Contents

PREFACE  page xvii

NOTATION  xxi

1  HISTORICAL INTRODUCTION  1

1.1  Photons  1
Black-body radiation □ Rayleigh–Jeans formula □ Planck formula □ Atomic constants
□ Photoelectric effect □ Compton scattering

1.2  Atomic Spectra  6
Discovery of atomic nuclei □ Ritz combination principle □ Bohr quantization condition
□ Hydrogen spectrum □ Atomic numbers and weights □ Sommerfeld quantization
condition □ Einstein A and B coefficients □ Lasers

1.3  Wave Mechanics  13
De Broglie waves □ Davisson–Germer experiment □ Schrödinger equation

1.4  Matrix Mechanics  16
Radiative transition rate □ Harmonic oscillator □ Heisenberg matrix algebra □
Commutation relations □ Equivalence to wave mechanics □ Quantization of radiation

1.5  Probabilistic Interpretation  24
Scattering □ Probability density and current □ Expectation values □ Equations of
motion □ Eigenvalues and eigenfunctions □ Uncertainty principle □ Born rule for
transition probabilities

Historical Bibliography  30

Problems  30
## Contents

### 2 PARTICLE STATES IN A CENTRAL POTENTIAL 32

#### 2.1 Schrödinger Equation for a Central Potential 32

- Hamiltonian for central potentials
- Orbital angular momentum operator $L$
- Spectrum of $L^2$
- Separation of wave function
- Boundary conditions

#### 2.2 Spherical Harmonics 39

- Spectrum of $L_3$
- Associated Legendre polynomials
- Construction of spherical harmonics
- Orthonormality
- Parity
- Legendre polynomials

#### 2.3 The Hydrogen Atom 43

- Radial Schrödinger equation
- Power series solution
- Laguerre polynomials
- Energy levels
- Selection rules

#### 2.4 The Two-Body Problem 47

- Reduced mass
- Relative and center-of-mass coordinates
- Relative and total momenta
- Hydrogen and deuterium spectra

#### 2.5 The Harmonic Oscillator 49

- Separation of wave function
- Raising and lowering operators
- Spectrum
- Normalized wave functions
- Radiative transition matrix elements

### Problems 54

### 3 GENERAL PRINCIPLES OF QUANTUM MECHANICS 55

#### 3.1 States 55

- Hilbert space
- Vector spaces
- Norms
- Completeness and independence
- Orthonormalization
- Probabilities
- Rays
- Dirac notation

#### 3.2 Continuum States 61

- From discrete to continuum states
- Normalization
- Delta functions
- Distributions

#### 3.3 Observables 64

- Operators
- Adjoint
- Matrix representation
- Eigenvalues
- Completeness of eigenvectors
- Schwarz inequality
- Uncertainty principle
- Dyads
- Projection operators
- Density matrix
- Von Neumann entropy
- Disentangled systems

#### 3.4 Symmetries 74

- Unitary operators
- Wigner’s theorem
- Antunitary operators
- Continuous symmetries
- Commutators

#### 3.5 Space Translation 78

- Momentum operators
- Commutation rules
- Momentum eigenstates
- Bloch waves
- Band structure
## Contents

### 3.6 Time Translation and Inversion

82

- Hamiltonians
- Time-dependent Schrödinger equation
- Conservation laws
- Time reversal
- Galilean invariance
- Boost generator
- Time-dependence of density matrix

### 3.7 Interpretations of Quantum Mechanics

86

- Copenhagen interpretation
- Measurement vs. unitary evolution of the density matrix
- Correlation of system and measuring apparatus
- Classical states
- Decoherence
- Stern–Gerlach experiment
- Schrödinger’s cat
- Where does the Born rule come from?
- Instrumentalist interpretations
- Decoherent histories
- Realist interpretations
- Many worlds?
- Approach to the Born rule
- Conclusion

### Problems

102

### 4 SPIN ET CETERA

104

#### 4.1 Rotations

106

- Finite rotations
- Rotation groups $O(3)$ and $SO(3)$
- Action on physical states
- Infinitesimal rotations
- Commutation relations
- Total angular momentum
- Spin

#### 4.2 Angular-Momentum Multiplets

112

- Raising and lowering operators
- Spectrum of $J^2$ and $J_3$
- Spin matrices
- Pauli matrices
- $J_3$-independence
- Stern–Gerlach experiment

