

Progress in Theoretical Chemistry and Physics B 23

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Mihail Atanasov, Claude Daul  
Philip L.W. Tregenna-Piggott, *Editors*

# Vibronic Interactions and the Jahn-Teller Effect

Theory and Applications

 Springer

# Vibronic Interactions and the Jahn-Teller Effect

# Progress in Theoretical Chemistry and Physics

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# Vibronic Interactions and the Jahn-Teller Effect

Theory and Applications

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# Preface

Since the discovery of the Jahn-Teller effect in 1937 the concept of vibronic coupling has become a source of inspiration for many researchers – theoreticians and experimentalists, chemists and physicists. The Jahn-Teller theorem states that degenerate electronic states of non-linear molecules are energetically unstable with respect to nuclear displacements which lift the orbital degeneracy. It has been later shown that mixing of electronic states by vibrational modes (vibronic coupling) can be very strong indeed even if degeneracy is absent and when energy separation between the interacting states is quite large. Thus the vibronic coupling is the sole mechanism responsible for structural distortions and dynamics in molecules and solids, and is at the very heart of reactivity in chemistry both in thermochemical and photochemically induced reactions. Jahn-Teller intersections are now being recognized as prototype cases of conical intersections, where the nuclear and electronic motions are known to be inherently nonadiabatic in nature and electrons interchange freely between different potential energy surfaces. In the condensed phase, the significance of the Jahn-Teller effect is increasingly recognized, appreciated and applied to the origin of high-temperature superconductivity, ferroelectric phase transitions in perovskite crystals, superconductivity in fullerenes, and of very large (“colossal”) magnetoresistance in manganites. These and other related vibronic coupling problems are particularly challenging because the Jahn-Teller interaction competes with electronic correlation and relativistic (spin-orbit coupling) effects.

The present volume reports on the state-of-art in the field of the Jahn-Teller effect and vibronic interactions. Starting in the mid-1970s, Jahn-Teller symposia – biannual conferences gathered together chemists and physicist, theoreticians and experimentalist working in this largely interdisciplinary field. In this volume we report a major part of the contributions to this field presented at the XX International Conference on the Jahn-Teller effect held in Fribourg, 16th–20th August in Switzerland, 2010. Several contributions to the conference (K.A. Müller, V.Z. Polinger, D. Khomskii, etc.) are published elsewhere.

The book starts with an introductory chapter by Isaac Bersuker (Chap. 1) – a pioneer in the field – who provides a thorough and critical overview of the



controversial issues related to the pseudo Jahn-Teller interactions in some cases of intersystem crossings. This chapter addresses the need of reinterpreting the experimental data in the Jahn-Teller system  $\text{Cu}^{2+}$  doped  $\text{MgO}$  in light of the new ab-initio results and the improvement of the latter result by (still missing) multimode Jahn-Teller treatments etc.

Part I deals with the developments of the DFT treatments of the multimode Jahn-Teller problem (Chap. 2, M. Zlatar et al.) and discusses the extensive use of symmetry which allows a better understanding of both static and dynamic Jahn-Teller phenomena (contributions by B. Tsukerblat – Chap. 3 and M. Breza – Chap. 4, respectively). Part II presents the Jahn-Teller effect due to impurity centers in crystals, such as  $\text{Cu}^{2+}$  doped  $\text{MgO}$  – a prototype of a dynamic Jahn-Teller effect thoroughly analysed in relation to temperature and field dependent EPR experiments (Chap. 5 by Riley et al.). The origin of the dynamic and static Jahn-Teller effect in the EPR spectra of transition metal impurities in insulators has been discussed in the light of ab-initio calculations by Garcia-Fernandez et al. (Chap. 6). The application of ultrasonic experiments to impurity centers in crystals with zinc-blende structure and tetrahedral coordination (Chap. 7 by V. Gudkov and I. Bersuker) offers the unique opportunity of evaluating empirically the linear Jahn-Teller coupling parameters. Vibronic coupling is manifested in Raman scattering in resonance with an electronic transition to a pseudo Jahn-Teller distorted excited state (Chap. 8 by I. Tehver et al.) and a theory of electronic transition from a non-degenerate to a two-fold degenerate state in an impurity is proposed by Hiznyakov et al. (Chap. 9). The many-electron multiplet theory as applied to oxygen vacancies in nanocrystalline  $\text{HfO}_2$  and non-crystalline  $\text{SiO}_2$  by Lucovsky et al. (Chap. 10) concludes this part.

