

# Contents

---

<b>Preface</b>	<b>xi</b>
<b>PART 1</b>	
<b>Spectroscopy and the quantum states of molecules</b>	<b>1</b>
<b>1 Molecular spectroscopy</b>	<b>3</b>
1.1 Molecular spectra	3
1.2 The energies of molecules in the gas phase	6
1.3 The positions of spectral lines	9
1.4 The intensities of spectral lines	11
1.5 The shapes of spectral lines	12
1.6 Raman spectra	14
1.7 Problems	15
<b>2 Quantum mechanics</b>	<b>17</b>
2.1 The Schrödinger equation	17
2.2 The postulates of quantum mechanics	18
2.2.1 Operators and eigenfunctions	19
2.3 Diagonalizing the Hamiltonian matrix	21
2.4 The molecular Schrödinger equation	26
2.5 The separation of translational energy	26
2.5.1 The translational Schrödinger equation	29
2.6 The rovibronic Schrödinger equation	32
2.7 The angular momentum operator	34
2.8 The dipole moment operator and line strengths	35
2.9 Matrices and matrix algebra	37
2.10 Problems	40
<b>3 Electronic states</b>	<b>42</b>
3.1 The Born–Oppenheimer approximation	42
3.2 Spin and the Pauli exclusion principle	46
3.3 Electronic wavefunctions and energies	48
3.3.1 The Slater determinant	49

3.3.2	The Hartree–Fock approximation and molecular orbitals	50
3.3.3	MOs as linear combinations of atomic orbitals	52
3.3.4	Configuration interaction	52
3.4	Molecular orbital theory	53
3.4.1	Bonding and antibonding orbitals	54
3.4.2	Hybridization	57
3.4.3	The Hückel approximation and benzene	61
3.4.4	Polyene chain molecules	62
3.5	Problems	65
<b>4</b>	<b>Vibrational states</b>	<b>68</b>
4.1	Space-fixed and molecule-fixed axes	68
4.2	The vibrational Hamiltonian	70
4.3	Vibrational wavefunctions and energies	72
4.4	Anharmonicity	78
4.5	Tunnelling	81
4.6	Problems	87
<b>5</b>	<b>Rotational states</b>	<b>89</b>
5.1	The Euler angles	89
5.2	The principal moments of inertia	90
5.3	The rigid-rotor Hamiltonian	92
5.3.1	Symmetric top molecules	92
5.3.2	Linear molecules	94
5.3.3	Spherical top molecules	95
5.3.4	Asymmetric top molecules	95
5.4	Rovibronic wavefunctions	96
5.5	The Hamiltonian and wavefunctions in detail	97
5.5.1	The derivation of the rigid-rotor Hamiltonian	97
5.5.2	The Euler angles and angular momentum	99
5.5.3	The symmetric top wavefunctions	101
5.5.4	The asymmetric top wavefunctions and energies	101
5.6	Problems	107
<b>PART 2</b>		
<b>Symmetry and symmetry groups</b>		<b>111</b>
<b>6</b>	<b>Geometrical symmetry</b>	<b>113</b>
6.1	Geometrical symmetry operations	113
6.2	Geometrical symmetry groups: Point groups	117
6.3	The point group symmetry of molecules	122
6.4	Problems	125

3.3.2	The Hartree–Fock approximation and molecular orbitals	50
3.3.3	MOs as linear combinations of atomic orbitals	52
3.3.4	Configuration interaction	52
3.4	Molecular orbital theory	53
3.4.1	Bonding and antibonding orbitals	54
3.4.2	Hybridization	57
3.4.3	The Hückel approximation and benzene	61
3.4.4	Polyene chain molecules	62
3.5	Problems	65
<b>4</b>	<b>Vibrational states</b>	<b>68</b>
4.1	Space-fixed and molecule-fixed axes	68
4.2	The vibrational Hamiltonian	70
4.3	Vibrational wavefunctions and energies	72
4.4	Anharmonicity	78
4.5	Tunnelling	81
4.6	Problems	87
<b>5</b>	<b>Rotational states</b>	<b>89</b>
5.1	The Euler angles	89
5.2	The principal moments of inertia	90
5.3	The rigid-rotor Hamiltonian	92
5.3.1	Symmetric top molecules	92
5.3.2	Linear molecules	94
5.3.3	Spherical top molecules	95
5.3.4	Asymmetric top molecules	95
5.4	Rovibronic wavefunctions	96
5.5	The Hamiltonian and wavefunctions in detail	97
5.5.1	The derivation of the rigid-rotor Hamiltonian	97
5.5.2	The Euler angles and angular momentum	99
5.5.3	The symmetric top wavefunctions	101
5.5.4	The asymmetric top wavefunctions and energies	101
5.6	Problems	107
<b>PART 2</b>		
<b>Symmetry and symmetry groups</b>		<b>111</b>
<b>6</b>	<b>Geometrical symmetry</b>	<b>113</b>
6.1	Geometrical symmetry operations	113
6.2	Geometrical symmetry groups: Point groups	117
6.3	The point group symmetry of molecules	122
6.4	Problems	125