#### 4.3 Addition of Angular Momenta

117

- Choice of basis
- Clebsch–Gordan coefficients
- Sum rules for coefficients
- Hydrogen states
- Symmetries of coefficients
- Addition theorem for spherical harmonics
- $3j$ symbols
- More sum rules
- $SU(2)$ formalism

#### 4.4 The Wigner–Eckart Theorem

128

- Operator transformation properties
- Theorem for matrix elements
- Parallel matrix elements
- Photon emission selection rules

#### 4.5 Bosons and Fermions

132

- Symmetrical and antisymmetrical states
- Connection with spin
- Hartree approximation
- Pauli exclusion principle
- Periodic table for atoms
- Magic numbers for nuclei
- Temperature and chemical potential
- Statistics
- Insulators, conductors, semi-conductors

#### 4.6 Internal Symmetries

141

- Charge symmetry
- Isotopic spin symmetry
- Pions
- $\Delta$s
- Strangeness
- $U(1)$ symmetries
- $SU(3)$ symmetry

#### 4.7 Inversions

150

- Space inversion
- Orbital parity
- Intrinsic parity
- Parity of pions
- Violations of parity conservation
- $P$, $C$, and $T$
## Contents

### 4.8 Algebraic Derivation of the Hydrogen Spectrum
- Runge–Lenz vector
- $SO(3) \otimes SO(3)$ commutation relations
- Energy levels
- Scattering states
- Four-dimensional interpretation

### 4.9 The Rigid Rotator
- Laboratory and body-fixed coordinates
- Rotational energy
- Moment-of-inertia tensor
- Body-fixed angular momentum operator
- Energy levels of symmetric rotators
- Energy levels of general rotators
- Rotator wave functions
- Rotation representation
- $D_{MK}^{IJ}(R)$
- Orthohydrogen and parahydrogen
- Estimated energies

### Problems

## 5 APPROXIMATIONS FOR ENERGY EIGENVALUES

### 5.1 First-Order Perturbation Theory
- Non-degenerate case: first-order energy and state vector
- Degenerate case: first-order energy, ambiguity in first-order state vector
- A classical analog

### 5.2 The Zeeman Effect
- Gyromagnetic ratio
- Landé $g$-factor
- Sodium D lines
- Normal and anomalous Zeeman effect
- Paschen–Back effect

### 5.3 The First-Order Stark Effect
- Mixing of $2S_{1/2}$ and $2P_{1/2}$ states
- Energy shift for weak fields
- Energy shift for strong fields

### 5.4 Second-Order Perturbation Theory
- Non-degenerate case: second-order energy and state vector
- Degenerate case: second-order energy, removal of ambiguity in first-order state vector
- Ultraviolet and infrared divergences
- Closure approximation
- Second-order Stark effect

### 5.5 The Variational Method
- Upper bound on ground state energy
- Excited states
- Approximation to state vectors
- Virial theorem
- Other states

### 5.6 The Born–Oppenheimer Approximation
- Reduced Hamiltonian
- Hellmann–Feynman theorem
- Estimate of corrections
- Electronic, vibrational, and rotational modes
- Effective theories

### 5.7 The WKB Approximation
- Approximate solutions
- Validity conditions
- Turning points
- Energy eigenvalues – one dimension
- Energy eigenvalues – three dimensions

### 5.8 Broken Symmetry
- Approximate solutions for thick barriers
- Energy splitting
- Decoherence
- Oscillations
- Chiral molecules
### Contents

5.9 Van der Waals Forces 208
- Expansion of interaction in spherical harmonics
- Second-order perturbation theory
- Dominance of the dipole–dipole term

Problems 212

6 APPROXIMATIONS FOR TIME-DEPENDENT PROBLEMS 214

6.1 First-Order Perturbation Theory 214
- Differential equation for amplitudes
- Approximate solution

6.2 Monochromatic Perturbations 215
- Transition rate
- Fermi golden rule
- Continuum final states

6.3 Ionization by an Electromagnetic Wave 218
- Nature of perturbation
- Conditions on frequency
- Ionization rate of hydrogen ground state

6.4 Fluctuating Perturbations 220
- Stationary fluctuations
- Correlation function
- Transition rate

6.5 Absorption and Stimulated Emission of Radiation 222
- Dipole approximation
- Transition rates
- Energy density of radiation
- $B$-coefficients
- Spontaneous transition rate

