

# Contents

<b>1</b>	<b>The Energy and Geometrical Structure of Molecules</b>	<b>1</b>
1.1	Absorption and Emission of Light by Dye Molecules	2
1.2	Infrared Radiation from the Earth	7
1.3	Microwaves Arriving from Outer Space	12
1.4	The Hierarchical Structure of Molecular Energy Levels	13
1.5	The Diffraction of Electron Beams and Molecular Structures	15
1.6	Methods of Molecular Structure Determination	18
<b>2</b>	<b>Vibrating Molecules</b>	<b>21</b>
2.1	How to Describe Vibrating Molecules	22
2.2	Molecular Vibration in Quantum Theory	26
2.2.1	Quantizing the Harmonic Oscillator	27
2.2.2	The Energy Level of the Harmonic Oscillator	27
2.2.3	Determination of Potentials by Infrared Absorption	32
2.2.4	Eigenfunctions of Harmonic Oscillators	34
2.2.5	The Hermite Recurrence Formula	36
2.2.6	The Eigenfunction System of a Harmonic Oscillator	38
2.3	The Harmonic Oscillator and Its Applications	40
2.3.1	Hermitian Operators and the Bracket Notation	41
2.3.2	Calculations of Expectation Values Using Eigenfunctions	45
2.3.3	Matrix Elements of $x$ and Selection Rules for Infrared Absorptions	47
2.3.4	Overtone Absorption	49
2.3.5	Matrix Elements of $x^2$ and the Expectation Value of the Potential Energy	52
2.3.6	Creation and Annihilation Operators	57
2.3.7	Evaluation of Perturbation Energy	61
2.3.8	Morse Potential	63
2.4	The Inversion Motion of Ammonia Molecules	68
2.4.1	The Infrared Absorption Spectrum	69
2.4.2	Parity of Wave Functions	71

2.4.3	Energy Level Splitting and Potential Barriers . . . . .	72
2.4.4	The Geometrical Structure of Ammonia and the Period of the Inversion Motion . . . . .	74
2.5	How to Treat the Vibration of Polyatomic Molecules . . . . .	77
2.5.1	Degrees of Freedom of Molecular Motions . . . . .	78
2.5.2	What Are Normal Modes? . . . . .	80
2.5.3	Normal Modes and Matrix Diagonalization . . . . .	87
2.5.4	The Vibrational Hamiltonian Represented by Normal Coordinates . . . . .	89
2.5.5	The Quantum Theory of Normal Mode Vibrations . . . . .	93
2.5.6	Normal Modes of a Polyatomic Molecule Composed of $n$ Atoms . . . . .	96
2.5.7	Representation of Normal Modes in Terms of Internal Coordinates . . . . .	101
2.5.8	Analysis of Normal Modes by the $GF$ Matrix Method . . .	105
2.5.9	Anharmonic Expansion of Potentials by Dimensionless Coordinates . . . . .	112
<b>3</b>	<b>Rotating Molecules . . . . .</b>	<b>119</b>
3.1	Molecular Rotation and Molecular Structure . . . . .	120
3.1.1	Microwave Spectroscopy . . . . .	120
3.1.2	The Quantum Theory of Molecular Rotation (Diatomic Molecules) . . . . .	121
3.1.3	Rotational Energy Levels of Linear Molecules and Structure Determination by Means of Isotope Substitution .	125
3.2	The Angular Momentum of Molecular Rotation . . . . .	128
3.2.1	Angular Momentum Operators . . . . .	129
3.2.2	Commutation Relations of Angular Momentum Operators .	130
3.2.3	Raising and Lowering Operators . . . . .	132
3.2.4	Eigenvalues of Angular Momentum Operators . . . . .	134
3.2.5	Eigenfunctions of Angular Momentum Operators . . . . .	136
3.3	Molecular Rotation from the Point of View of Classical Mechanics	141
3.3.1	Molecular Rotation and Euler Angles . . . . .	141
3.3.2	Matrix Representation of the Coordinate Rotation . . . . .	144
3.3.3	The Kinetic Energy and Angular Momentum of the Rotation of a Molecule . . . . .	146
3.3.4	Classification of Molecules by Values of the Moments of Inertia . . . . .	149
3.4	Molecular Rotation from the Point of View of Quantum Mechanics	152
3.4.1	Quantum Mechanical Hamiltonians of Molecular Rotations	152
3.4.2	Angular Momenta of Overall Rotations in Molecule-Fixed Coordinate Systems . . . . .	157
3.4.3	Energy Level Diagrams of Prolate and Oblate Top Molecules . . . . .	161

3.4.4	Energy Levels of Diatomic and Linear Molecules . . . . .	163
3.4.5	Energy Levels of Spherical Top Molecules . . . . .	164
3.4.6	Energy Levels of Asymmetric Top Molecules . . . . .	164
3.4.7	Calculating the Rotational Energy Levels of an Asymmetric Top Molecule for $J = 0$ and $J = 1$ . . . . .	166
3.4.8	Wang's Transformation . . . . .	170
3.4.9	Symmetry in the Rotational Levels of an Asymmetric Top Molecule . . . . .	173
3.5	Determination of Molecular Structures Based on Rotational Spectra	176
3.5.1	Molecular Structures of Symmetric Top Molecules . . . . .	176
3.5.2	Determining the Rotational Constants of Asymmetric Top Molecules . . . . .	179
3.5.3	Molecular Structures of Asymmetric Top Molecules . . . . .	183
3.6	Rotating and Vibrating Molecules . . . . .	188
3.6.1	Rotational Structures of Vibrational Transitions . . . . .	188
3.6.2	Rotational Structures of Electronic Transitions . . . . .	193
<b>4</b>	<b>Scattering Electrons</b> . . . . .	197
4.1	Scattering Electron Waves . . . . .	198
4.2	Electron Scattering by Atoms . . . . .	204
4.2.1	The Schrödinger Equation for Scattering . . . . .	204
4.2.2	Representation of the Scattering Amplitude by Use of the Born Approximation . . . . .	208
4.2.3	Electron Scattering by Atoms . . . . .	210
4.3	Electron Scattering by Molecules . . . . .	212
4.3.1	The Scattering Amplitude of Electron Scattering by a Molecule . . . . .	212
4.3.2	The Scattering and Interference of an Electron Beam by a Diatomic Molecule . . . . .	214
4.4	Phase Shift of the Scattering Electron Wave . . . . .	218
4.4.1	Partial-Wave Expansions of Scattered Waves . . . . .	218
4.4.2	The Behavior of Partial Waves in the Asymptotic Region . . . . .	222
4.4.3	The Partial Wave Expansion of Plane Waves . . . . .	224
4.4.4	The Partial Wave Expansion of Scattering Amplitudes . . . . .	226
4.4.5	Phase Shift in Electron Diffraction . . . . .	230
4.5	The Effect of Molecular Vibration . . . . .	232
4.5.1	Mean Square Amplitudes . . . . .	232
4.5.2	The $r_a$ Structure and the $r_g$ Structure . . . . .	238
4.6	Electron Beam Scattering by Polyatomic Molecules . . . . .	241
4.6.1	Molecular Scattering Curves and Radial Distribution Curves . . . . .	241
4.6.2	From a Molecular Scattering Curve to the Molecular Structure . . . . .	244
4.6.3	The Shrinkage Effect . . . . .	246

4.6.4 The  $r_{\alpha}^0$  Structure . . . . . 250

4.6.5 An Example of Structure Determination . . . . . 255

**For Further Reading** . . . . . 259

Figure Sources . . . . . 260

**Subject Index** . . . . . 261

**Formula Index** . . . . . 267