Contents

Preface ix
Acknowledgements xii

1. Energy, probability and electrons 1
   1.1 Energy quantization 1
   1.2 The wave–particle duality, observations and probability 6
   1.3 Wavefunctions and the indeterminacy principle 10

2. An introduction to the dynamics of microsystems 18
   2.1 Operators and observables 18
   2.2 Expectation values of observables 21
   2.3 Commuting operators 23
   2.4 Important operators 24
   2.5 The Schrödinger equation 27
   2.6 A simple system: translational motion of a particle 30
   2.7 Relativity theory, quantum mechanics and spin 42

3. One-electron atoms: atomic orbitals 45
   3.1 Wave equation and angular momentum 45
   3.2 Atomic orbitals 51
   3.3 Spin 67

4. The one-electron molecule H$_2^+$: molecular orbitals 70
   4.1 The wave equation and molecular orbitals 70
   4.2 Molecular orbitals from atomic orbitals 74
   4.3 Classifying molecular orbitals and electronic states 75
5. Many-electron atoms and the orbital concept  85
   5.1 Wavefunction and the Pauli principle  85
   5.2 Electron repulsion: orbitals, an approximation  90
   5.3 Total electronic energy  95
   5.4 Orbital energies  97
   5.5 Electronic configurations  101
   5.6 Beyond electronic configurations: terms, levels, states  105
   5.7 Density-functional theory and Kohn–Sham orbitals  111
   5.8 Relativistic corrections  112

6. Orbitals in diatomic molecules  114
   6.1 The approximations  114
   6.2 The simple diatomics H₂, He₂⁺ and ‘He₂’  115
   6.3 Molecular orbitals in X₂ molecules  120
   6.4 Heterodiatomic molecules  129
   6.5 Electronegativity  136

7. Orbitals in polyatomic molecules  139
   7.1 New features relative to diatomic molecules  139
   7.2 Molecular orbitals in AHₙ molecules  140
   7.3 Other molecules and quantitative m.o. theory  156

8. Molecular orbitals and electron pair bonding  167
   8.1 Atoms in molecules and structural formulae  167
   8.2 The theory of atoms in molecules  169
   8.3 Structural formulae and non-independent bonds  175
   8.4 Orbitals and electron pairing in valence-bond theory  180
   8.5 Molecular geometry and the valence-shell electron pair repulsion model  185
   8.6 Canonical molecular orbitals and localized functions  193
   8.7 Use and misuse of the hybrid orbital concept  201

9. π Molecular orbitals: conjugation and resonance  205
   9.1 The σ–π separation  205
   9.2 The CO₂ molecule and the CO₃²⁻ ion  206
   9.3 The ethylene and acetylene molecules  214
   9.4 The butadiene molecule  217
   9.5 The benzene molecule  223
   9.6 π Electron densities and bond orders  227
## Contents

10. Patterns in localized chemical bonds  230  
   10.1 Back to structural formulae  230  
   10.2 Bond energies and the Periodic Table  232  
   10.3 The octet rule and the writing of structural formulae  236  
   10.4 The conservation of the sum of bond orders  242  

11. The concept of molecular orbitals in other systems  245  
   11.1 The C₆₀ molecule  245  
   11.2 Octahedral complexes of transition metals  248  
   11.3 The band theory of solids  258  

12. Orbitals in action  265  
   12.1 Orbitals and chemical reactivity  265  
   12.2 Orbitals and spectroscopy  273  

Answers to problems  290  

References  303  

Index  311