

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).

In the 1970s most of the further efforts in this field were devoted to spectroscopic consequences of the JTE (Chapter 6), as well as to cooperative phenomena in crystals (Sections 8.2 and 8.3). During the 1980s, alongside applications of the JTE to physical and chemical phenomena, new developments of the theory emerged. First, numerical calculations of vibronic coupling effects became more widespread, allowing a more detailed insight into observable JTE (here we stop citing the names of contributors because they are many; they can be found in the books and reviews cited below, as well as in the corresponding sections with more detailed description).

Among chemical applications attention was paid to the JTE in stereochemistry and chemical activation (Section 7.1), and in mixed-valence compounds (Section 7.6.2). In the general theory more attention was also paid to the multimode problem (Section 5.4). Quite a number of papers in the 1970s and 1980s were devoted to the JTE in impurity centers in crystals (Section 8.1). At this point the geography of JT symposia became more widespread and they attracted more participants: the Vth Symposium took place in Oxford (1980), the VIth in Nijmegen (1981), the VIIth in Liblice (1983), the VIIIth in Marburg (1985), the IXth in Nottingham (1987), the Xth in Kishinev (1989), the XIth in Ovronnaz (1992), the XIIth in Tartu (1994), the XIIIth in Berlin (1996), the XIVth in Erice (1998), the XVth in Boston (2000), and the XVIth in Leuven (2002), and an international workshop was organized in Beijing (2004).

The next important achievement of the theory was made by proving that the PJTE not only explains possible structural instabilities of systems in pseudo-degenerate electronic states, but also is the only possible source of instability of such systems (Section 4.1). Moreover, it was shown that any instability of high-symmetry configurations of any system is of JT (in degenerate states), PJT (in nondegenerate states), or RT (in linear systems) origin. With this result all polyatomic systems became subject to JT vibronic coupling effects, and any of their spontaneous distortions is of JT, PJT, or RT origin.

A new wave of increasing interest in the JTE emerged in the late 1980s and early 1990s following the discovery of high-temperature superconductivity, which was inspired by the JTE, and the colossal magnetoresistance, the origin of which is explained in essence by the JTE (Section 8.4). In the 1990s several other advances emerged in this field. First, the theory of the JTE was enriched by exploring its tight relation to the so-called topological phase problem (Section 5.7), with important consequences for observable properties of JT systems (Section 5.3). Also the JTE was shown to be very instrumental in explaining the properties of fullerenes, including their superconductivity (Sections 3.4, 5.6, and 7.5.3). Further achievements were reached in treating

phase transition with the CJTE (Section 8.2). Novel fields of applications emerged in reactivity and mechanisms of chemical reactions (Chapter 7).

Thus the evolution of understanding of the JTE went from the simple idea of spontaneous distortions of some very specific systems to a general method of solving molecular and crystal problems via revealing the complex JT dynamics, tunneling splitting, cooperative phenomena, and the essential role of the PJTE which includes all the polyatomic systems under the same JT vibronic coupling approach. The role and place of this approach in modern physics and chemistry is outlined in Section 1.2. Earlier stages of development of this field are presented in a series of books and reviews [1.22–1.57]; the intention of this book is to present a full account of the trend as a whole.

1.2 The role and place of the JTE in modern physics and chemistry

As mentioned in the previous section, in the evolution of understanding and development of the theory the JTE grew into a general approach to understanding and solving molecular and crystal problems. Now we intend to explain why this approach is different from other existing approaches and how they are interrelated.

First we notice that the main interaction which results in the JTE is the vibronic (electron–vibrational) coupling between electronic and nuclear motions. Vibronic interaction in molecules or electron–phonon interaction in crystals is one of the main elements of any theory of matter; it has been well studied since the very inception of quantum mechanics. So what is novel in the JT approach to the problem?

