

Contents

Preface to the Second Edition xiii
Preface to the First Edition xv

1 Review of the Quantum Mechanical Background 1

- 1 State Vector Notation 1
- 2 Wave Function and Matrix Representations 4
- 3 Basis Functions for the Energy 7
- 4 Perturbation Theory of Energy Corrections 8
- 5 Time-Dependent Perturbations: Absorption and Emission of Electromagnetic Radiation 14
- 6 The Electric Dipole Interaction 19
- 7 Optical Constants of Atoms and Molecules 25
- 8 Homogeneous and Inhomogeneous Line Shapes 31
- 9 The Road Ahead 36
- Problems 36
- References 38

2 Atomic Spectra 39

- 1 The Hydrogen Atom—a One-Electron System 39
- 2 Two- and Many-Electron Atoms 40
- 3 Spin-Orbit Coupling in a One-Electron Atom 48
- 4 Vector Precession Diagrams: LS and jj Coupling 51
- 5 Examples of Energy Levels and Spectra 52
- 6 Nuclear Hyperfine Interactions in Atoms 60
- 7 The Stark Effect 64
- 8 The Zeeman Effect 67
- Problems 74
- References 75

3 Diatomic Molecules 77

- 1 The Born-Oppenheimer Approximation 77
- 2 Electronic Energy Levels for Molecules with Stationary Nuclei 79
- 3 Determination of Molecular States from Separated Atom States 85

4	Selection Rules for Electronic Transitions	87
5	Simple Molecular Orbital Theory and Molecular Potential Curves	92
	Problems	111
	References	112
4	Rotation and Vibration of Diatomic Molecules	113
1	Rigid Rotor Hamiltonian, Eigenfunctions, and Spectra	113
2	Harmonic Oscillator Hamiltonian, Eigenfunctions, and Spectra	120
3	Combination of Rotational and Vibrational Motions	124
4	The Nonrigid Rotor: Centrifugal Distortions	127
5	The Anharmonic Oscillator	128
6	Rotational and Vibrational Raman Spectra	134
	Problems	142
	References	144
5	Electronic Spectra of Diatomic Molecules	145
1	“Ro-vibronic” Energy Levels	145
2	The Franck-Condon Principle	145
3	Vibrational Band Analysis	150
4	Rotational Fine Structure of Bands	157
5	Angular Momentum Coupling Cases	161
6	Selection Rules in Electronic Transitions	167
7	Perturbations and Predissociation	171
8	Zeeman Effect in Molecules	179
9	Stark Effect in Molecules	183
10	Magnetooptic Rotation (Faraday Effect) in Molecules	184
11	Photofragment Spectroscopy of Continuum States	187
	Problems	192
	References	196
6	Rudimentary Group Theory	198
1	Symmetry Elements E , C_n , σ , and i	199
2	Point Groups for Molecules	202
3	Group Properties and Multiplication Tables	202

4 Representations and Character Theory	205
5 Direct Products of Representations	207
6 Selected Applications	209
Problems	211
References	212
7 Rotational Spectra of Polyatomic Molecules	214
1 Rigid Body Hamiltonian, Eigenfunctions, and Spectra	214
2 Microwave Spectroscopy of Rotational Levels	219
3 Additional Topics in Rotational Spectroscopy	223
Problems	226
References	228
8 Vibrational Spectra of Polyatomic Molecules	230
1 Lagrangian Mechanics	230
2 Normal Coordinate Analysis of a Linear Triatomic Molecule	232
3 "FG" Matrix Method and Symmetry of Normal Vibrations	241
4 Selection Rules for Vibrational Transitions	248
5 Rotational Structure of Vibrational Bands	252
Problems	256
References	261
9 Electronic Spectra of Polyatomic Molecules	262
1 Energy Levels and Spectra	262
2 Electronic States of Polyatomic Molecules: Walsh's Rules	263
3 Electronic Spectroscopy of Formaldehyde	268
4 The 2,600-Å System of Benzene	272
5 Molecular Photoelectron Spectroscopy	280
6 Radiationless Transitions	285
Problems	290
References	292
10 From Molecular Beams to Masers to Lasers	293
1 Hyperfine Structure and Line Width	293
2 Optical Pumping	296

3	Optical Level-Crossing Spectroscopy	300
4	Molecular Beam Methods	301
5	Supersonically Cooled Molecular Beam Spectroscopy	307
6	Molecular Beam Masers	308
7	Optical Masers	311
	References	325

11 Optical Resonance Spectroscopy 327

1	The Idealized Two-Level System	327
2	The Rabi Solution for a Two-Level System	329
3	Saturation in a Two-Level System	334
4	Feynman-Vernon-Hellwarth Theorem	337
5	Optical Bloch Equations	340
6	Magnetic Resonance Analogues of Coherent Optical Spectroscopy	347
	Problems	353
	References	355

12 Coherent Transient Spectroscopy 356

1	Transient Nutation	356
2	Photon Echo	364
3	Fourier Transform Spectroscopy	373
4	Self-Induced Transparency	374
5	Saturation Revisited	388
6	Saturated Absorption Spectroscopy: The "Lamb Dip"	391
7	Double-Resonance Spectroscopy	394
	Problems	402
	References	402

13 Multiple-Photon Spectroscopy 404

1	Nonlinear Polarizability and Second-Harmonic Generation	404
2	Optical Parametric Oscillation	413
3	Multiphoton Spectra of Molecules	415
4	Infrared Multiple-Photon Absorption	426

5	Resonant Multiphoton Ionization	429
6	Stimulated Raman Scattering	429
7	Coherent Anti-Stokes Raman Scattering	434
8	Production and Detection of Picosecond Light Pulses	438
	Problem	442
	References	443
14	Spectroscopy beyond Molecular Constants	444
1	Molecules at High Excitation Levels	444
2	Spectra from Molecular Dynamics	448
	References	453
Appendix A	Direct Product Tables	454
Appendix B	Lagrangian Mechanics	459
Appendix C	Density Matrix Methods	463
Appendix D	Dipole Correlation and Spectral Density Functions	471
Appendix E	The Literature of Spectroscopy	475
Appendix F	IUPAC/IUPAP Energy Conversion Constants (Revised 1973)	483
Index		485