

The Jahn-Teller Effect

Fundamentals and Implications for Physics and Chemistry

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1st Edition. 2009. Buch. xxi, 915 S. Hardcover

ISBN 978 3 642 03431 2

Format (B x L): 15,5 x 23,5 cm

Gewicht: 1421 g

Weitere Fachgebiete > Chemie, Biowissenschaften, Agrarwissenschaften >
Physikalische Chemie

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Preface

The Jahn–Teller (JT) effect continues to be a paradigm for structural instabilities and dynamical processes in molecules and in the condensed phase. While the basic theorem, first published in 1937, had to await experimental verification for 15 years, the intervening years saw rapid development, initially in the theoretical arena, followed increasingly by experimental work on molecules and crystals. The International Jahn–Teller Symposium was established in the mid-1970s, to foster the exchange of ideas between researchers in the field. Among the many important developments in the field, we mention cooperative phenomena in crystals, the general importance of pseudo-Jahn–Teller (PJT) couplings for symmetry-lowering phenomena in molecular systems, nonadiabatic processes at conical intersections of potential energy surfaces and extensions of the basic theory in relation to the discovery of fullerenes and other icosahedral systems.

It is the objective of this volume to provide the interested reader with a collection of tutorial reviews by leading researchers in the field. These reviews provide a comprehensive overview of the current status of the field, including important recent developments. This volume is targeted at both the non-expert scientist as well as the expert who wants to expand his/her knowledge in allied areas. It is intended to be a complement to the existing excellent textbooks in the field. Guided by the idea of tutorial reviews, we provide here short introductory remarks to the various sections, as they appear in the table of contents. These are followed by a brief characterization of the individual papers to make their basic contents, as well as their interrelation, more transparent.

1. Jahn–Teller Effect and Vibronic Interactions: General Theory

The first set of reviews deals with general formal aspects of the theory, its range of application and implementation. While the original formulation of the JT theorem applies to orbitally degenerate electronic states, it was later recognized that similar mechanisms for structural instabilities are operative also in nondegenerate states (PJT effect). In the first paper of this volume, Bersuker emphasizes the even more general implications of the JT and related couplings, by demonstrating that they may affect ground state structural properties, even when operative in the excited state manifold (hidden JT effect). This may be associated with spin-crossover effects and orbital disproportionation. The following two papers (by Ceulemans and Lijnen, and

by Breza) address group theoretical aspects. A desire has sometimes been expressed to gain more insight into the nature of the JT theorem than is afforded by the original proof (which consists in enumerating all topologically distinct realizations of all molecular point groups). This goal is indeed achieved in the article by Ceulemans and Lijnen. Poluyanov and Domcke advocate the use of the microscopic Breit-Pauli operator for the spin-orbit coupling rather than the phenomenological form often adopted. They point out that the resulting dependence of the spin-orbit coupling on the nuclear coordinates can lead to novel effects, of relevance to molecular spectra. Sato and coworkers present a scheme for analyzing vibronic coupling constants in terms of densities, which allows them to investigate their local properties and visualize their electronic origin. Finally, an efficient method to compute multimode JT coupling constants with density functional theory is presented by Zlatař et al. The approach uses information from the JT distorted structure, which is decomposed into contributions from the various relevant normal modes.

2. Conical Intersections and Nonadiabatic Dynamics in Molecular Processes

Conical intersections can be considered generalizations of the JT intersections in less symmetric cases, the latter being also conical in shape owing to the presence of the linear coupling terms predicted by the JT theorem. In molecular physics, conical intersections have emerged in the past one or two decades as paradigms for nonadiabatic excited-state dynamics, triggering a plethora of studies of elementary photophysical and photochemical processes. The article by Blancafort et al. reports on modern developments in the characterization of conical intersections by *ab initio* techniques. Their second-order analysis shows, for example, how to distinguish between minima and saddle points in the subspace of electronic degeneracy and to identify photochemically active coordinates. The paper by Bouakline et al. presents a quantum dynamical analysis of the smallest JT active system, triatomic hydrogen. This prototypical reactive scattering system is subject to geometric phase effects which, however, almost completely cancel out in the integral cross section. On the other hand, strong nonadiabatic couplings/geometric phase effects govern the upper-cone resonances (Rydberg states) of the system. The papers by Faraji et al. and by Reddy and Mahapatra present multimode quantum dynamical treatments of JT and PJT systems with more than two intersecting potential energy surfaces. Pronounced effects of the couplings in the spectral intensity distribution and in femtosecond (fs) internal conversion processes are identified. A systematic dependence of the phenomena on the (fluoro) substituents as well as the importance for the photostability of hydrocarbons is demonstrated. In the article by McKinlay and Paterson, similar phenomena, including nonadiabatic photodissociation processes and fs pump-probe spectroscopy, are discussed for transition metal complexes, thus providing a bridge between the JT effect and photochemistry.