Part III is dedicated to the manifestation of the Jahn-Teller effect in fullerenes, fullerides and related systems. The imaging of molecular orbitals of fullerene molecules on surface substrates by using scanning tunnelling microscopy and their splitting by static or dynamic Jahn-Teller effect is the subject of the very transparent and nicely visualized contribution by Dunn et al. (Chap. 11). The same group of authors analyses the Jahn-Teller effect in  $p^3 \otimes h$  of  $\text{C}_{60}^{3-}$  as found in the  $T_c = 40$  K superconductor  $\text{A}_3\text{C}_{60}$  (Chap. 12 by A. Lakin et al.), whereas Iwahara et al. (Chap. 13) focus on deriving vibronic coupling constants from experiment and (Muya et al., Chap. 14) deal with the theory and the investigation of pseudo-Jahn-Teller effect and chemical reactivity in the boron buckyball  $\text{B}_{80}$ .

Part IV examines the conical intersection and the interplay between Jahn-Teller coupling and spin-orbit coupling. Here Adhikari et al. (Chap. 15), using the  ${}^2E'$  and  ${}^2A'_1$  electronic states in a case study of the trimer of sodium, carry out a nuclear dynamics study employing diabatic ab-initio derived potential energy surfaces and non-adiabatic coupling terms proving the validity of the so-called “Curl condition”. W. Ernst et al. (Chap. 16), present a thorough study that combines spectroscopy and theory and manifests the quenching of the  $E \otimes \epsilon$  Jahn-Teller coupling with increasing spin-orbit coupling across the series  $\text{K}_3, \text{Rb}_3, \text{Cs}_3$ . Along the same line, R. Fishman (Chap. 17) reviews the interaction between Jahn-Teller coupling due to the high-spin

Fe(II) and spin-orbit coupling of the same ion in Fe(II)Fe(III) bimetallic oxalates as well as their relevance for the temperature- dependent magnetic properties.

Part V focuses on mixed valence compounds and their spectroscopic and magnetic properties that lead to exciting phenomena where Jahn-Teller coupling or pseudo Jahn-Teller coupling and electronic delocalization interfere. A vibronic pseudo Jahn-Teller coupling model for mixed valence dimers belonging to Robin and Day class II compounds is the subject of the contribution by Palii et al. (Chap. 18). This chapter elucidates the factors controlling the non-adiabatic Landau-Zener tunnelling between vibronic levels induced by a pulsed electric field. A mixed valence iron dimer  $[L^I\text{Fe}_2(\mu\text{-OAc})_2](\text{ClO}_4)$  is investigated by Ostrovsky (Chap. 19) in the framework of the generalized vibronic model which takes into account both the local vibrations on the metal sites (Piepho-Krausz-Schatz model) and the molecular vibrations changing the intermetallic distance (suggested by Piepho).

Lucovsky et al. (Chap. 20) complete this part by presenting the many-electron multiplet theory as applied to the spectroscopic detection of hopping induced mixed valence Ti and Sc in  $\text{GdSc}_{1-x}\text{Ti}_x\text{O}_3$ .