Consider polyatomic systems with discrete energy spectra. For them the essential difference between the usual approaches that include vibronic (or electron–phonon) coupling and the JT approach is in *the number of electronic states and hence the kind of vibrations* involved in this procedure. While the traditional approaches consider the coupling of phonons (vibrations) to a given (usually ground) electronic state, the JT approach requires necessarily two or more (degenerate or pseudodegenerate) electronic states that are mixed under these vibrations in a *nonadiabatic coupling*. In other words, the JTE involves *a new quality*, namely, the mixing of electronic states by vibrations, and the back influence of this mixing on the nuclear motion, resulting in special coupled electron–nuclear dynamics that influences all the properties of the polyatomic system.

Since the “one-state” coupling may be described by the diagonal matrix element of the operator of vibronic coupling, while the mixing of different electronic states is an off-diagonal (nonadiabatic) effect, the two

approaches, “usual” and JT, may be related as diagonal and off-diagonal vibronic (electron–phonon) coupling. The diagonal coupling is nonzero for totally symmetric vibrations only, and therefore they do not distort the symmetry of the system, whereas the off-diagonal elements involve low-symmetry JT distortions.

In the case of metals or semiconductors with states that are continuous or very close in energy the traditional theory includes all possible interactions with the phonons, but in a simplified manner without involving the nonadiabatic coupling between the electronic and nuclear motions. In other words the non-JT approach ignores the mixing of electronic states by nuclear displacements and the back influence of this mixing on the phonon spectrum. The JT electron–phonon coupling in metals involves many electronic states, which in our classification is a combination of JT (at the Fermi level) and PJT problems (Section 4.2). This is the so-called *band JTE* considered in Section 8.2.5.

An illustration of the JT approach to electron–phonon coupling in solids may be found in the modern attempts to explain the origin of high-temperature superconductivity (HTSC) (Section 8.4). Experimental data show that the electron–phonon interaction is essential in this phenomenon. The existing Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity takes into account the electron–phonon interaction “in general” as an interaction of the electrons with the “bath of phonons” without detailed analysis of the local aspects of this interaction leading to the JTE. As shown in Section 8.2.5, for broad-band metals with widely delocalized electrons the JT electron–phonon coupling is weak and the JTE may be ignored. This is why the BCS theory explains the origin of superconductivity at low temperatures without taking into account the JTE. For narrower bands (which are characteristic of systems with HTSC) the JTE becomes significant, and the application of the achievements of the JTE theory to the HTSC problem seems to be most appropriate. This is indeed the subject of most current attempts to treat the HTSC yielding reasonable (reassuring) results (Section 8.4).

Another important point is the *universality of JT symmetry breaking*. The most widespread knowledge about the JTE is that it results in distortion of high-symmetry configurations of polyatomic systems. As mentioned above, this statement may be inaccurate, but under certain conditions the JTE does indeed trigger a breaking of the high symmetry of the system (Sections 7.1 and 8.2). Symmetry breaking is an important phenomenon employed to explain the evolution of the universe by cooling, beginning from the big bang. In condensed matter (atoms, molecules, crystals) symmetry breaking looks like a phase transition that takes place under the condition that at a

certain temperature both the symmetry and the entropy of the system become lower at lower temperatures, and this condition is satisfied in the presence of the JTE (Sections 4.5 and 8.2). Moreover, since the JTE has been shown to be the only source of spontaneous distortion of high-symmetry configurations, we come to the conclusion that *the JTE is a unique mechanism of all the symmetry breakings in condensed matter* (Section 8.2).

With regard to computational chemistry and physics another question emerges. As follows from that said above and in more detail from Section 2.5, the JTE is basically a perturbational approach in which two or more electronic states are mixed by the vibronic coupling. The main result of this perturbation is the instability of the reference configuration meaning the lack of minimum on the APES at the point of degeneracy or pseudodegeneracy. On the other hand, modern computational (numerical) methods allow one to (relatively easily) calculate the APES with its main features including the extrema points. These computationally revealed features of the APES obviously cover the predictions of the JTE with regard to instabilities. Then where is the heuristic role of the JTE in these problems?

