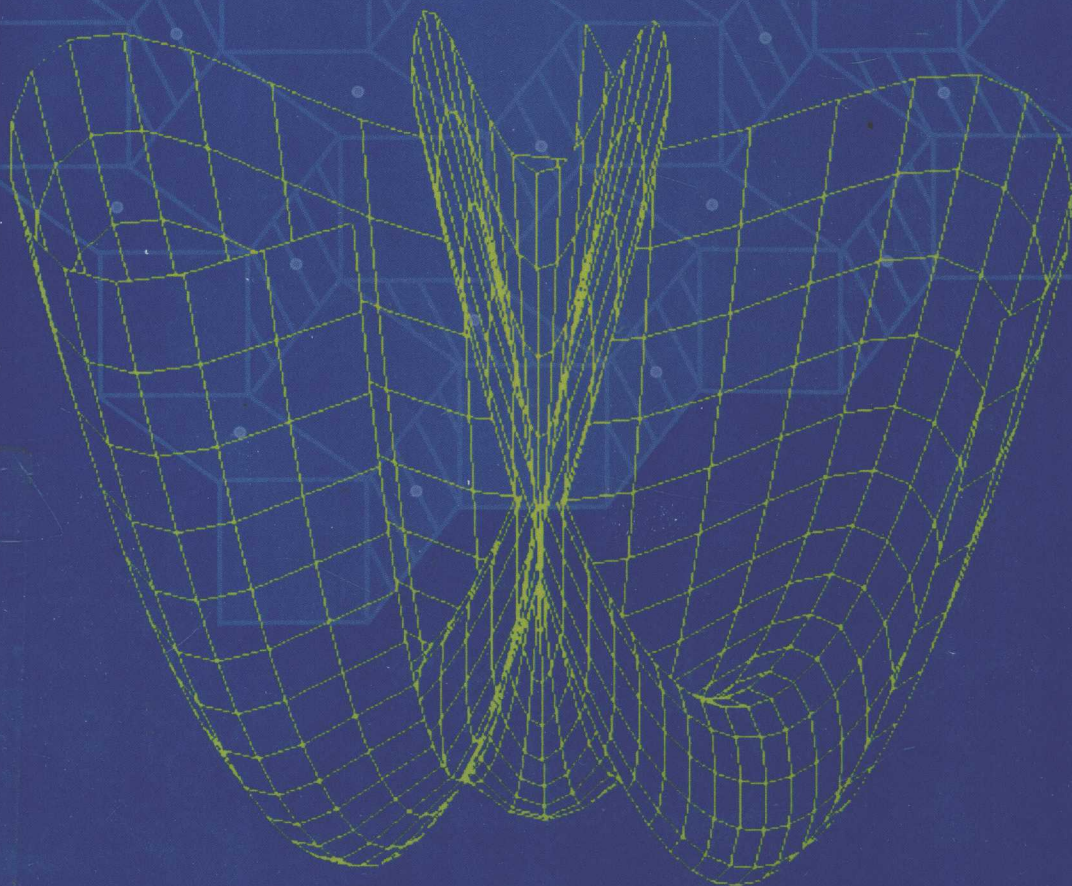


The Jahn-Teller Effect

Isaac B. Bersuker



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THE JAHN–TELLER EFFECT

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In memory of my wife Liliya Bersuker

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. Eksping, 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

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.

I acknowledge the cooperation of many publishers of academic journals and books for their kind permission to reprint figures, including the American Chemical Society, the American Institute of Physics, the American Physical Society, Elsevier Science Publishers, Helvetica Chimica Acta Verlag, the Institute of Physics, John Wiley & Sons, Kluwer Academic Publishers, NRC Research Press, Princeton University Press, the Royal Society London, Springer Verlag, and Taylor & Francis. I am grateful to the team of Cambridge University Press for help and cooperation in the copy-editing and production of this book.

