular Polarizers *512*
16.8.3 Quantum Mechanical Description of Polarized Photons *513*

Online Supplement

1 The Principle of Wave–Particle Duality: An Overview
OS1.1 Review Quiz
OS1.1 Determining Planck's Constant from Everyday Observations

2 The Schrödinger Equation and Its Statistical Interpretation
OS2.1 Review Quiz
OS2.2 Further Study of Hermitian Operators: The Concept of the Adjoint Operator
OS2.3 Local Conservation of Probability: The Probability Current

3 The Uncertainty Principle
OS3.1 Review Quiz
OS3.2 Commutator Algebra: Calculational Techniques
OS3.3 The Generalized Uncertainty Principle
OS3.4 Ehrenfest's Theorem: Time Evolution of Mean Values and the Classical Limit

4 Square Potentials. I: Discrete Spectrum—Bound States
OS4.1 Review Quiz
OS4.2 Square Well: A More Elegant Graphical Solution for Its Eigenvalues
OS4.3 Deep and Shallow Wells: Approximate Analytic Expressions for Their Eigenvalues

5 Square Potentials. II: Continuous Spectrum—Scattering States
OS5.1 Review Quiz
OS5.2 Quantum Mechanical Theory of Alpha Decay

6 The Harmonic Oscillator
OS6.1 Review Quiz
OS6.2 Algebraic Solution of the Harmonic Oscillator: Creation and Annihilation Operators

7 The Polynomial Method: Systematic Theory and Applications
OS7.1 Review Quiz
OS7.2 An Elementary Method for Discovering Exactly Solvable Potentials
OS7.3 Classic Examples of Exactly Solvable Potentials: A Comprehensive List

8 The Hydrogen Atom. I: Spherically Symmetric Solutions
OS8.1 Review Quiz

9 The Hydrogen Atom. II: Solutions with Angular Dependence
OS9.1 Review Quiz
OS9.2 Conservation of Angular Momentum in Central Potentials, and Its Consequences
OS9.3 Solving the Associated Legendre Equation on Our Own

10 Atoms in a Magnetic Field and the Emergence of Spin
OS10.1 Review Quiz
OS10.2 Algebraic Theory of Angular Momentum and Spin

11 Identical Particles and the Pauli Principle
OS11.1 Review Quiz
OS11.2 Dirac's Formalism: A Brief Introduction

12 Atoms: The Periodic Table of the Elements
OS12.1 Review Quiz
OS12.2 Systematic Perturbation Theory: Application to the Stark Effect and Atomic Polarizability

13 Molecules. I: Elementary Theory of the Chemical Bond
OS13.1 Review Quiz

14 Molecules. II: The Chemistry of Carbon
OS14.1 Review Quiz
OS14.2 The LCAO Method and Matrix Mechanics
OS14.3 Extension of the LCAO Method for Nonzero Overlap

15 Solids: Conductors, Semiconductors, Insulators
OS15.1 Review Quiz
OS15.2 Floquet's Theorem: Mathematical Study of the Band Structure for an Arbitrary Periodic Potential V(x)
OS15.3 Compressibility of Condensed Matter: The Bulk Modulus
OS15.4 The Pauli Principle and Gravitational Collapse: The Chandrasekhar Limit

16 Matter and Light: The Interaction of Atoms with Electromagnetic Radiation

OS16.1 Review Quiz

OS16.2 Resonance Transitions Beyond Fermi's Rule: Rabi Oscillations

OS16.3 Resonance Transitions at Radio Frequencies: Nuclear Magnetic Resonance (NMR)

Appendix *519*

Bibliography *523*

Index *527*