To begin with, numerical computations of APES are (so far) limited to molecular systems and clusters of moderate size and limited numbers of vibrational degrees of freedom, and this does not allow one to consider extended systems. The JTE has no such limitations, but this is not the main point of importance of the JTE. More important is the *general relevance of the JTE*. Indeed, it is well known that the mainstream computational chemistry calculations of electronic structure at fixed nuclei that reveal the APES of specific molecular systems may be regarded as (have all the features of) *computer experiments*; the results cannot be transferred directly to other molecules. To rationalize such computer data, i.e., to explain their origin, they should be put in correspondence with more general models obtained by simplification and reasonable assumptions introduced in the first principles. *The JTE serves as an approved general model, which allows one to rationalize the results on molecular structure and properties obtained by other methods.*

Note that in the presence of degeneracy or pseudodegeneracy conventional electronic structure calculations with fixed nuclei, strictly speaking, do not predict observable properties; the calculated APES in these cases loses its physical meaning of the potential energy of the nuclei because of the strong nonadiabaticity (Sections 2.1 and 2.5). The vibronic coupling theory thus remains here the only criterion of reliability of the results. To calculate observable magnitudes, the system of coupled equations (2.6) should be solved, and this contributes to a higher level of computational chemistry and physics.

1.3 Main goals of this book and means of their realization

The main goal of this book is to present a generalized picture of the status quo in the theory and applications of the JTE with a stronger emphasis on the latest achievements. Following the request of the publisher and our experience with previous books on related subjects, the presentation of the material is given in a way suitable for a wide circle of college-level physicists and chemists. This means that we avoid bulky mathematical deductions (or give them in a way that they may be skipped, if not necessary) and restrict heavy professional language, where possible. On the other hand, detailed citations and a full list of references to each chapter are included to allow the reader to go to original work for more details, if necessary. With regard to the citations (of which there are thousands) we tried to avoid listing the authors' names in the text (but they are all given in the citations!). Several names mentioned above in the brief history are exceptions made for the "founders" of this trend, meaning people who contributed essentially to the first stages of its development; without their names there is no history of this subject.

The material of this book is arranged as follows. Chapter 2 introduces the problem of vibronic coupling and the JT theorem. Chapters 3 and 4 formulate in general the JT, PJT, and RT problems and reveal their APES, while Chapter 5 discusses the solutions of the JT problems, including perturbation theory, numerical methods, tunneling splitting, the multimode problem, vibronic reduction factors, and the topological phase implications.

The theoretical background of the JTE in one of the most widely used experimental methods of investigation – spectroscopy – is given in Chapter 6. Chapter 7 (largest in volume and number of cited publications) deals with all kinds of applications of the JT theory to specific molecular formations, including molecules, radicals, and ions from different classes of compounds, plus clusters, coordination compounds, and mixed-valence systems, as well as some more general chemical problems. Chapter 8 is devoted to specific JT problems in solid-state physics, including impurity centers in crystals, the cooperative JTE in phase transitions (the largest part of the chapter), and contributions to the JTE in HTSC and colossal magnetoresistance.

The appendix, subject index and formula index are deemed to help the reader navigate through the vast material of this book with a large number of cross-references. The Formula Index is of special interest, allowing the reader to easily find the specific molecular and solid-state systems considered with regard to the JTE, thus contributing to the attempt to introduce encyclopedia features with regard to the trend under consideration. The list of abbreviations is intended to play a similar helpful role.

