

Contents

Preface

v

1 Preliminary Survey

1	The Interaction Between Light and Matter	1
2	The Photoelectric Effect	2
3	Photoelectron Spectroscopy	3
4	Rydberg Series	5
5	Angular Momentum	9
6	Electronic Orbitals of Hydrogen	12
7	Transition Probability	14
8	Polyelectronic Atoms	16
9	Electron Spin	17
10	Atomic States	18
11	Electron–Electron Repulsion in Atoms	19
12	Slater Orbitals	22
13	The Variation Method	24
14	Self-Consistent Fields	25
15	Atomic Relaxation Energy	28
16	Problems	30

2 Molecular Orbitals

17	Hydrides Isoelectronic with Neon	31
18	Molecular Orbitals	33
19	Examples of Molecular Orbital Calculations	36
20	Hydrogen Fluoride	37
21	Water	42
22	Ammonia	45

3 Vibrational Structure

23	The Nuclear Motion of Molecules	50
24	Simple Harmonic Motion	52
25	Potential Energy and Bond Length	54
26	The Franck–Condon Factor	55
27	Vibrational Interval	57
28	Vibrational Structure of Hydrogen Halide Spectra	58
29	Hydrogen Cyanide	62
30	Linear Conjugated Molecules	64
31	Changes in Bond Length and Angle on Ionisation	67
32	Vibrational Inversion	69

33	The Jahn-Teller Effect	72
34	Jahn-Teller-Active Vibrations	75
35	The Jahn-Teller Effect in Cyclopropane	76
4	Spin–Orbit Coupling	
36	The Spin–Orbit Coupling Constant	81
37	The Spin–Orbit Effect in Carbon and its Congeners	84
38	Double Groups	87
39	The Boron Trihalides	89
40	The Ham Effect	91
41	The Halides of Methane	93
42	Inner Shells	95
43	The Spin–Orbit Effect in O ₂ and its Congeners	96
5	The Angular Distribution of Photoelectrons	
44	The Asymmetry Parameter, β	101
45	Angular Distribution in the Noble Gases	103
46	Angular Distribution in O ₂	105
6	Diatomic Molecules	
47	Carbon Monoxide	108
48	The Nitrogen Molecule	109
49	The Oxygen Molecule	111
50	Nitric Oxide, NO	113
51	The Halogens	114
7	Molecules Related to Ethylene	
52	Acetylene, Ethylene and Ethane	117
53	Diborane, B ₂ H ₆	120
54	Ethylene Glycol, (CH ₂ OH) ₂	121
55	Butadiene and Hexatriene	123
56	Inner Valence Orbitals of the Alkanes	125
57	Benzene	127
58	Pyridine and Pyrazine	130
8	Molecules Related to Xenon Difluoride	
59	Xenon Difluoride, XeF ₂	134
60	Carbon Dioxide and its Derivatives	138
61	Nitrous Oxide, N ₂ O, and its Derivatives	139
62	Fluorine and Chlorine Monoxides	141
9	Tetrahedral Molecules	
63	Tetrahedrally Disposed p Orbitals	144
64	Molecular Orbitals Formed by Tetrahedrally Disposed p Orbitals	146
65	Energies of Tetrahedral Orbitals	147
66	Tetraphosphorus, P ₄	149

67	Tetraboron tetrachloride, B_4Cl_4	151
68	Group IV Tetrahalides	153
69	Group IV Tetramethyls	155
70	Transition Metal Chlorides	156
71	Ruthenium and Osmium Tetroxides	159
72	Nickel Tetracarbonyl	160
73	Trifluorophosphine Complexes, $Ni(PF_3)_4$ and $Pt(PF_3)_4$	162
10	Octahedral Molecules	
74	Octahedrally Disposed p Orbitals	163
75	Hexafluorides	165
76	Hexacarbonyls	168
77	Hexatrifluorophosphine Complexes	169
Appendix 1	Physical Constants	173
Appendix 2	The Greek Alphabet	174
Appendix 3	Valence Orbital Ionisation Energies	175
Appendix 4	Symmetric and Antisymmetric Wavefunctions	177
Appendix 5	The Raising and Lowering Operators	179
Appendix 6	Spin–Orbit Interaction Between $\Psi(^3\Sigma_g^-)$ and $\Psi(^1\Sigma_g^+)$ of O_2	181
References		183
Index		187