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

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1

Introduction

This introductory chapter has two goals. The first one is usual for books of this kind and is aimed at providing the reader with a brief outline of the background history of the subject, its main content, form of presentation, and correlation with other related subjects. The second goal is to give this introduction in a way which allows the reader to get a general (although maybe rather rough and superficial) impression of the whole subject and its possibilities, a very brief insight into this trend without reading the corresponding chapters or sections. This is done keeping in mind that quite a number of physicists, chemists, and biologists, who at present are not engaged in the use of the Jahn–Teller effect, may be interested to know in general the status quo in this field and make a fast choice of the parts of it they may be interested in. In other words, the introduction is aimed at giving a very brief qualitative description of the main features of the Jahn–Teller effect theory in a way useful also for the reader who has no intention to read the whole book or its parts. The applications of the theory to chemical problems and molecular systems are given in Chapter 7, while the Jahn–Teller effect in specific solid-state problems is considered in Chapter 8.

1.1 The history and evolution of understanding of the Jahn–Teller effect

The so-called Jahn–Teller (JT) effect (JTE), which includes the proper JTE, pseudo JTE (PJTE), and Renner–Teller effect (RTE), nowadays forms a whole trend in the theory of structure and properties of molecules and crystals jointly termed *JT vibronic coupling effects*, or abbreviated JTE (this abbreviation is used throughout the whole book). In fact the JT theory is *an approach* to (*a tool* for) general understanding and solving of molecular and crystal problems, which is in principle applicable to any system with more than two atoms.

As for many other fundamental properties of matter, the JTE was first formulated in the early thirties of the twentieth century [1.1–1.4]. There were four persons who initiated this trend: L. Landau, E. Teller, H. Jahn, and R. Renner. In 1934 L. D. Landau in a discussion with E. Teller about his student's (R. Renner's) work first formulated the statement that *a molecule in an orbitally degenerate electronic state is unstable with respect to spontaneous distortion of the nuclear configuration that removes the degeneracy* (see in [1.4]). Presumably, Landau's arguments were based on ideas similar to that used in the proof of the von Neumann–Wigner theorem about crossing electronic terms [1.5]. This Landau statement was later verified by E. Teller and H. Jahn and more rigorously formulated as (what is now known as) the Jahn–Teller theorem [1.1].

The proof of this theorem (Section 2.5) is based on perturbation theory, in which the influence of the nuclear displacements (vibrations) via *electron–vibrational (vibronic) interactions* is considered as a perturbation to the degenerate states, and only linear terms of this *vibronic coupling* of the electronic states to the nuclear displacements are taken into account. Qualitatively (roughly) the origin of instability of molecules in high-symmetry configurations with orbital degeneracy can be easily understood if one takes into account that *when there are two or more electronic distributions with the same energy, they are necessarily nontotally symmetric with regard to the environment* (cf. three atomic p states, p_x , p_y , and p_z), and hence the electron on any one of them distorts the otherwise symmetrical environment, thus lowering its energy (Section 2.5).

In the linear approximation (first order in the vibronic coupling) linear geometries are exceptions from the JT theorem (Renner's molecule CO_2 was just such an exception, with regard to which, at first sight, Landau was wrong). However, linear molecules are subject to similar instabilities when the quadratic terms of vibronic coupling are taken into account [1.3], and then it is called the RTE (Section 4.4). Another exception from the JT theorem is a spin double degenerate (Kramers) term, which cannot be split by nuclear displacements (it splits under magnetic fields only).

Before World War II only one more paper was devoted to the JTE, that of Van Vleck [1.6]. In this paper the simplest JT problem of a twofold degenerate electronic term E interacting with twofold degenerate e vibrations (hereafter the vibrational modes are indicated with small letters), the $E \otimes e$ problem, was explored, and it was shown that in this case the *adiabatic potential energy surface* (APES) has the form of a “Mexican hat” (Section 3.2).

Among other things the author of this publication Van Vleck, wrote that “it is a great merit of the JTE that it disappears when not needed.” This declaration reflects the situation when there was very poor understanding

of what observable effects should be expected as a consequence of the JT theorem. The point is that the simplified formulation of the consequences of the JT theorem as “spontaneous distortion” is incomplete and therefore inaccurate, and may lead to misunderstanding. In fact, there are several (or an infinite number of) equivalent directions of distortion (like in the three p -state directions in the example above), and the system may resonate between them (the *dynamic JTE*). In a more rigorous treatment (Chapters 3–5) the lack of minimum of the APES results in a variety of novel properties, but it does not necessarily lead to observable nuclear configuration distortion, and this explains why such distortions often cannot be observed directly (Section 7.1).