<b>7</b>	<b>The symmetry of the Hamiltonian</b>	<b>126</b>
7.1	Hamiltonian symmetry operations	126
7.2	Nuclear permutations and the inversion $E^*$	127
7.3	Symmetry labels	132
7.4	Symmetry groups	133
7.5	The vanishing integral rule	136
7.5.1	Proof of the vanishing integral rule for the water molecule	138
7.6	Selection rules	139
7.7	The rovibronic symmetry label $J$	140
7.8	Diagonalizing the Hamiltonian matrix using symmetry	141
7.9	The Stark effect	142
7.10	The symmetry of $H_3^+$	143
7.11	Group theory	149
7.12	Problems	156
<b>8</b>	<b>The symmetry groups of rigid molecules</b>	<b>158</b>
8.1	The CNPI group	158
8.2	The molecular symmetry (MS) group	162
8.3	The MS group and the point group	164
8.3.1	The $H_2O$ molecule	164
8.3.2	The $H_3^+$ molecule	168
8.3.3	General rules for rigid molecule symmetry groups	171
8.3.4	Linear rigid molecules	172
8.3.5	The ethylene molecule $C_2H_4$	173
8.4	Problems	175
<b>PART 3</b>		
	<b>Applications of symmetry</b>	<b>177</b>
<b>9</b>	<b>Nuclear spin, statistical weights and hyperfine structure</b>	<b>179</b>
9.1	The fifth postulate of quantum mechanics	179
9.2	Statistical weights	180
9.3	Missing levels	184
9.3.1	$CO_2$	184
9.3.2	$H_3^+$	185
9.4	Statistical weights for $CH_3F$	186
9.5	Nuclear spin hyperfine structure	187
9.6	Problems	191
<b>10</b>	<b>The symmetry of electronic wavefunctions</b>	<b>193</b>
10.1	The water molecule	193
10.2	The benzene molecule	197
10.3	The butadiene molecule	205
10.4	Conservation of orbital symmetry	207
10.5	The non-crossing rule	217

10.6	The $C_6$ and $\sigma_v$ operations for benzene	218
10.7	Problems	220
<b>11</b>	<b>The symmetry of rotation–vibration wavefunctions</b>	<b>222</b>
11.1	The transformation properties of the Euler angles	222
11.2	The symmetry of rotational wavefunctions	224
11.2.1	$H_3^+$	226
11.2.2	$H_2O$	229
11.3	The symmetry of normal coordinates	230
11.3.1	$H_2O$	232
11.3.2	Benzene	233
11.4	The symmetry of vibrational wavefunctions	236
11.4.1	$H_2O$	236
11.4.2	$H_3^+$	236
11.5	Rotation–vibration coupling	238
11.6	Problems	244
<b>12</b>	<b>Symmetry selection rules for optical transitions</b>	<b>245</b>
12.1	Forbidden and allowed transitions	245
12.2	Zero-order transition moment integrals	247
12.3	Transitions within an electronic state	249
12.3.1	Vibrational transition moments and Hönl–London factors	249
12.3.2	The rotational spectrum of the CO molecule	255
12.3.3	Parallel and perpendicular bands of $CH_3F$	255
12.3.4	Rotation–vibration interaction	261
12.4	Transitions between electronic states	264
12.5	Raman transitions	266
12.6	Problems	272
<b>13</b>	<b>The symmetry groups of non-rigid molecules</b>	<b>274</b>
13.1	The MS group of a non-rigid molecule	274
13.2	The ammonia molecule	275
13.3	Torsionally tunnelling ethylene	278
13.4	Intensity alternations for HSSH and DSSD	280
13.5	The water dimer and the water trimer	282
13.5.1	Water dimer	282
13.5.2	Water trimer	287
13.6	Ethylene and its Raman spectrum	288
13.7	Problems	290

<b>PART 4</b>	
<b>Other symmetries and symmetry violation</b>	<b>291</b>
<b>14 Other symmetries</b>	<b>293</b>
14.1 The fourth postulate of quantum mechanics	293
14.2 Conservation laws	294
14.3 Electron permutation symmetry	295
14.4 Translational symmetry	296
14.5 Rotational symmetry	301
14.6 Charge conjugation	304
14.7 Parity	305
14.8 Time reversal	308
<b>15 Symmetry violation</b>	<b>310</b>
15.1 The electroweak Hamiltonian	310
15.2 Parity (P) violation	311
15.3 CP violation	313
15.4 T violation	315
15.5 Testing for CPT violation	316
15.6 Testing for permutation symmetry violation	316
<b>A Answers to selected problems</b>	<b>320</b>
<b>B Character tables</b>	<b>331</b>
<b>C Books for further reading</b>	<b>352</b>
<b>Index</b>	<b>354</b>

Throughout the text, we introduce 'shadow boxes' such as this to focus attention on a particularly significant statement.

At the end of each chapter in parts 1, 2 and 3, we have included problems involving the application of the ideas developed in the chapter. The answers to selected problems are given in appendix A at the end of the book; the problems