6.6 The Adiabatic Approximation 224
- Slowly varying Hamiltonians
- Dynamical phase
- Non-dynamical phase
- Degenerate case

6.7 The Berry Phase 227
- Geometric character of the non-dynamical phase
- Closed curves in parameter space
- General formula for the Berry phase
- Spin in a slowly varying magnetic field

6.8 Rabi Oscillations and Ramsey Interferometers 232
- Two-state approximation
- Rabi oscillation frequency
- The Ramsey trick
- Precision measurements of transition frequencies

6.9 Open Systems 237
- Linear non-unitary evolution of density matrix
- Properties of evolution kernel
- Expansion of kernel in eigenmatrices
- Rate of change of density matrix
- Positivity
- Complete positivity
- Lindblad equation
- Increasing entropy
- Measurement

Problems 246
7 POTENTIAL SCATTERING

7.1 In-States
Wave packets □ Lippmann–Schwinger equation □ Wave packets at early times □ Spread of wave packet

7.2 Scattering Amplitudes
Green’s function for scattering □ Definition of scattering amplitude □ Wave packet at late times □ Differential cross section

7.3 The Optical Theorem
Derivation of theorem □ Conservation of probability □ Diffraction peak

7.4 The Born Approximation
First-order scattering amplitude □ Scattering by shielded Coulomb potential

7.5 Phase Shifts
Partial wave expansion of plane wave □ Partial wave expansion of “in” wave function □ Partial wave expansion of scattering amplitude □ Scattering cross section □ Scattering length and effective range

7.6 Resonances
Thick barriers □ Breit–Wigner formula □ Decay rate □ Alpha decay □ Ramsauer–Townsend effect

7.7 Time Delay
Wigner formula □ Causality

7.8 Levinson’s Theorem
Conservation of discrete states □ Growth of phase shift

7.9 Coulomb Scattering
Separation of wave function □ Kummer functions □ Scattering amplitude

7.10 The Eikonal Approximation
WKB approximation in three dimensions □ Initial surface □ Ray paths □ Calculation of phase □ Calculation of amplitude □ Application to potential scattering □ Classical cross section □ Phase of scattering amplitude □ Long-range forces

Problems

8 GENERAL SCATTERING THEORY

8.1 The S-Matrix
“In” and “out” states □ Wave packets at early and late times □ Definition of the S-matrix □ Normalization of the “in” and “out” states □ Unitarity of the S-matrix
## Contents

8.2 Rates 287
- Transition probabilities in a spacetime box
- Decay rates
- Cross sections
- Relative velocity
- Connection with scattering amplitudes
- Final states

8.3 The General Optical Theorem 291
- Optical theorem for multiparticle states
- Two-particle case

8.4 The Partial Wave Expansion 292
- Discrete basis for two-particle states
- Two-particle S-matrix
- Total and scattering cross sections
- Phase shifts
- High-energy scattering

8.5 Resonances Revisited 299
- S-matrix near a resonance energy
- Consequences of unitarity
- General Breit–Wigner formula
- Total and scattering cross sections
- Branching ratios

8.6 Old-Fashioned Perturbation Theory 303
- Perturbation series for the S-matrix
- Functional analysis
- Square-integrable kernel
- Sufficient conditions for convergence
- Upper bound on binding energies
- Distorted-wave Born approximation
- Coulomb suppression

8.7 Time-Dependent Perturbation Theory 309
- Time-development operator
- Interaction picture
- Time-ordered products
- Dyson perturbation series
- Lorentz invariance
- “In–in” formalism

8.8 Shallow Bound States 315
- Low equation
- Low-energy approximation
- Solution for scattering length
- Neutron–proton scattering
- Solution using Herglotz theorem

8.9 Time Reversal of Scattering Processes 320
- Time reversal of free-particle states
- Time reversal of in and out states
- Detailed balance
- Time reversal in Born approximation
- Time reversal in distorted-wave Born approximation
- Watson–Fermi theorem

Problems 323

9 THE CANONICAL FORMALISM 325

9.1 The Lagrangian Formalism 326
- Stationary action
- Lagrangian equations of motion
- Example: spherical coordinates

9.2 Symmetry Principles and Conservation Laws 327
- Noether’s theorem
- Conserved quantities from symmetries of Lagrangian
- Space translation
- Rotations
- Symmetries of action

