

Contents

<i>Preface</i>	<i>page</i> xi
<i>Abbreviations</i>	xv
1 Introduction	1
1.1 The history and evolution of understanding of the Jahn–Teller effect (JTE)	1
1.2 The role and place of the JT vibronic coupling effects in modern molecular structure and condensed matter theory	6
1.3 The main goals of this book and means of their realization	9
References	10
2 Vibronic interactions	12
2.1 The adiabatic approximation	12
2.2 Vibronic interactions. Vibronic coupling constants	17
2.3 Orbital vibronic constants	27
2.4 Force constants, anharmonicity, and instability	31
2.5 The Jahn–Teller theorem	35
References	43
3 Formulation of Jahn–Teller problems. Adiabatic potentials	45
3.1 Basic formulations. The simplest $E \otimes b_1$ and $E \otimes (b_1 + b_2)$ problems	45
3.2 The $E \otimes e$ problem	52
3.3 $T \otimes e$, $T \otimes t_2$, $T \otimes (e + t_2)$, and $\Gamma_8 \otimes (e + t_2)$ problems	62
3.4 $T \otimes h$, $p^n \otimes h$, $G \otimes (g + h)$, and $H \otimes (g + h)$ problems for icosahedral systems	73
3.5 Adiabatic potentials in the multimode problem	91
3.6 Multicenter systems	95
References	106

viii	<i>Contents</i>	
4	Pseudo Jahn–Teller, product Jahn–Teller, and Renner–Teller effects	110
4.1	Two-level and multilevel pseudo JT (PJT) problems. Uniqueness of the PJT origin of configuration instability and its bonding nature	110
4.2	Pseudo JT $(A + E) \otimes e$, $(A + T) \otimes t$, $(T_1 + T_2) \otimes e$, and combined JT and PJT problems	122
4.3	Product JTE problems	135
4.4	The Renner–Teller effect	151
4.5	Reformulation of the JT theorem	155
	References	160
5	Solutions of vibronic equations. Energy spectra and JT dynamics	162
5.1	Weak vibronic coupling, perturbation theory	162
5.2	Strong vibronic coupling	169
5.3	Tunneling in JT systems	179
5.4	Numerical methods and general solutions	198
5.5	Solutions of multimode problems	212
5.6	Vibronic reduction factors	227
5.7	The topological phase problem	248
	References	254
6	The JTE in spectroscopy: general theory	263
6.1	Electronic spectra	263
6.1.1	Optical band shapes	263
6.1.2	Vibronic fine structure, zero-phonon lines, and tunneling splitting	278
6.1.3	The JTE in excited-state decay	289
6.2	Vibronic infrared and Raman spectra	291
6.2.1	Vibronic infrared absorption	291
6.2.2	Raman spectra and birefringence	305
6.3	Magnetic resonance and related spectra	318
6.3.1	The JTE in electron paramagnetic resonance spectra	318
6.3.2	Random strain and relaxation in EPR	325
6.3.3	Nuclear γ -resonance, microwave absorption, and ultrasonic attenuation	340
	References	345
7	Geometry, spectra, and reactivity of molecular systems	353
7.1	General: JT vibronic coupling effects in geometry and reactivity	353
7.1.1	Dynamic molecular shapes of JT systems. Pseudorotation	354

<i>Contents</i>		ix
7.1.2	Types of JT and PJT distortions. The lone-pair effect	361
7.1.3	JT-induced reactivity and chemical activation	367
7.1.4	Mutual influence of ligands	373
7.2	Linear configurations of simple molecules	377
7.2.1	Linear triatomic and tetraatomic systems	377
7.2.2	“Quasilinear” molecules	388
7.3	Trigonal molecular systems	393
7.3.1	Triangular triatomics X_3	393
7.3.2	Trigonal tetraatomic AB_3 systems	402
7.3.3	Other systems with a threefold symmetry axis	406
7.4	Distorted tetrahedral and square-planar systems	410
7.4.1	Tetraatomic X_4 and pentaatomic MX_4 systems	410
7.4.2	Cyclobutadiene, cyclobutane, and tetrahedrane radical cations	416
7.5	The benzene and cyclopentane families and some larger systems	422
7.5.1	The benzene-family molecular and radical cation and anion systems	422
7.5.2	The cyclopentadienyl radical and cyclopentane: puckering	427
7.5.3	Larger organic systems	431
7.6	Clusters, coordination and mixed-valence compounds	437
7.6.1	JT clusters and coordination systems	438
7.6.2	Vibronic coupling in mixed-valence systems	452
	References	461
8	Solid-state problems: local properties and cooperative phenomena	479
8.1	The JTE in local properties of solids	479
8.1.1	Impurity centers in crystals	479
8.1.2	The local JTE in formation of special crystal structures	495
8.2	Cooperative phenomena	504
8.2.1	Ordering of JT distortions and structural phase transitions	504
8.2.2	The simplest cooperative JT $E \otimes b_1$ problem: rare-earth zircons	511
8.2.3	Ordering of JT tri-minima distortions	519
8.2.4	Helicoidal structures, incommensurate phases, and structural–magnetic ordering	525
8.2.5	The band JTE, Peierls distortions, and first-order phase transitions. A general view on symmetry breaking	539

x	<i>Contents</i>	
8.3	The cooperative PJTE. Ferroelectric phase transitions	551
8.4	The JTE in high-temperature superconductivity and colossal magnetoresistance	566
	References	581
	<i>Appendix</i>	598
	<i>Subject index</i>	605
	<i>Formula index</i>	609