The last Part II of the book deals with the cooperative Jahn-Teller effect and spin-coupling phenomena. A vibronic approach to the cooperative spin transitions in crystals based on cyano-bridged trigonal bipyramidal  $\text{M}_2\text{Fe}_3$  complexes ( $\text{M}=\text{Co},\text{Os}$ ) subject of the report by Klokishner et al. (Chap. 21) allows one to determine the type and temperature of spin transitions in spin clusters originating from the changes of the spin in a single metal ion or caused by charge transfer between different ions in the cluster. Based on a model by Kamimura and Suwa (interplay between Jahn-Teller physics and Mott physics) the mechanism of the high- $T_c$  superconductivity and a new phase diagrams of high- $T_c$  oxo-cuprates has been proposed (Chap. 22, Ushio et al.). Completing this part are two chapters on a vibronic theory of ferroelectric transitions in hydrogen bonded phosphates (Chap. 23, Levin et al.) and on virtual phonon exchange influence on the magnetic properties of Jahn-Teller crystals with Jahn-Teller centers in a triply degenerate electronic states (Chap. 24, Kaplan et al.).

The editors hope that this volume will be of valuable use for researchers working in the field of Jahn-Teller coupling and vibronic coupling and in all closely related experimental and theoretical disciplines of physics and chemistry.

M. Atanasov  
C.A. Daul  
P.L.W. Tregenna-Piggott\*

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\*It is with great sadness that we report the death of P.L.W. Tregenna-Piggott, the initiator of the Jahn-Teller Conference in 2010 and of the present volume.



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# Chapter 1

## Critical Review of Contributions to the Jahn-Teller Symposium JT2010 and Beyond

Isaac B. Bersuker

**Abstract** A review of some important problems presented at the XX International Symposium on the Jahn-Teller effect (JTE) is given, outlining also the author's view on some controversial issues. It is shown that the presentation of the pseudo JTE (PJTE) as a second order perturbation-theory correction (and hence called "second order JTE") is misleading. The PJTE is a two-level (multilevel) problem that can only be reduced to a second order perturbation in very limited cases when there is no term crossover or when the crossing between the interaction states is avoided. This statement is illustrated by several examples demonstrating also the possibilities of the PJTE as a tool for molecular and solid state problem solving. The possible reason of the puzzling, drastically different results obtained for the magnitude of tunneling splitting in the impurity system  $\text{MgO}:\text{Cu}^{2+}$  by experimental EPR measurements and theoretical ab initio calculations is discussed. More specifically, it is suggested that a reinterpretation of the experimental results is needed, while the calculations can be improved by taking into account the multimode nature of the problem. A brief discussion of the relation between orbital ordering and the cooperative JTE is given in view of a talk presented to the Symposium under an incorrect (wrong) title of "failure of the JTE physics". More elaborate is the controversy around the origin of ferroelectricity in perovskite type crystals, mostly  $\text{BaTiO}_3$ , discussed in a plenary talk to the Symposium. The vibronic PJT origin and order-disorder nature of the ferroelectric phase transitions in these crystals, predicted many years ago and presently fully confirmed experimentally, serves also as an indication of the predictive ability of the PJTE and should be

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recognized as such. Some historical notes were also made with regard of the JT origin of high-temperature superconductivity discussed in a plenary talk to the Symposium.

## 1.1 Introduction

This review paper resulted from the analysis of some up-to-date problems presented at the XX Symposium on the Jahn-Teller effect (JTE) and related issues, and prepared on request of the Organizing Committee. Obviously, only a few questions were reported in the talk to the Symposium and can be discussed in this paper of limited volume, and their choice is solely that of the author's.

In light of our experience in the field and of the presentations given at the Symposium, we found that one of the basic notions in the JTE theory, the pseudo JTE (PJTE), lacks both a precise definition and a unique interpretation in the current literature, leading to confusion and misunderstanding. Meanwhile, the PJTE has become one of the most important applications of the vibronic coupling theory which in many aspects surpasses the importance of the JTE itself. In this paper we tried to clarify this situation and demonstrate the importance of a proper understanding of the PJTE showing also several molecular and solid state examples from our papers illustrating this problem.

