

## THE JAHN–TELLER EFFECT

The Jahn–Teller effect is one of the most fascinating phenomena in modern physics and chemistry, providing a general approach to understanding the properties of molecules and crystals and their origins. The effect inspired one of the most important recent scientific discoveries, the concept of high-temperature superconductivity. This comprehensive volume presents the background of the theory and its main applications in physics and chemistry, along with more recent achievements. Full descriptions are presented alongside thorough references to original material. The book contains over 200 figures to aid visual explanation and avoids bulky mathematical deductions and overly technical language. It is intended for graduate students and academic researchers working in solid-state physics, theoretical, physical, and quantum chemistry, crystallography, spectroscopy, and materials science.

ISAAC B. BERSUKER is a Senior Research Scientist and Adjunct Professor of Theoretical Chemistry at the University of Texas at Austin. His main scientific interest is in the theory of vibronic interactions and Jahn–Teller Effect with applications to solid-state physics, chemistry, and biology. He is the author and co-author of 12 books, 25 major reviews, and more than 300 original publications.

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ISAAC B. BERSUKER

*The University of Texas at Austin*



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In memory of my wife Liliya Bersuker

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## Preface

The Jahn–Teller effect (JTE) is one of the most fascinating phenomena in modern physics and chemistry. It emerged in 1934 in a discussion between two famous physicists, L. Landau and E. Teller, and grew into a general tool for understanding and an approach to solving molecular and crystal problems, which is applicable to any polyatomic system. The first formulation of this effect as *instability of molecular configurations in electronically degenerate states* proved to be the beginning of a whole trend which rationalizes the origin of *all possible instabilities* of high-symmetry configurations, and the peculiar nuclear dynamics resulting from these instabilities as well as the origins of all structural symmetry breakings in molecular systems and condensed matter.

Intensive development of the JTE theory began in the late 1950s together with a wave of main applications to spectroscopy, stereochemistry, and structural phase transitions, which lasted a couple of decades. The next significant resurgence of interest in the Jahn–Teller effect is related to the late 1980s and is still continuing. It was triggered by one of the most important Nobel Prize discoveries in physics of our times inspired by the Jahn–Teller effect: the *high-temperature superconductivity*. As explained by the authors of this discovery, “*the guiding idea in developing this concept was influenced by the Jahn–Teller polaron model*” (J. G. Bednorz and K. A. Müller, in *Nobel Lectures: Physics*, Ed. G. Ekspong, World Scientific, Singapore, 1993, p. 424).

Another recent discovery in solid-state physics, the *colossal magnetoresistance*, is also explained with essential implication of the Jahn–Teller effect. With regard to recent achievements in application to molecular systems, in addition to vast numbers of solutions of *structural, spectroscopic, and magnetic problems*, the Jahn–Teller effect has been most instrumental in explaining the properties of a novel class of compounds, the fullerenes, and it is now invoked in growing applications to the origin of *reactivity and mechanisms of chemical reactions*.

This book is devoted to presenting the JTE phenomenon in its integral unity, including the background of the theory and its main applications in physics and chemistry with emphasis on more recent achievements (as explained in more detail in the introduction). The goal is also to make the JTE more accessible to a wider circle of readers, meaning more visual explanation of the origin of the effects, omitting bulk mathematical deductions, where possible, and, in view of the multidisciplinary nature of the subject, trying to avoid heavy professional language specific for narrow groups of researchers. To compensate for any possible inconvenience for some of the readers created by this style, detailed references and cross-references have been included, allowing one to reach the desired level of description. We tried to address all aspects of the JTE theory and applications to all kinds of molecular systems and crystals, *making the book almost encyclopedic* in this respect.