3. Impurities; Spectroscopy of Transition Metal Complexes

Transition metal complexes have represented, for a long time, the archetypical system for which the JT effect plays a crucial role, especially with regard to crystal field splitting and spin-orbit interaction (Ham effect). This affects optical as well

as EPR spectra of 3d group ions, for example. In the review by Brik and Avram these are studied for various coordination sites using an effective Hamiltonian formalism. Useful relations for the Ham reduction factors are derived, and the JT parameters obtained from the Ham effect are compared with those obtained from the JT-distorted minima of the potential energy surfaces. Tregenna-Piggott and Riley present in their review a very pedagogic introduction to the Exe JT effect, and the Ham effect as one of its consequences. Applications to various types of spectra of different transition metal complexes underline the usefulness of the theoretical concepts. Garcia-Fernandez et al. address the question of structural instabilities of doped materials and their type and origin. They argue, and present convincing evidence, that these are frequently not due to differences in atomic sizes (as is often assumed in the literature) but rather to vibronic coupling, that is, the PJT effect. Finally in their review, Reinen and Atanasov analyze in their review, the effects of JT coupling on the changes from a high-spin to a low-spin electronic ground state in hexacoordinate fluoride complexes of Mn(III), Co(III), Ni(III) and Cu(III), an aspect which is frequently ignored in the literature on spin-crossover systems. In particular, the strong links to coordination and solid state chemistry are set out in this contribution.

4. Fullerenes and Fullerides

In the mid 1980s and subsequent years, the discovery of C₆₀ and other fullerenes opened a route to the analysis of JT systems with higher than threefold degeneracies (G and H irreducible representations). This led to substantial developments from the point of view of pure theory as well as applications. This volume includes two important papers in this area. Structural aspects of fulleride salts, i.e. fullerene anions in various charge states in the solid state, are covered by Klupp and Kamaras. Evidence, based mostly on infrared spectroscopy, is used to discuss issues including static vs. dynamic JT effect, unusual phases, and relation to conductivity. The review by Hands et al. addresses the further complication of fullerenes being adsorbed on surfaces. The lowering in symmetry due to the surface interactions is considered, as well as the rather slow time-scale of the experimental technique of scanning tunneling microscopy proposed. Detailed simulations of the corresponding images shed useful light on their possible significance in establishing the presence and shape of JT distortions.

5. Jahn–Teller Effect and Molecular Magnetism

Molecular magnetism concerns the synthesis, characterization and application of molecular-based materials that possess the typical properties of magnets – slow relaxation, quantum tunneling and blocking of the magnetization at low temperatures (single molecular magnets (SMM)). It is an interdisciplinary research field which requires the combined efforts (cooperation) of chemists, molecular and solid state physicists, as well as theoreticians (quantum chemists). This is the point where the JT effect enters into the game. The magnetic properties of SMMs are affected by the structural influences caused by vibronic coupling and these influences are further manifested in the optical band shapes, the interactions between magnetic molecules

with degenerate ground states (cooperative JT effect), and the dynamical JT and PJT effects (which impact upon the magnetic relaxation and spin coherence times). In their review, Tsukerblat, Klokishner and Palii address these points in spin-frustrated systems with threefold symmetry, mixed valence systems, photoswitchable spin systems, and magnetic molecules which undergo tautomeric transformations leading to long-lived (metastable) states. The Jahn–Teller effect plays a crucial role in magnetic clusters built up from magnetic centers in orbitally degenerate ground states. Using a combination of ligand field theory and density functional theory Atanasov and Comba show how small structural changes due to Jahn–Teller activity and/or structural strains induce a dramatic lowering of the magnetic anisotropy. The same authors also show for the first time, using cyanide-bridged systems as model examples, how one can deduce the parameters of the spin Hamiltonian from first principles.