9.3 The Hamiltonian Formalism 329
- Time translation and Hamiltonian
- Hamiltonian equations of motion
- Spherical coordinates again
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.4</td>
<td>Canonical Commutation Relations</td>
<td>332</td>
</tr>
<tr>
<td></td>
<td>Conserved quantities as symmetry generators</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Commutators of canonical variables and conjugates</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Momentum and angular momentum</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Poisson brackets</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jacobi identity</td>
<td></td>
</tr>
<tr>
<td>9.5</td>
<td>Constrained Hamiltonian Systems</td>
<td>335</td>
</tr>
<tr>
<td></td>
<td>Example: particle on a surface</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Primary and secondary constraints</td>
<td></td>
</tr>
<tr>
<td></td>
<td>First- and second-class constraints</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dirac brackets</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Application to example</td>
<td></td>
</tr>
<tr>
<td>9.6</td>
<td>The Path-Integral Formalism</td>
<td>340</td>
</tr>
<tr>
<td></td>
<td>Derivation of the general path integral</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Integrating out momenta</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The free particle</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Two-slit experiment</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Interactions</td>
<td></td>
</tr>
<tr>
<td>Problems</td>
<td></td>
<td>347</td>
</tr>
</tbody>
</table>

10 CHARGED PARTICLES IN ELECTROMAGNETIC FIELDS 348

10.1 Canonical Formalism for Charged Particles 348

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equations of motion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Scalar and vector potentials</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lagrangian</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hamiltonian</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Commutation relations</td>
<td></td>
</tr>
<tr>
<td>10.2</td>
<td>Gauge Invariance</td>
<td>351</td>
</tr>
<tr>
<td></td>
<td>Gauge transformations of potentials</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gauge transformation of Lagrangian</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gauge transformation of Hamiltonian</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Commutation of energy eigenvalues</td>
<td></td>
</tr>
<tr>
<td>10.3</td>
<td>Landau Energy Levels</td>
<td>353</td>
</tr>
<tr>
<td></td>
<td>Hamiltonian in a uniform magnetic field</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Energy levels</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Near degeneracy</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fermi level</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Periodicity in $1/B_z$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shubnikov–de Haas and de Haas–van Alphen effects</td>
<td></td>
</tr>
<tr>
<td>10.4</td>
<td>The Aharonov–Bohm Effect</td>
<td>356</td>
</tr>
<tr>
<td></td>
<td>Application of the eikonal approximation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Interference between alternate ray paths</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Relation to Berry phase</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Effect of field-free vector potential</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Periodicity in the flux</td>
<td></td>
</tr>
<tr>
<td>Problems</td>
<td></td>
<td>360</td>
</tr>
</tbody>
</table>

11 THE QUANTUM THEORY OF RADIATION 361

11.1 The Euler–Lagrange Equations 361

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>General field theories</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Variational derivatives of Lagrangian</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lagrangian density</td>
<td></td>
</tr>
<tr>
<td>11.2</td>
<td>The Lagrangian for Electrodynamics</td>
<td>363</td>
</tr>
<tr>
<td></td>
<td>Maxwell equations</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Charge density and current density</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Field, interaction, and matter Lagrangians</td>
<td></td>
</tr>
<tr>
<td>Problems</td>
<td></td>
<td>360</td>
</tr>
</tbody>
</table>
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.3 Commutation Relations for Electrodynamics</td>
<td>365</td>
</tr>
<tr>
<td>11.4 The Hamiltonian for Electrodynamics</td>
<td>368</td>
</tr>
<tr>
<td>11.5 Interaction Picture</td>
<td>370</td>
</tr>
<tr>
<td>11.6 Photons</td>
<td>375</td>
</tr>
<tr>
<td>11.7 Radiative Transition Rates</td>
<td>380</td>
</tr>
<tr>
<td>11.8 Quantum Key Distribution</td>
<td>387</td>
</tr>
<tr>
<td>12 Entanglement</td>
<td>392</td>
</tr>
<tr>
<td>12.1 Paradoxes of Entanglement</td>
<td>392</td>
</tr>
<tr>
<td>12.2 The Bell Inequalities</td>
<td>398</td>
</tr>
<tr>
<td>12.3 Quantum Computation</td>
<td>402</td>
</tr>
</tbody>
</table>

**Problems**

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>390</td>
</tr>
</tbody>
</table>

**AUTHOR INDEX**

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>407</td>
</tr>
</tbody>
</table>

**SUBJECT INDEX**

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>412</td>
</tr>
</tbody>
</table>