THE ROLE OF DEGENERATE STATES IN CHEMISTRY

ADVANCES IN CHEMICAL PHYSICS
VOLUME 124

Edited by

MICHAEL BAER and GERT DUE BILLING

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A SPECIAL VOLUME OF ADVANCES IN CHEMICAL PHYSICS

VOLUME 124

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

I. Prigogine
Stuart A. Rice

INTRODUCTION TO THE ADVANCES OF CHEMICAL PHYSICS VOLUME ON:

THE ROLE OF DEGENERATE STATES IN CHEMISTRY

The study of molecular systems is based on the Born–Oppenheimer *treatment*, which can be considered as one of the most successful theories in physics and chemistry. This treatment, which distinguishes between the fast-moving electrons and the slow-moving nuclei leads to electronic (adiabatic) eigenstates and the non-adiabatic coupling terms. The existence of the adiabatic states was verified in numerous experimental studies ranging from photochemical processes through photodissociation and unimolecular processes and finally bimolecular interactions accompanied by exchange and/or charge-transfer processes. Having the well-established adiabatic states many studies went one step further and applied the Born–Oppenheimer *approximation*, which assumes that for low enough energies the dynamics can be carried out on the lower surface only, thus neglecting the coupling to the upper states. Although on numerous occasions, this approximation was found to yield satisfactory results, it was soon realized that the relevance of this approximation is quite limited and that the interpretation of too many experiments whether based on spectroscopy or related to scattering demand the inclusion of several electronic states. For a while, it was believed that perturbation theory may be instrumental in this respect but this idea was not found in many cases to be satisfactory and therefore was only rarely employed.

In contrast to the successful introduction, of the electronic adiabatic states into physics and mainly into chemistry, the incorporation of the complementary counterpart of the Born–Oppenheimer treatment, that is, the electronic non-adiabatic coupling terms, caused difficulties (mainly due to their being “extended” vectors) and therefore were ignored. The non-adiabatic coupling terms are responsible for the coupling between the adiabatic states, and since for a long time most studies were related to the ground state, it was believed that the Born–Oppenheimer approximation always holds due to the weakness of the non-adiabatic coupling terms. This belief persisted although it was quite early recognized, due to the Hellmann–Feynman theorem, that non-adiabatic coupling terms are not necessarily weak, on the contrary, they may be large and eventually become infinite. They become infinite (or singular) at those instances when two successive adiabatic states turn out to be degenerate. Having singular non-adiabatic coupling terms not only leads to the breakdown of the Born–Oppenheimer approximation but also rules out the possibility of keeping it while applying perturbation theory. Nevertheless the Born–Oppenheimer approximation can be partly "saved," in particular while studying low-energy processes, by extending it to include the relevant non-adiabatic coupling terms. In this way, a new equation is obtained, for which novel methods to solve it were developed—some of them were discussed in this volume.

This volume in the series of *Advances of Chemical Physics* centers on studies of effects due to electronic degenerate states on chemical processes. However, since the degenerate states affect chemical processes via the singular non-adiabatic coupling terms, a major part of this volume is devoted to the study of features of the non-adiabatic coupling terms. This is one aspect related to this subject. Another aspect is connected with the Born–Oppenheimer Schrödinger equation which, if indeed degenerate states are common in molecular systems, frequently contains singular terms that may inhibit the possibility of solving this equation within the original Born–Oppenheimer adiabatic framework. Thus, an extensive part of this volume is devoted to various transformations to another framework—the diabatic framework—in which the adiabatic coupling terms are replaced by potential coupling—all analytic smoothly behaving functions.

In Chapter I, Child outlines the early developments of the theory of the geometric phase for molecular systems and illustrates it primarily by application to doubly degenerate systems. Coverage will include applications to given to $(E \times \epsilon)$ Jahn–Teller systems with linear and quadratic coupling, and with spin–orbit coupling. The origin of vector potential modifications to the kinetic energy operator for motion on well-separated lower adiabatic potential surfaces is also be outlined.

In Chapter II, Baer presents the transformation to the diabatic framework via a matrix—the adiabatic-to-diabatic transformation matrix—calculated employing a line-integral approach. This chapter concentrates on the theoretical–mathematical aspects that allow the rigorous derivation of this transformation matrix and, following that, the derivation of the diabatic potentials. An interesting finding due to this treatment is that, once the non-adiabatic coupling terms are arranged in a matrix, this matrix has to fulfill certain *quantization* conditions in order for the diabatic potentials to be single valued. Establishing the quantization revealed the existence of the topological matrix, which contains the topological features of the electronic manifold as related to closed contours in configuration space. A third feature fulfilled by the non-adiabatic coupling matrix is the curl equation, which is reminiscent of the Yang–Mills field. This suggests, among other things, that *pseudomagnetic* fields may "exist" along *seams* that are the lines formed by the singular points of the non-adiabatic coupling terms. Finally, having the curl equation leads to the proposal of calculating non-adiabatic coupling terms by solving this equation rather than by performing the tedious ab initio treatment. The various theoretical derivations are accompanied by examples that are taken from *real* molecular systems.