6. The Cooperative Jahn–Teller Effect and Orbital Ordering

It has long been recognized for JT crystals, i.e., crystals containing a JT center in each unit cell, that the intrinsic instability of JT complexes against distortions may give rise to an effective interaction between JT ions, mediated by the surrounding ligands of the ions. Below a critical temperature, this interaction may lead to the cooperative JT effect (CJTE), a structural phase transition where the whole crystal distorts. There are two main approaches to the CJTE, differing in the form of the effective ion–ion interaction. Kaplan’s review is partly based on Kanamori’s treatment, who generated this interaction by the transformation from local vibrational modes to phonons. This treatment, in combination with the canonical Hamiltonian shift transformation and a subsequent mean-field approximation, is the most popular approach to the CJTE. Although this concept, also referred to as virtual phonon exchange, has led to impressive results for some simpler systems, it cannot be applied to systems characterized by the Exe JT effect because of insurmountable technical difficulties. Such systems are conveniently treated by means of an alternative approach, developed by Thomas and co-workers and described in Polinger’s article. This method assumes a bilinear lattice-dynamical interaction between the normal coordinates belonging to nearest-neighbor cells. However, the main emphasis of this article lies in a detailed comparison of the CJTE with the orbital-ordering (or Kugel-Khomskii) approach. A typical example of the orbital-ordering approach is presented in Ishihara’s review. The main emphasis of this article is on the intrinsic orbital frustration effect, meaning that no orbital configuration exists, whereby the bond energies in all equivalent directions are simultaneously minimized. It is shown that the orbital frustration effect leads to several nontrivial phenomena in strongly correlated systems with orbital degrees of freedom. The influence of the CJTE and of JT impurities on material properties is elucidated in the reviews by Gudkov and Lucovsky. The review by Gudkov deals mainly with the influence of JT impurities on the elastic moduli and ultrasonic wave attenuation in diluted crystals. The elastic-wave technique broadens the facilities of JT spectroscopy in its low-energy part and provides new information, mostly about the properties of the ground state and its tunneling splitting. That the JT effect even plays an important role in semiconductor technology is convincingly demonstrated in Lucovsky’s article. Here the CJTE

manifests itself in the group IVB transition-metal oxides, designed as replacement gate dielectrics for advanced metal-oxide-semiconductor devices.

7. Jahn–Teller Effect and High-T_c Superconductivity

The explanation of high-temperature superconductivity (HTSC) in copper oxides (cuprates) is one of the most difficult problems in modern physics. The undoped cuprates are antiferromagnetic Mott insulators, where the insulating behavior is caused by a strong on-site Coulomb repulsion. HTSC arises upon hole doping, whereupon the originally immobile electrons in the half-filled conduction band become mobile. The basic problem is to find the proper mechanism for the formation of Cooper pairs, the necessary ingredient of all superconductors. There are mainly two antagonistic views on the problem amounting to the question of whether the participation of phonons is indispensable for the pair formation or whether the electrons alone can do the job. The review by Miranda Mena tries to answer this question by gathering all available evidence in favor of electron–phonon mechanisms such as (bi)polarons and JT (bi)polarons. Seen in this perspective, the article gives a fair account of the state of the art in HTSCs. A more detailed theory of JT polarons and bipolarons with application to the fullerene superconductors is presented in the article by Hori and Takada. In addition to offering a thorough mathematical analysis, the authors also make the interesting observation that, for stronger coupling, JT polarons acquire a smaller effective mass than the Holstein polaron. Such a reduction of the polaron effective mass is essential for the existence of superconductivity, as the polaron mass increases with increasing coupling so that, for sufficiently strong coupling, the polaron becomes immobile and cannot contribute to the electric current. These remarks apply, in particular, to Koizumi’s work, which proposes that the doped holes become small polarons and not, as is supposed in all electron-based theories of HTSC, constituents of Zhang-Rice singlets. As the mobility of the polarons is very limited, a novel mechanism is required to facilitate a macroscopic electric current. The author solves the problem by a loop current generation around each spin vortex due to the spin Berry phase. The macroscopic current is then the collection of all these loop currents.

This set of tutorial reviews has been created on the occasion of the 19th International Jahn–Teller Symposium, held in Heidelberg, University Campus, 25–29 August 2008. The volume does not, however, reflect directly the conference contents. Full coverage of the 46 oral presentations given at the meeting (plus a similar number of posters) was not attempted. Conversely, the 27 papers collected here go into considerably more depth than would be normal for a proceedings volume. We hope that this volume constitutes a valuable reference, for beginners and experts alike.

Heidelberg
Stuttgart
Baltimore
May 2009

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