This period of “stagnation,” misunderstanding of the JTE, lasted almost two decades. Even in 1960 Low in his book [1.7] stated that “*it is a property of the JTE that whenever one tries to find it, it eludes measurements.*”

In 1950 Abragam and Price [1.8] first revealed the dynamic nature of the JT distortions by analyzing the temperature dependence of ESR spectra of Cu(II) compounds [1.9] (Section 6.3.1). The usually well-defined anisotropy of the ESR signal from octahedral complexes of Cu(II) disappeared at certain temperatures due to the thermal averaging over the different directions of JT distortions in the $E \otimes e$ problem (in fact the JT dynamics is more complicated, involving tunneling splitting, Sections 5.3 and 6.3.1). This was seemingly the first experimental observation of the JTE.

In 1957 Öpik and Pryce [1.10] developed a method of calculation of the possible JT distortions (Section 3.3) and revealed the number and kind of extrema points of the APES for threefold degenerate states interacting with both e and threefold degenerate t_2 vibrations, the *linear $T \otimes (e + t_2)$ problem* (Section 3.3), showing that in this case either tetragonal or trigonal distortions are possible. In this paper the *PJTE problem* was formulated for the first time. The idea behind the PJTE is that not only exact degeneracy (required by the JT theorem), but sufficiently close-in-energy (*pseudodegenerate*) states may produce instabilities, similar to those of the JTE (Section 4.1). The condition of the PJT instability requires that the energy gap between the mixing states is sufficiently small in comparison with other vibronic parameters of the system. The PJTE became most important later when it was shown that it is the only source of instability of high-symmetry configurations of polyatomic systems in nondegenerate states.

In 1957–58 Longuet-Higgins *et al.* [1.11] and independently Moffit and Thorson [1.12] calculated the vibronic energy levels of systems with the linear $E \otimes e$ problem, transitions to and from these states, and band shapes of optical spectra involving such degenerate states. It was the first demonstration of the

JTE in optical spectroscopy showing that it results in specific forms of the band shape (Section 6.3.1). Liehr and Ballhausen [1.13] explored the JT $E \otimes e$ problem with quadratic terms of vibronic interactions and revealed the so-called warping of the Mexican-hat-type APES. This warping results in the formation of three equivalent minima along the bottom of the trough, which correspond to three directions of tetragonal distortions of the system (Section 3.2).

An explosion of publications began at this point, from which we mention here a few main contributions, which explored in detail the origin of different kinds of JT dynamics. An account for the publications of the whole period from inception up to 1979 inclusive is given in the bibliographic review [1.14].

In 1961–63 Bersuker [1.15] first considered the splitting of the lowest vibronic energy levels due to the *tunneling* of the system between the equivalent distorted configurations (Section 5.3) and its influence on ESR spectra (Section 6.3.3). In 1964 O'Brien [1.16] calculated numerically the vibronic energy levels in the $E \otimes e$ problem with linear and quadratic terms of vibronic coupling included (Section 3.2). In 1965 Ham [1.17] generalized the idea of *vibronic reduction factors* (Section 5.6). The latter are of special interest since they allow one to calculate physical properties of electronic origin without fully solving the vibronic coupling problem.

An important development of the JTE theory began with the treatment of interactions of JT centers, especially regular JT centers in crystals, known as the *cooperative JTE* (CJTE) (Sections 8.2–8.4). Kanamori [1.18] in 1960 first explicitly explored such cooperative phenomena in JT crystals, while Elliot *et al.* [1.19] and other authors essentially advanced this important trend in application to rare-earth zircons (Section 8.2.1). In 1966 Bersuker [1.20] first suggested the vibronic theory of ferroelectricity as a *cooperative PJTE* (Section 8.3). While the idea of interactions between JT centers in crystals and the consequent ordering of JT distortions was physically transparent and quite understandable, the very possibility of the PJTE in dielectric crystal centers with relatively large band energy gaps and their interaction to lead to ferroelectric (and other) phase transitions was questionable at that time.

The book of Englman in 1972 was the first to give a comprehensive review of this field as a whole [1.21] (before that a review of this topic was published by M. D. Sturge [1.22]). With this book the first stage of the JTE theory was accomplished, resulting in a full understanding of the basics of this phenomenon: the JTE became a firmly established trend in the theory of matter. This was also marked by the beginning of separate JT symposia; the first four symposia took place in Bad Honnef (1976), Leoni (1977), Trento (1978), and Chantilly (1979).