Another topic brought up at the Symposium is that one of tunneling splitting in JT systems, which was one of the first experimental demonstrations of the dynamical JTE predicted by the theory. A very puzzling situation emerged in the publications and in the contributions presented at the Symposium and related to the two-orders-of-magnitude difference between the experimentally (EPR) observed and ab initio calculated magnitude of the tunneling splitting in the impurity crystal  $\text{MgO} : \text{Cu}^{2+}$  which is subject to the JTE problem  $E \otimes e$ . We show here our perceived inconsistencies in the interpretation of the experimental data and the possible improvement to the calculations that could solve this embarrassing problem.

There is already some history in the relation between the problems of orbital ordering (OO) in crystals with electronically degenerate centers and the cooperative JTE (CJTE) in such systems. A part of it was discussed at the previous Symposium on the JTE in Heidelberg. Orbital ordering that ignores the vibronic coupling (the JTE) is an easy way to try to handle the problems of JT crystals, but in most cases it is not the correct way. As the local vibronic coupling is much stronger than the orbital-orbital interaction between metal centers (which are not adjacent), there is not much sense to consider the latter ignoring the former. In this context, the talk presented to the Symposium under title of "failure of the JTE physics" looks provocative. A brief critical discussion of this subject is given in this review.

More attention is devoted to the problem of vibronic origin of ferroelectricity in perovskite type crystals, which demonstrates the prediction abilities of the JTE

theory. Indeed, based on the vibronic theory (the PJTE), it was predicted that the fundamental property of ferroelectric phase transitions in so-called displacive ferroelectrics is triggered by the local vibronic coupling, being hence of order-disorder type, not displacive! This prediction was made when there was none experimental evidence that could confirm it, and therefore it was not well accepted at the time. Unfortunately, it remains obscure even now after full experimental confirmation of all basic predictions of the PJTE theory. There was a talk about this subject at the Symposium, and the present paper is to further defend this important contribution of the vibronic coupling theory and its prediction power.

Finally, the role of the JTE in the modern problem of high-temperature superconductivity (HTSC) presented at the Symposium by one of its two authors, K.A. Muller, is augmented here by some additional historical notes.

## 1.2 The Pseudo Jahn-Teller Effect: Definition, Understanding, and Misunderstanding

The theory of vibronic coupling defined as the coupling between electronic states and nuclear displacements has already a long history. Starting with the equilibrium configuration of the system in a non-degenerate electronic state and considering the nuclear displacements as a perturbation one can easily find that only totally symmetric vibrations contribute to the vibronic coupling because the matrix elements of lower symmetry displacements are zero by symmetry. This understanding has been dominating the vibronic coupling theory for many decades being widely used in molecular problems to explain vibrational implications in observable properties and, more elaborate, in solid state physics as electron-phonon interaction.

The situation became more complicated for some particular cases of molecular systems and local properties in crystals in degenerate electronic states after it was shown by Jahn and Teller [1] that in these cases the coupling to low-symmetry nuclear displacements is non-zero too, with the result that the starting high-symmetry configuration is no more in equilibrium with respect to the latter, it distorts spontaneously. This Jahn-Teller effect (JTE) has been developed forming now a whole trend which serves as a tool for problem solving when there is electronic degeneracy (see, e.g., in [2]). Obviously, a sufficiently small splitting of the electronic term that removes the degeneracy may not destroy completely the JTE (albeit modifying it), so the system remains unstable in this configuration and distorts spontaneously. This was shown by Opik and Pryce [3]. A small splitting at the point of crossing terms looks like a “pseudo crossing” (avoided crossing). Therefore the JTE in this situation is termed pseudo JTE (PJTE). Thus from the very beginning the PJTE was introduced as a two-level (multi-level) problem of a slightly destroyed degeneracy. If we denote the energy gap between

the two states  $|1\rangle$  and  $|2\rangle$  by  $\Delta$ , we get for the condition of instability of the ground state  $|1\rangle$  in the direction of the low-symmetry displacements  $Q$  induced by the PJT coupling to the excited state  $|2\rangle$  the following inequality ( $H$  is the Hamiltonian) [2, 3]:

