

CONTENTS

PREFACE

xi

CHAPTER 1

INTRODUCTION

1

1.1

Leaping to a start

1

1.2

Some basic hardware

4

1.3

Atomic Hamiltonians

7

CHAPTER 2

ANGULAR MOMENTUM

12

2.1

Angular momentum operators

12

2.2

The commutation rules

15

2.3

Observables

16

2.4

Eigenvalues and orbital quantum numbers

19

2.5

The eigenfunctions—spherical harmonics

20

2.6

The shapes of some spherical harmonics

25

2.7

The relationship with atomic orbitals

27

2.8

Electron spin

29

CHAPTER 3

MANY-ELECTRON ATOMS

34

3.1

Angular momentum operators and commutators

34

3.2

Terms and term symbols

39

3.3

Relationships between l and L ; between s and S

43

3.4

Terms arising from the d^2 configuration

45

3.5

Configurations, terms and Hund's first two rules

52

3.6

Ground terms quickly

55

CHAPTER 4	SPIN-ORBIT COUPLING	57
4.1	Electrostatic versus magnetic coupling	57
4.2	Electrostatic and magnetic coupling together	60
4.3	The Russell–Saunders coupling scheme	63
4.4	Hund's third rule and Landé's interval rule	64
4.5	Hole formalisms	68
4.6	Russell–Saunders coupling review: configurations, terms, levels	69
4.7	Magnitudes of spin-orbit coupling coefficients	70
4.8	The j – j coupling scheme	74
4.9	Intermediate coupling	77
4.10	Deviations from Landé's rule	77
4.11	The effects of applied magnetic and electric fields	81
4.12	Atomic orbitals, configurations, terms, levels and states	84
CHAPTER 5	ANTISYMMETRY	86
5.1	The exclusion principle	86
5.2	Antisymmetrized triplets and singlets	91
5.3	Coulomb and exchange integrals	95
CHAPTER 6	BASES	101
6.1	The expansion theorem	101
6.2	Hilbert space	104
6.3	Crystal-field potentials	109
6.4	Perturbation theory	111
6.5	The non-crossing rule I	116
6.6	The variation method	118
6.7	Molecular orbitals	120
6.8	The secular equations	123
6.9	Diagonalization	126
6.10	The non-crossing rule II	127
CHAPTER 7	DIATOMIC MOLECULAR ORBITALS	129
7.1	Conserved angular momentum in linear molecules	129
7.2	Spectroscopic versus chemical labels	132

7.3	Symmetry classification	135
7.4	Eigenvalues of symmetry operators	138
7.5	Real and complex orbitals	143
7.6	Review of orbital symmetry labels	150

PREFACE

CHAPTER 8	DIATOMIC MOLECULAR STATES	153
8.1	Diatomic molecular configurations	153
8.2	Closed shells and open shells	156
8.3	The open shell $(\pi_g)^2$	158
8.4	The open shell $(\sigma_u)^1 (\pi_g)^3$	162
8.5	The open shell $(\pi_u)^3 (\pi_g)^3$	166
8.6	Diatomic molecular states: concluding remarks	170
	REFERENCES AND FURTHER READING	173
	INDEX	174

I believe that many chemistry students are unclear about the nature of orbitals, terms, levels and states, and that they feel a need for a text that has been published many times in various standard texts—it has, and some are splendid—but it is a fact that those sources are either dated, slanted too much towards physics, or too comprehensive. If the latter, the area is not unfolded as much as clear pedagogy might require and is, in any case, lost within the daunting length of a large work. So I have presented here a selection from atomic and molecular spectroscopy, from quantum mechanics and bonding theory, that I hope forms a satisfying nucleus from which understanding of those subjects can grow. In addition to the title topics, I offer brief introductions to the expansion theorem and the concept of basis functions; perturbation theory and the variational principle; secular equations and determinants; Slater determinants and antisymmetry; real versus complex orbitals; quantum numbers and symmetry labels. Explanations of, and simple manipulations with, the angular momentum operators L^2 , L_z , S^2 , S_z , F^2 , J_z are provided within the contexts of both free ions and linear molecules. And central to full discussions of angular momentum presented here, are the meanings of symbols like:

s, p, d, f, \dots

S, P, D, F, \dots

$l, s, i, m_l, m_s, m_j, \dots$

$L, S, J, M_L, M_S, M_J, \dots$

d^2, d^3, \dots

$^2D, ^4F, ^3F_4, ^4S_{3/2}, \dots$

$^1\Sigma_g^+, ^3\Delta_u$

I have attempted to minimize the mathematical content as far as possible but commensurate with reality. However, I have