

CONTENTS

Preface ix

1	SYMMETRY VERSUS SPLITTING PARAMETERS	<i>page 1</i>
	Introduction: the role of symmetry and group theory in ligand-field theory; the Spectrochemical Series; crystal-field and molecular-orbital viewpoints on the interpretation of Δ	1
2	THE CRYSTAL-FIELD FORMALISM	17
	Expansion of functions	17
	The crystal-field potential as an expansion	20
	Series terminators	21
	The vector triangle rule	23
	The tetrahedral potential from symmetry	25
	Matrix elements	28
	The point-charge model	31
	Definitions of Δ_{oct} , Δ_{tet} and $10Dq$	35
	Summary and outlook	36
3	INTERELECTRON REPULSION PARAMETERS	39
	Many-electron systems	39
	Matrix elements of V	41
	Evaluation of V matrix elements	43
	The crystal-field fundamental character	47
	Interelectron repulsion parameters	48
	Refinements of the theory	51
	The Trees correction	54
4	RADIAL PARAMETERS FOR ANGULARLY-DISTORTED SYSTEMS	60
	Low-symmetry crystal-field potentials defined by symmetry	60
	Low-symmetry and the point-charge model	63
	Matrix elements: the definition of Cp	64
	Distortion parameters and radial parameters	65
	Magnetic properties of trigonally-distorted octahedra	67
	Examples from spectra	77
	Spectra of distorted tetrahedral ions	82
	Second-order terms are not always very important	85

5 RADIAL PARAMETERS FOR QUADRATE SYMMETRY	page 88
Definitions of Dt and Ds	88
Relationships between Dt , Ds and Cp , Dq	90
Tetragonal nickel(II) complexes	94
Pseudo-tetragonal chromium(III) complexes	97
Tetragonal octahedral iron(II) molecules	98
Dq values: further examples	101
Summary	104
6 THE NATURE AND CALCULATION OF $10Dq$	106
The electrostatic or ionic crystal-field theory	107
The molecular-orbital formalism	109
The molecular-orbital method	110
Covalency	113
One-electron calculations	114
The Heitler–London approach	123
Many-electron MO calculations	124
Orbital energies and definitions of $10Dq$	127
Conclusion	131
7 A CRYSTAL-FIELD APPROACH TO RADIAL PARAMETERS	132
The radial integrals G^l	133
Pictorial representation of the G^l integrals	135
Properties of the radial integrals	136
Bond lengths	137
Charge distributions	140
Summary of trends	141
Radial parameters and coordination number	141
Inverse trends in Dq and Cp/Dq : effective bond lengths	143
Factorizability of the Spectrochemical Series	146
Some difficulties	146
A pictorial representation of Ds and Dt values: the ‘strength’ of a ligand field	147
Summary	149
Appendix 7A. Evaluation of electrostatic radial integrals	151
8 SEMI-EMPIRICAL MOLECULAR-ORBITAL APPROACHES	157
The principles of semi-empirical molecular-orbital methods	159
Approximation 1: the Hückel model	161
Approximation 2: the Wolfsberg–Helmholz model	162

Contents

vii

Approximation 3: the angular overlap model	<i>page</i> 163
Angular overlap integrals	165
Group overlap integrals	170
The angular overlap model in ML_N complexes	173
The octahedron versus the tetrahedron	174
Lower symmetries	176
Distorted molecules	178
Applications of the angular overlap model	180
Parameters in the angular overlap and crystal-field models	183
Appendix 8A. The transformation properties of the d -orbitals	189
Appendix 8B. Evaluation of group overlap integrals	191
9 THE NEPHELAUXETIC EFFECT	197
The Nephelauxetic Series	198
Interpretations I	200
Different experimental Nephelauxetic ratios	201
Early conclusions	212
The views of Ferguson and Wood	214
The consequences of 'inner' and 'outer' properties	216
Interpretations II	219
Interpretations III	221
Summary of trends	223
<i>References</i>	229
<i>Index</i>	233