In Chapter III, Adhikari and Billing discuss chemical reactions in systems having conical intersections. For these situations they suggest to incorporate the effect of a geometrical phase factor on the nuclear dynamics, even at energies well below the conical intersection. It is suggested that if this phase factor is incorporated, the dynamics in many cases, may still be treated within a one-surface approximation. In their chapter, they discuss the effect of this phase factor by first considering a model system for which the two-surface problem can also easily be solved without approximation. Since many calculations involving heavier atoms have to be considered using approximate dynamical theories such as classical or quantum classical, it is important to be able to include the geometric phase factor into these theories as well. How this can be achieved is discussed for the three-particle problem. The connection between the so-called extended Born–Oppenheimer approach and the phase angles makes it possible to move from two-surface to multisurface problems. By using this approach a three-state model system is considered. Finally, the geometric phase effect is formulated within the so-called quantum dressed classical mechanics approach.

In Chapter IV, Englman and Yahalom summarize studies of the last 15 years related to the Yang–Mills (YM) field that represents the interaction between a set of nuclear states in a molecular system as have been discussed in a series of articles and reviews by theoretical chemists and particle physicists. They then take as their starting point the theorem that when the electronic set is complete so that the Yang–Mills field intensity tensor vanishes and the field is a pure gauge, and extend it to obtain some new results. These studies throw light on the nature of the Yang–Mills fields in the molecular and other contexts, and on the interplay between diabatic and adiabatic representations.

In Chapter V, Kuppermann and Abrol present a detailed formulation of the nuclear Schrödinger equation for chemical reactions occurring on multiple potential energy surfaces. The discussion includes triatomic and tetraatomic systems. The formulation is given in terms of hyperspherical coordinates and accordingly the scattering equations are derived. The effect of first and second derivative coupling terms are included, both in the adiabatic and the diabatic representations. In the latter, the effect of the non-removable (transverse) part of the first derivative coupling vector are considered. This numerical treatment led, finally, to the potential energy surfaces that are then employed for the scattering calculations. The coverage includes a detailed asymptotic analysis and expressions for the reactive scattering matrices, the associated scattering amplitudes and differential cross-sections. The inclusion of the geometric phase in these equations is discussed, as well as results of representative calculations.

In Chapter VI, Ohrn and Deumens present their electron nuclear dynamics (END) time-dependent, nonadiabatic, theoretical, and computational approach to the study of molecular processes. This approach stresses the analysis of such processes in terms of dynamical, time-evolving states rather than stationary molecular states. Thus, rovibrational and scattering states are reduced to less prominent roles as is the case in most modern wavepacket treatments of molecular reaction dynamics. Unlike most theoretical methods, END also relegates electronic stationary states, potential energy surfaces, adiabatic and diabatic descriptions, and nonadiabatic coupling terms to the background in favor of a dynamic, time-evolving description of all electrons.

In Chapter VII, Worth and Robb discuss techniques known as direct, or on-the-fly, molecular dynamics and their application to non-adiabatic processes. In contrast to standard techniques, which require a predefined potential energy surfaces, here the potential function, is provided by explicit evaluation of the electronic wave function for the states of interest. This fact makes the method very general and powerful, particularly for the study of polyatomic systems where the calculation of a multidimensional potential function is expected to be a complicated task. The method, however, has a number of difficulties that need to be solved. One is the sheer size of the problem—all nuclear and electronic degrees of freedom are treated explicitly. A second is the restriction placed on the form of the nuclear wave function as a local- or trajectory-based representation is required. This introduces the problem of including quantum effects into methods that are often based on classical mechanics. For non-adiabatic processes, there is the additional complication of the treatment of the non-adiabatic coupling. In this chapter these authors show how progress has been made in this new and exciting field, highlighting the different problems and how they are being solved.

In Chapter VIII, Haas and Zilberg propose to follow the phase of the total electronic wave function as a function of the nuclear coordinates with the aim of locating conical intersections. For this purpose, they present the theoretical basis for this approach and apply it for conical intersections connecting the two lowest singlet states (S_1 and S_0). The analysis starts with the Pauli principle and is assisted by the permutational symmetry of the electronic wave function. In particular, this approach allows the selection of two coordinates along which the conical intersections are to be found.