$$K = K_0 + K_v = K_0 - \frac{F_{12}^2}{\Delta} < 0 \quad (1.1)$$

where

$$F_{12} = \left\langle 1 \left| \left( \frac{\partial H}{\partial Q} \right)_0 \right| 2 \right\rangle \quad (1.2)$$

$$K_0 = \left\langle 1 \left| \left( \frac{\partial^2 H}{\partial Q^2} \right)_0 \right| 1 \right\rangle \quad (1.3)$$

and

$$K_v = - \frac{|F_{12}|^2}{\Delta} \quad (1.4)$$

is the PJTE contribution to the curvature of the lower state.

Hence the initial understanding of the PJTE introduced by Opik and Pryce [3] was that it may produce instability similar to the JTE one, provided the  $\Delta$  value is sufficiently small. So the PJTE enlarged the applicability of the JTE adding to the particular cases of electronic degeneracy some more cases of “quasi-degeneracy” where the degeneracy is slightly removed. This understanding (“paradigm”) changed when it was shown that the energy gap  $\Delta$  in Eq. 1.4 is not a small parameter, it may be very large as the other parameters  $F$  and  $K_0$  in this inequality vary significantly [2, 4]. By means of ab initio calculations it was shown that PJT instability may be induced by excited states with energy gaps of tenths of electronvolts (for instance, the instability of planar  $\text{NH}_3$  is induced by the excited state at  $\Delta \sim 14\text{eV}$  [4]). Moreover, further developments in this understanding resulted in the *theorem of instability* which states that any instability of any polyatomic system in a high-symmetry configuration in a non-degenerate electronic state is due to and only to the PJTE. In the presentation of Eqs. 1.1–1.4, it was shown that  $K_0 > 0$  always, and hence instability may occur only due to the PJTE contribution  $|K_v| > K_0$  [2, 4, 5] (see also Sect. 1.5 below).

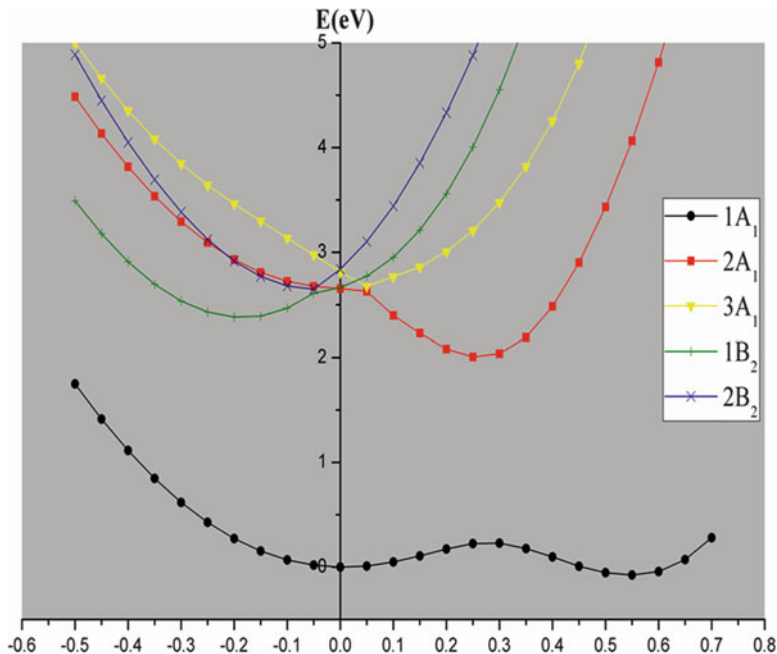
If there are many excited states that contribute to the instability of the ground state, then Eq. 1.4 in the linear approximation with respect to the vibronic coupling changes to  $K_v = \sum_n |F_{1n}|^2 / \Delta_{1n}$ , so the total PJT contribution to the instability becomes similar to a second order perturbation theory correction, provided the  $\Delta_{1n}$  values are sufficiently large. Second order perturbation corrections that lower the

curvature of the ground state under low-symmetry nuclear displacements have been well known before, irrelevant to the PJTE [6, 7]. They were employed to explain the softening of some molecular systems in the direction of chemical reactions. But for small  $\Delta_{1n}$  (in the sense of inequality (1.1)!) the perturbation theory becomes inapplicable and two-level (multi-level) problems should be formulated similar to the two-level case above.

