

Contents

<i>Preface</i>	xi
<i>Acknowledgments</i>	xiii
1. How Science Deals with Complex Problems	1
1.1 Introduction: Levels in Science	2
1.2 What are Molecules Made Of?	4
1.3 Interactions Between Atoms	6
1.4 The Simplest examples: H ₂ and LiH	8
1.4.1 The Hydrogen Molecule	8
1.4.2 The Lithium Hydride Molecule	10
1.4.2.1 What About the Other Li Electrons?	14
1.4.2.2 What About the Nuclear Repulsions?	14
1.4.3 Comments on H ₂ and LiH	15
1.5 How to Proceed?	16
Appendix A How to Interpret 3D Contours	19
A.1 Thinking in 3D	19
A.2 The Electron Distribution of the Lithium 2s Electron	22
A.2.1 How does this relate to the Text-Book “Orbitals” . .	25
A.2.2 What if the Distribution is not Spherical?	25
Appendix B <i>Must</i> We Use Quantum Theory?	29
B.1 Connections to Laws of Nature	29
B.2 Stable Molecules	30
B.3 The Equipartition of Energy	31

B.4 Quantum Summary	33
2. What We Know about Atoms and Molecules	35
2.1 Atomic Electronic Structure	35
2.1.1 The Hydrogen Atom	36
2.1.2 Many-electron Atoms	38
2.1.3 The Pauli Principle	40
2.1.3.1 Statement of the Pauli Principle	40
2.1.4 Current Summary for Atoms	41
2.2 Empirical Chemistry	41
Appendix C The Interpretation of Orbitals	45
C.1 What is an Orbital?	45
C.2 Orbitals: Atomic and Molecular	48
3. A Strategy for Electronic Structure	49
3.1 Review	49
3.2 Lithium Hydride Again	52
3.2.1 Polarisation and Hybrid AOs	53
3.2.2 Molecular Orbitals	55
3.2.2.1 Quick Summary	59
Appendix D Is Hybridisation a Real Process?	61
4. The Pauli Principle and Orbitals	63
4.1 A Difficulty with Helium	64
4.2 When are Orbitals Mutually Exclusive?	66
4.3 Does This Work for AOs?	69
4.4 The Helium Molecule—Again	72
4.5 The Rôle of Atomic Orbitals in Valence Theory	75
4.6 Current Summary for LiH and “He ₂ ”	76
5. A Model Polyatomic: Methane	79
5.1 The Methane Molecule: CH ₄	79
5.2 The Electronic Structure of Methane	81
5.3 The Shape of the Methane Molecule	83
5.4 What About the Pauli Principle?	84
5.4.1 Preliminary Summary for Methane	85

5.5	The Chemist's Description of Methane	86
5.5.1	How to Use these Structures: the Valence Bond Method	88
5.6	Summary for Methane	91
6.	Lone Pairs of Electrons	93
6.1	Why are Not All Electrons Involved in Bonding?	93
6.2	What is a Lone Pair?	96
6.2.1	The Ammonia Molecule	97
6.2.2	The Water Molecule	101
6.3	The Shapes of Simple Molecules	102
6.3.1	The Water Molecule—Again	103
6.4	“Reactions” of Lone pairs	105
6.5	A Working Summary	106
7.	Organic Molecules with Multiple Bonds	107
7.1	Double and Triple Bonds	108
7.2	The Possibilities	110
7.3	Ethene and Methanal	112
7.4	The Double Bond in Ethene and Methanal	113
7.4.1	Sigma (σ) and Pi (π) Notation in Planar Molecules .	115
7.5	The σ and π Orbitals in C_2H_4 and CH_2O	117
7.5.1	Ethene Contours	117
7.5.2	Methanal Contours	120
7.5.3	Relative Energies of the Two Bonds	122
7.6	Reactivity of a Double Bond	123
7.7	Multiple Bonds in General	124
8.	Molecular Symmetry	125
8.1	The Question of Symmetry	125
8.2	Symmetry: Generalisation	128
8.3	Case Studies: H_2O and Benzene	129
8.3.1	The H_2O Molecule	129
8.3.2	The Benzene σ system	132
8.4	Bond MOs and Symmetry MOs	135
8.5	A Cautionary Note	136
9.	Diatomics with Multiple Bonds	139
9.1	Motivation	140

9.2	The Nitrogen Molecule: N ₂	140
9.2.1	Energies of the N ₂ MOs	143
9.2.2	Symmetry and the N ₂ Molecule	146
9.3	The Carbon Monoxide Molecule: CO	148
9.4	Other Homonuclear Diatomics	150
9.4.1	The Oxygen Molecule: O ₂	151
9.5	Lessons from Diatomics	153
10.	Dative Bonds	155
10.1	Introduction: Familiar Reactions	155
10.1.1	“Solvation”	156
10.1.2	A Reactive Lone Pair: the CO Molecule	159
10.1.3	CO and Transition-metal Atoms	161
10.2	The Dative Bond: Summary	161
11.	Delocalised Electronic Substructures: Aromaticity	163
11.1	The Benzene Molecule	163
11.2	Delocalised Electrons	167
11.3	Environment-insensitive π Substructures?	172
11.4	Nomenclature and Summary	175
12.	Organic and Inorganic Chemistry	177
12.1	Commentary on Results	177
12.2	Nitric Acid and Related Molecules	178
12.2.1	The Nitrate Ion NO ₃ ⁻	183
12.3	Carbonic acid and Carbonates	185
12.4	Sulphuric Acid and Sulphates	185
13.	Further Down the Periodic Table	187
13.1	The Effect of Increasing Atomic Number	188
13.2	The Possible Demise of Lone Pairs	189
13.3	A Particular Case: Sulphur	190
13.4	The General Case: “Hypervalence”	192
13.4.1	Single or double bonds?	194
13.4.2	The Steric Effect	195
13.5	How to Describe These Bonds?	196
13.5.1	A Comparison: 16 valence electrons	198
13.6	An Updated Summary	203

14. Reconsidering Empirical Rules	205
14.1 Limitations of the Octet Rule	205
14.2 The Basis of the Octet Rule	206
14.3 Population Analysis	209
14.4 Resonance and Resonance Hybrids	212
14.5 Oxidation Number	213
14.6 Summary for Number Rules	215
15. Mavericks and other Lawbreakers	219
15.1 Exceptions to the Rules	220
15.2 Boron Hydrides and Bridges	221
15.2.1 The Expected Compound: BH_3	222
15.2.2 The Compounds Which Are Found	223
15.2.3 Bridged, Three-Centre, Bonds	223
15.3 Other Three-Centre Bonds?	226
15.4 Metals and Crystals	229
15.4.1 Metals	230
15.4.2 Crystals	231
15.5 The Hydrogen Bond	233
15.6 Lawbreakers?	234
16. The Transition Elements	235
16.1 The Background	236
16.2 Transition Metals: effects of “ <i>d</i> ” electrons	237
16.3 “Screening” in the Electronic Structure of Atoms	238
16.4 History and Apology	241
16.4.1 The “Crystal” Model	241
16.4.2 The Molecular Orbital Model	242
16.4.3 The “Chemical” Model	245
16.4.4 Apology	246
16.5 Comments	247
17. Omissions and Conclusions	251
17.1 Omissions	251
17.1.1 Intermolecular Forces	252
17.1.2 Chemical Reactions	252
17.2 Conclusions	255

