

Contents

Preface *xi*

Introduction *xv*

1	Transition from Classical Physics to Quantum Mechanics	1
1.1	Description of Light as an Electromagnetic Wave	2
1.2	Blackbody Radiation	3
1.3	The Photoelectric Effect	5
1.4	Hydrogen Atom Absorption and Emission Spectra	7
1.5	Molecular Spectroscopy	10
1.6	Summary	12
	References	12
	Problems	12
2	Principles of Quantum Mechanics	15
2.1	Postulates of Quantum Mechanics	16
2.2	The Potential Energy and Potential Functions	20
2.3	Demonstration of Quantum Mechanical Principles for a Simple, One-Dimensional, One-Electron Model System: The Particle in a Box	21
2.3.1	Definition of the Model System	21
2.3.2	Solution of the Particle-in-a-Box Schrödinger Equation	23
2.3.3	Normalization and Orthogonality of the PiB Wavefunctions	25
2.4	The Particle in a Two-Dimensional Box, the Unbound Particle, and the Particle in a Box with Finite Energy Barriers	27
2.4.1	Particle in a 2D Box	27
2.4.2	The Unbound Particle	28
2.4.3	The Particle in a Box with Finite Energy Barriers	29
2.5	Real-World PiBs: Conjugated Polyenes, Quantum Dots, and Quantum Cascade Lasers	31
2.5.1	Transitions in a Conjugated Polyene	31
2.5.2	Quantum Dots	33

- 2.5.3 Quantum Cascade Lasers 33
 - References 34
 - Problems 35

- 3 Perturbation of Stationary States by Electromagnetic Radiation 37**
 - 3.1 Time-Dependent Perturbation Treatment of Stationary-State Systems by Electromagnetic Radiation 37
 - 3.2 Dipole-Allowed Absorption and Emission Transitions and Selection Rules for the Particle in a Box 40
 - 3.3 Einstein Coefficients for the Absorption and Emission of Light 42
 - 3.4 Lasers 45
 - References 47
 - Problems 47

- 4 The Harmonic Oscillator, a Model System for the Vibrations of Diatomic Molecules 49**
 - 4.1 Classical Description of a Vibrating Diatomic Model System 49
 - 4.2 The Harmonic Oscillator Schrödinger Equation, Energy Eigenvalues, and Wavefunctions 51
 - 4.3 The Transition Moment and Selection Rules for Absorption for the Harmonic Oscillator 56
 - 4.4 The Anharmonic Oscillator 59
 - 4.5 Vibrational Spectroscopy of Diatomic Molecules 62
 - 4.6 Summary 65
 - References 66
 - Problems 66

- 5 Vibrational Infrared and Raman Spectroscopy of Polyatomic Molecules 69**
 - 5.1 Vibrational Energy of Polyatomic Molecules: Normal Coordinates and Normal Modes of Vibration 69
 - 5.2 Quantum Mechanical Description of Molecular Vibrations in Polyatomic Molecules 73
 - 5.3 Infrared Absorption Spectroscopy 76
 - 5.3.1 Symmetry Considerations for Dipole-Allowed Transitions 76
 - 5.3.2 Line Shapes for Absorption and Anomalous Dispersion 77
 - 5.3.2.1 Line Shapes and Lifetimes 77
 - 5.3.2.2 Anomalous Dispersion 79
 - 5.4 Raman Spectroscopy 81
 - 5.4.1 General Aspects of Raman Spectroscopy 81
 - 5.4.2 Macroscopic Description of Polarizability 81
 - 5.4.3 Quantum Mechanical Description of Polarizability 83
 - 5.5 Selection Rules for IR and Raman Spectroscopy of Polyatomic Molecules 87

5.6	Relationship between Infrared and Raman Spectra: Chloroform	88
5.7	Summary: Molecular Vibrations in Science and Technology	90
	References	91
	Problems	91
6	Rotation of Molecules and Rotational Spectroscopy	93
6.1	Classical Rotational Energy of Diatomic and Polyatomic Molecules	94
6.2	Quantum Mechanical Description of the Angular Momentum Operator	97
6.3	The Rotational Schrödinger Equation, Eigenfunctions, and Rotational Energy Eigenvalues	99
6.4	Selection Rules for Rotational Transitions	104
6.5	Rotational Absorption (Microwave) Spectra	105
6.5.1	Rigid Diatomic and Linear Molecules	105
6.5.2	Prolate and Oblate Symmetric Top Molecules	108
6.5.3	Asymmetric Top Molecules	110
6.6	Rot-Vibrational Transitions	110
	References	113
	Problems	113
7	Atomic Structure: The Hydrogen Atom	115
7.1	The Hydrogen Atom Schrödinger Equation	116
7.2	Solutions of the Hydrogen Atom Schrödinger Equation	118
7.3	Dipole Allowed Transitions for the Hydrogen Atom	124
7.4	Discussion of the Hydrogen Atom Results	124
7.5	Electron Spin	126
7.6	Spatial Quantization of Angular Momentum	129
	References	130
	Problems	130
8	Nuclear Magnetic Resonance (NMR) Spectroscopy	131
8.1	General Remarks	131
8.2	Review of Electron Angular Momentum and Spin Angular Momentum	132
8.3	Nuclear Spin	134
8.4	Selection Rules, Transition Energies, Magnetization, and Spin State Population	137
8.4.1	Electric Dipole Selection Rules for a One-Spin Nuclear System	137
8.4.2	Transition Energies	138
8.4.3	Magnetization	138
8.4.4	Spin State Population Analysis	139
8.5	Chemical Shift	140
8.6	Multispin Systems	141
8.6.1	Noninteracting Spins	141
8.6.2	Interacting Spins: Spin-Spin Coupling	143