The similarity to the second order perturbation formulas in some multilevel problems led to some controversies in terminology and interpretation of the PJTE in publications on this topic, including some presentations to this conference. An unacceptable statement is that the PJTE is a second order perturbation correction to the ground state often called *second order JTE*. This is not just a terminology issue. To begin with, it instills the impression that the PJTE is a small effect, smaller than the JTE, which, generally speaking, is wrong (see below). But the main failure of this definition is that it does not include the novel effects that are not possible in the JT presentation. In addition to the instability of the ground state which is similar to that of the JTE (but richer in its varieties) the PJTE may produce spin crossover that changes also the ground electronic state spin multiplicity, with far going consequences, in particular, in their magnetic and dielectric properties. There are no first and second order JTE, *both the JTE and the PJTE are induced by the first order vibronic coupling terms* in the Hamiltonian, but *are applied to different situations and produce different results* that may have some similar features.

The essential difference between the JTE and the PJTE is first of all in the different situations to which the vibronic coupling terms of the Hamiltonian are applied. While the JTE is applicable to limited classes of system with electronic degeneracy, the *PJTE is applicable to any polyatomic system without limitations*. In particular, the PJTE is present also in systems with the JTE, in which case there is no way to state that the PJTE is of second order (see below). The correct definition is that the PJTE is a nondegenerate two- or multi-level vibronic coupling problem (in case of more than two states some of them may be degenerate); in the particular case of only corrections to the ground state when there is no avoided crossing with the excited states (meaning the interaction between them is sufficiently small) the PJTE contribution can be estimated by means of the second order perturbation theory.

Let us illustrate the said above by some examples. In a recent publication on ab initio calculation of the CO<sub>3</sub> molecule [8] it was shown that involving the PJTE in a multilevel seven-state six-mode problem (that takes into account also the JTE in the excited states) we get the correct description of the adiabatic potentials energy surface (APES) with three equivalent global minima of C<sub>2v</sub> symmetry in addition to the more shallow minimum at the high-symmetry configuration D<sub>3h</sub> (Figs. 1.1 and 1.2). Note that starting with the latter configuration and involving second order perturbation theory we obtain just the curvature in the central minimum, but not the distorted configurations in the three global minima. This is also an example of the “hidden JTE” which we introduced earlier [9]; it emerges only when the excited