The presentation in this book is based on our experience in this field. I started thinking on the Jahn–Teller effect in 1959 when reading a paper on the crystal field theory and have continued to work in this field ever since, so I witnessed and participated in its main achievements. My first book on this topic in English was published in 1984 (the first book on the JTE was published by R. Englman in 1972). Another book prepared together with V. Z. Polinger for a narrower circle of theoreticians was published in English in 1989 (the Russian version of this book was published in 1983). Together with my coworkers we published in 1984 a bibliographic review of the JTE publications. The new book follows the style of presentation of my first book and it uses some materials from, and references to, the book of 1989. In essence the new book is quite novel with regard to both the content and the level of presentation: in view of the achievements of the last two decades, the previous books, mentioned above, look rather incomplete (and in some respects obsolete). However, the book of 1989 authored with V. Z. Polinger remains valid with respect to many theoretical derivations referred to in the new book.

During the preparation of this book I benefited from the cooperation with my previous and present coworkers and colleagues from the community of scientists working in this field. My thanks are due to C. A. Bates, G. Bevilacqua, G. I. Bersuker, J. E. Boggs, S. A. Borshch, L. S. Cederbaum, A. Ceulemans, L. F. Chibotaru, J. T. Devreese, J. L. Dunn, R. Englman, J. P. Fackler, Jr., P. Garcia-Fernandez, M. D. Kaplan, H. Koizumi, H. Köppel, N. N. Kristoffel, A. A. Levin, L. Yu, W. J. A. Maaskant, N. Manini, L. Martinelli, T. A. Miller, M. Moreno, K. A. Müller, I. Ya. Ogurtsov, Yu. E. Perlin, V. Z. Polinger, D. Reinen, S. S. Stavrov, E. Teller, B. S. Tsukerblat, C.-L. Wang, and Yu. V. Yablokov. I am especially thankful to V. Z. Polinger for continuing discussion of JT problems of this book, and to J. E. Boggs for support and

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cooperation. I am thankful also to E. Teller for an encouraging chat on some aspects of the JTE; unfortunately, he did not survive to write the (promised) foreword to this book.

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Isaac B. Bersuker  
Austin, Texas, January 2005

## Abbreviations

- AA – adiabatic approximation  
AO – atomic orbitals  
APES – adiabatic potential energy surface  
BCS – Bardeen–Cooper–Schrieffer  
BLYP – Becke–Lee–Yang–Parr (DFT functional)  
BOD – bicyclooctadienediyl  
CASSCF – complete active space SCF  
CI – configuration interaction  
CJTE – cooperative JTE  
CNDO – complete neglect of differential overlap  
COT – cyclooctatetraene  
CPJTE – cooperative PJTE  
DFT – density functional theory  
DPH – diphenylhexatriene  
EPR (ESR) – electron paramagnetic resonance (electron spin resonance)  
EXAFS – extended X-ray absorption fine structure  
HF – Hartree–Fock  
HOMO – highest occupied MO  
HTSC – high-temperature superconductivity  
INDO – intermediate neglect of differential overlap  
IR – infrared  
JT – Jahn–Teller  
JTE – Jahn–Teller effect  
LSD – local spin density  
LUMO – lowest unoccupied MO  
MCSCF – multicenter SCF  
MCZDO – multicenter zero differential overlap  
MFA – mean-field approximation

MINDO – modified INDO  
MO – molecular orbitals  
MO LCAO – MO linear combination of AOs  
MP – metal porphyrin  
MPc – metal phthalocyanine  
MP2 – Möller–Plesset 2 (second-order perturbation theory)  
MRCI – multireference CI  
MRSDCI – MRCI with single and double excitations  
MV – mixed valence  
NMR – nuclear magnetic resonance  
NGR – nuclear gamma resonance  
phen – phenanthroline  
PJT – pseudo JT  
PJTE – pseudo JTE  
QCISD – quadratic CI with single and double excitations  
QM/MM – quantum mechanics/molecular mechanics  
RF – reductions factor  
RMP2 – restricted MP2  
ROHF – restricted open-shell HF  
RT – Renner–Teller  
RTE – Renner–Teller effect  
SB – symmetry breaking  
SCF – self-consistent field  
SP – square-pyramidal  
STO – Slater-type orbitals  
TBP – trigonal-bipyramidal  
TCNE – tetracyanoethylene  
TCNQ – 7,7,8,8-tetracyano-*p*-quinodimethane  
TTF – tetrathiofulvalene  
UQCISD – unrestricted QCISD  
ZEKE – zero electron kinetic energy