References

- 1.1. H. A. Jahn and E. Teller, *Proc. R. Soc. London A* **161**, 220 (1937).
- 1.2. H. A. Jahn, *Proc. R. Soc. London A* **164**, 117 (1938).
- 1.3. R. Renner, *Z. Phys.* **92**, 172 (1934).
- 1.4. E. Teller, in R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, London, Wiley, 1972 (Foreword); *Electron–Phonon Dynamics and Jahn–Teller Effects*, Eds. G. Bevilacqua, L. Martinelli, and N. Terzi, Singapore, World Scientific, 1999, p. 1; and in *Vibronic Interactions: Jahn–Teller Effect in Crystals and Molecules*, Eds. M. D. Kaplan and G. O. Zimmerman, NATO Science Series II, Vol. 39, Dordrecht, Kluwer, 2001, p. 1.
- 1.5. J. von Neumann and E. Wigner, *Phys. Z.* **30**, 467 (1929).
- 1.6. J. H. Van Vleck, *J. Chem. Phys.* **7**, 61 (1939).
- 1.7. W. Low, *Paramagnetic Resonance in Solids*, New York, Academic Press, 1960.
- 1.8. A. Abragam and M. H. L. Pryce, *Proc. R. Soc. London A* **63**, 409 (1950).
- 1.9. B. Bleaney and D. J. F. Ingram, *Proc. Phys. Soc. A* **63**, 408 (1950).
- 1.10. U. Öpik and M. H. L. Pryce, *Proc. R. Soc. London A* **238**, 425 (1957).
- 1.11. H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, *Proc. R. Soc. London A* **244**, 1 (1958).
- 1.12. W. Moffitt and W. Thorson, *Phys. Rev.* **108**, 1251 (1957).
- 1.13. A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N.Y.)* **3**, 304 (1958).
- 1.14. *The Jahn–Teller Effect. A Bibliographic Review*, Ed. I. B. Bersuker, New York,IFI/Plenum, 1984.
- 1.15. I. B. Bersuker, *Opt. Spektrosk.* **11**, 319 (1961); *Zh. Eksp. Teor. Fiz.* **43**, 1315 (1962) (English transl.: *Sov. Phys. – JETP* **16**, 933 (1963)); **44**, 1238 (1963).
- 1.16. M. C. M. O'Brien, *Proc. R. Soc. London A* **281**, 323 (1964).
- 1.17. F. S. Ham, *Phys. Rev.* **138**, 1727 (1965).
- 1.18. J. Kanamori, *J. Appl. Phys.* **31**, 14 (1960).
- 1.19. R. J. Elliot, R. T. Harley, W. Hayes, and S. R. P. Smith, *Proc. R. Soc. London A* **328**, 217 (1972).
- 1.20. I. B. Bersuker, *Phys. Lett. A* **20**, 589 (1966).
- 1.21. R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, London, Wiley, 1972.
- 1.22. M. D. Sturge, *The Jahn–Teller Effect in Solids*, in *Solid State Physics*, Vol. 20, Eds. F. Seitz, D. Turnbull, and H. Ehrenreich, New York, Academic Press, 1967.
- 1.23. I. B. Bersuker, *Coord. Chem. Rev.* **14**, 357 (1975).
- 1.24. I. B. Bersuker, B. G. Vekhter, and I. Ya. Ogurtsov, *Uspekhi Fiz. Nauk (Sov. Phys. – Uspekhi)* **116**, 605 (1975).
- 1.25. J. Gazo, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, M. Langfelderova, M. Melnik, M. Serator, and F. Valach, *Coord. Chem. Rev.* **19**, 253 (1976).
- 1.26. F. S. Ham, in *Electron Paramagnetic Resonance*, Ed. S. Geschwind, New York, Plenum, 1972.
- 1.27. D. Reinen and C. Friebel, *Struct. Bonding* **37**, 1 (1979).
- 1.28. L. K. Burdett, *Molecular Shapes. Theoretical Models of Inorganic Stereochemistry*, New York, Wiley, 1980.
- 1.29. I. B. Bersuker and V. Z. Polinger, *Adv. Quant. Chem.* **15**, 85 (1982).
- 1.30. *Dynamical Jahn–Teller Effect in Localized Systems*, Eds. Yu. E. Perlin and M. Wagner, Amsterdam, Elsevier, 1984.