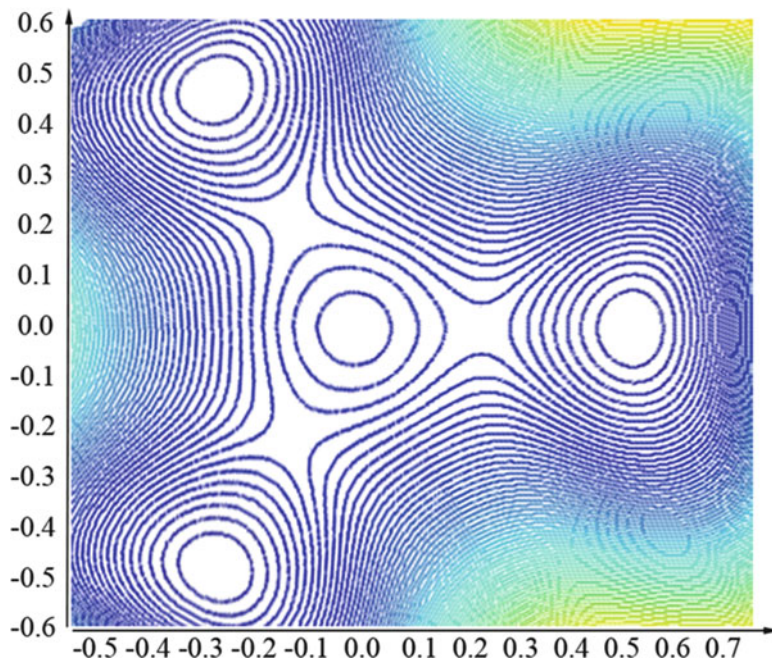


**Fig. 1.1** Ground  $1A_1$  and four excited states energy levels ( $2A_1$  and  $1B_2$ ,  $3A_1$  and  $2B_2$  correspond to  $E_1$  and  $E_2$  in  $D_{3h}$  symmetry, respectively) of  $\text{CO}_3$  in the cross section of the APES along the interaction mode  $q_\vartheta$  obtained by the MRCI+Q//SA-CASSCF (16/13) method of ab initio electronic structure calculations [8]

states (sometimes high in energy excited states) are involved in the problem via the JTE or PJTE.

Another example of the hidden JTE revealed by the PJTE is from a whole class of molecular systems and crystals with  $e^2$  and  $t^3$  electronic configurations. It was shown that in such systems a very strong PJTE between two excited electronic states in the high-symmetry configuration results in a spin crossover in which the lower component of the two PJT mixing states goes down and crosses the former ground state producing a global minimum with lower symmetry and changed spin multiplicity [10]. Figure 1.3 illustrates how these two minima are formed by the PJTE using the molecule  $\text{Si}_3$  as an example [10]. Similar to such two molecular configurations, two crystalline configurations (phases) may be produced by the PJTE in crystals with  $e^2$  or  $t^3$  centers; Fig. 1.4 shows the results of calculations performed for  $\text{LiCuO}_2$  [11] in which the  $\text{Cu}^{3+}$  centers have the electronic configuration  $e^2$ .

Finally, an example of the particular case when the PJTE can be taken into account by means of perturbation theory is illustrated in Table 1.1. It shows that when the two effects, JTE and PJTE, are present simultaneously the latter may be more important than the former. For a series of linear molecules in which there is no



**Fig. 1.2** Equipotential curves on the APES of the ground state of  $\text{CO}_3$  in the cross section of the  $(q_\theta, q_\epsilon)$  plane of the interaction  $e$  mode obtained by ab initio calculations with the BCCD(T) method. In the central shallower minimum the molecule has the undistorted  $D_{3h}$  configuration, whereas in the three equivalent global minima it is distorted to an acute triangular  $C_{2v}$  geometry

ground state crossing or avoided crossing with excited states ab initio calculation of the Renner-Teller effect (RTE) and the PJTE taken into account as a second order perturbation effect were performed [12].

The potential energy Hamiltonian in this case is (this equation and the values of  $g$  in Table 1.1 are formally different from that in Ref. [12] as the constant  $g$  there was defined as  $1/2$  of the present one):

$$\hat{U} = \frac{1}{2}(K_0 - p)(Q_x^2 + Q_y^2)\sigma_0 + \left(g - \frac{1}{2}p\right)[(Q_x^2 - Q_y^2)\sigma_z + 2Q_x Q_y \sigma_x] \quad (1.5)$$

where  $p$  and  $g$  are the PJTE and RTE contribution, respectively,  $K_0$  is the primary force constant defined in Eq. 1.3,  $\sigma_0$ ,  $\sigma_z$ , and  $\sigma_x$  are Pauli matrices, and  $Q_x$  and  $Q_y$  are the bending coordinates. The first term in Eq. 1.5 describes the bending and the second term stands for the term splitting. Hence the PJTE represented by the constant  $p$  influences both effects. From the results given in Table 1.1 we see that in all the cases under consideration the PJTE contribution  $p$  to both the instability of the ground state and the RTE splitting is significantly larger than the pure RTE splitting constant  $g$  [12]. For a JT ground state the Hamiltonian contains also linear