- 8.6.3 Interaction of Multiple Spins 144
- 8.7 Pulse FT NMR Spectroscopy 146
 - 8.7.1 General Comments 146
 - 8.7.2 Description of NMR Event in Terms of the “Net Magnetization” 147
 - References 148
 - Problems 149

- 9 Atomic Structure: Multi-electron Systems 151**
 - 9.1 The Two-electron Hamiltonian, Shielding, and Effective Nuclear Charge 151
 - 9.2 The Pauli Principle 152
 - 9.3 The Aufbau Principle 153
 - 9.4 Periodic Properties of Elements 155
 - 9.5 Atomic Energy Levels 156
 - 9.5.1 Good and Bad Quantum Numbers and Term Symbols 156
 - 9.5.2 Selection Rules for Transitions in Atomic Species 159
 - 9.6 Atomic Spectroscopy 160
 - 9.7 Atomic Spectroscopy in Analytical Chemistry 161
 - References 162
 - Problems 162

- 10 Electronic States and Spectroscopy of Polyatomic Molecules 163**
 - 10.1 Molecular Orbitals and Chemical Bonding in the H_2^+ Molecular Ion 163
 - 10.2 Molecular Orbital Theory for Homonuclear Diatomic Molecules 168
 - 10.3 Term Symbols and Selection Rules for Homonuclear Diatomic Molecules 171
 - 10.4 Electronic Spectra of Diatomic Molecules 173
 - 10.4.1 The Vibronic Absorption Spectrum of Oxygen 173
 - 10.4.2 Vibronic Transitions and the Franck–Condon Principle 175
 - 10.5 Qualitative Description of Electronic Spectra of Polyatomic Molecules 177
 - 10.5.1 Selection Rules for Electronic Transitions 178
 - 10.5.2 Common Electronic Chromophores 178
 - 10.5.2.1 Carbonyl Chromophore 178
 - 10.5.2.2 Olefins 179
 - 10.5.2.3 Benzene 180
 - 10.5.2.4 Other Aromatic Molecules 180
 - 10.5.2.5 Transition Metals in the Electrostatic Field of Ligands 181
 - 10.6 Fluorescence Spectroscopy 181
 - 10.6.1 Fluorescence Energy Level (Jablonski) Diagram 182
 - 10.6.2 Intersystem Crossing and Phosphorescence 183
 - 10.6.3 Two-Photon Fluorescence 183

- 10.6.4 Summary of Mechanisms for Raman, Resonance Raman, and Fluorescence Spectroscopies 184
- 10.7 Optical Activity: Electronic Circular Dichroism and Optical Rotation 185
 - 10.7.1 Circularly Polarized Light and Chirality 185
 - 10.7.2 Manifestation of Optical Activity: Optical Rotation, Optical Rotatory Dispersion and Circular Dichroism 187
 - 10.7.3 Optical Activity of Asymmetric Molecules: The Magnetic Transition Moment 188
 - 10.7.4 Optical Activity of Dissymmetric Molecules: Transition Coupling and the Exciton Model 191
 - 10.7.5 Vibrational Optical Activity 192
- References 193
- Problems 194

11 Group Theory and Symmetry 199

- 11.1 Symmetry Operations and Symmetry Groups 200
- 11.2 Group Representations 204
- 11.3 Symmetry Representations of Molecular Vibrations 211
- 11.4 Symmetry-Based Selection Rules for Dipole-Allowed Processes 214
- 11.5 Selection Rules for Raman Scattering 217
- 11.6 Character Tables of a Few Common Point Groups 218
 - References 219
 - Problems 219

Appendix 1 Constants and Conversion Factors 221

Appendix 2 Approximative Methods: Variation and Perturbation Theory 223

- A2.1 General Remarks 223
- A2.2 Variation Method 224
- A2.3 Time-independent Perturbation Theory for Nondegenerate Systems 225
- A2.4 Detailed Example of Time-independent Perturbation: The Particle in a Box with a Sloped Potential Function 226
- A2.5 Time-dependent Perturbation of Molecular Systems by Electromagnetic Radiation 230
 - Reference 231

Appendix 3 Nonlinear Spectroscopic Techniques 233

- A3.1 General Formulation of Nonlinear Effects 233
- A3.2 Noncoherent Nonlinear Effects: Hyper-Raman Spectroscopy 234
- A3.3 Coherent Nonlinear Effects 235
 - A3.3.1 Second Harmonic Generation 236
 - A3.3.2 Coherent Anti-Stokes Raman Scattering (CARS) 237

A3.3.3 Stimulated Raman Scattering (SRS) and Femtosecond Stimulated Raman Scattering (FSRS) 240

A3.4 Epilogue 242
References 242

Appendix 4 Fourier Transform (FT) Methodology 243

A4.1 Introduction to Fourier Transform Spectroscopy 243

A4.2 Data Representation in Different Domains 244

A4.3 Fourier Series 244

A4.4 Fourier Transform 247

A4.5 Discrete and Fast Fourier Transform Algorithms 248

A4.6 FT Implementation in EXCEL or MATLAB 249
References 251

Appendix 5 Description of Spin Wavefunctions by Pauli Spin Matrices 253

A5.1 The Formulation of Spin Eigenfunctions α and β as Vectors 254

A5.2 Form of the Pauli Spin Matrices 255

A5.3 Eigenvalues of the Spin Matrices 256
Reference 257

Index 259