In Chapter IX, Liang et al. present an approach, termed as the "crude Born–Oppenheimer approximation," which is based on the Born–Oppenheimer approximation but employs the straightforward perturbation method. Within their chapter they develop this approximation to become a practical method for computing potential energy surfaces. They show that to carry out different orders of perturbation, the ability to calculate the matrix elements of the derivatives of the Coulomb interaction with respect to nuclear coordinates is essential. For this purpose, they study a diatomic molecule, and by doing that demonstrate the basic skill to compute the relevant matrix elements for the Gaussian basis sets. Finally, they apply this approach to the H_2 molecule and show that the calculated equilibrium position and force constant fit reasonable well those obtained by other approaches.

In Chapter X, Matsika and Yarkony present an algorithm for locating points of conical intersection for odd electron molecules. The nature of the singularity at the conical intersection is determined and a transformation to *locally* diabatic states that eliminates the singularity is derived. A rotation of the degenerate electronic states that represents the branching plane in terms of mutually orthogonal vectors is determined, which will enable us to search for confluences intersecting branches of a single seam.

In Chapter XI, Perić and Peyerimhoff discuss the Renner–Teller coupling in triatomic and tetraatomic molecules. For this purpose, they describe some of their theoretical tools to investigate this subject and use the systems FeH_2, CNC, and HCCS as adequate examples.

In Chapter XII, Varandas and Xu discuss the implications of permutational symmetry on the total wave function and its various components for systems having sets of identical particles. By generalizing Kramers' theorem and using double group theory, some drastic consequences are anticipated when the nuclear spin quantum number is one-half and zero. The material presented may then be helpful for a detailed understanding of molecular spectra and collisional dynamics. As case studies, they discuss, in some detail, the spectra of trimmeric species involving ^2S atoms. The effect of vibronic interactions on the two conical intersecting adiabatic potential energy surfaces will then be illustrated and shown to have an important role. In particular, the implications of the Jahn–Teller instability on the calculated energy levels, as well as the involved dynamic Jahn–Teller and geometric phase effects, will be examined by focusing on the alkali metal trimmers. This chapter was planned to be essentially descriptive, with the mathematical details being gathered on several appendixes.

MICHAEL BAER
GERT DUE BILLING

CONTENTS

EARLY PERSPECTIVES ON GEOMETRIC PHASE

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CONTENTS

I. INTRODUCTION

Subsequent chapters deal largely with developments in the theory of geometric phase and non-adiabatic coupling over the past 10 years, but the editors agreed with me that there would be some value in including a chapter on early contributions to the field, to provide a historical perspective. No doubt the choice of material will seem subjective to some. Others will find it redundant to repeat well-established results in an "Advances" volume, but this chapter is not addressed to the experts; it is primarily intended for students seeking a pedagogical introduction to the subject. Discussion is limited to what is now known as the quantal adiabatic (Longuet-Higgins or Berry) phase, associated with motion on a single adiabatic electronic surface, on the assumption that the nuclear motion occurs far from any points of electronic degeneracy. The geometric phase and an associated vector potential term in the nuclear kinetic energy operator will be seen to arise from the presence of singularities in the non-adiabatic coupling operator, at so-called conical intersection points, but the wave function will appear as a product of a single electronic and a single nuclear factor.

The story begins with studies of the molecular Jahn–Teller effect in the late 1950s [1–3]. The Jahn–Teller theorems themselves [4,5] are 20 years older and static Jahn–Teller distortions of electronically degenerate species were well known and understood. Geometric phase is, however, a dynamic phenomenon, associated with nuclear motions in the vicinity of a so-called conical intersection between potential energy surfaces.

The simplest and most widely studied case is the $E \times \epsilon$ Jahn–Teller model [2,6,7] for which a double degeneracy at say an equilateral triangular geometry is relieved *linearly* by nuclear distortions in a doubly degenerate nuclear vibration. In the language of later discussions [8], the nuclear coordinates Q define a two-dimensional (2D) parameter space containing the intersection point Q_0, and the geometric phase is associated with evolution of the real adiabatic electronic eigenstates, say $|x_+(Q)\rangle$ and $|x_-(Q)\rangle$, on parameter paths around Q_0. The important points are that $|x_\pm(Q)\rangle$ are undefined at Q_0, but that they can be taken elsewhere as smooth functions of Q, in the sense that $\langle x_\pm(Q)|x_\pm(Q+\delta Q)\rangle \to 1$ as $\delta Q \to 0$, over any region free of other degeneracies. It is then a simple matter to demonstrate that the linearity of the separation between the two adiabatic potential surfaces, say $W_\pm(Q)$, also requires a sign change in $|x_\pm(Q)\rangle$, as they are transported around Q_0 [2,6,7]. Note that there is no corresponding geometric phase associated with symmetry determined electronic degeneracies in linear molecules for which the degeneracy is relieved quadratically in the bending coordinate [9]; in other words the two linear molecule adiabatic potential surfaces touch at Q_0 but do not intersect. Conical intersections, with associated geometric phase, do, however, arise at accidental degeneracies in linear molecules, between, for example, Σ and Π electronic states [6]; they can also occur in quite general geometries for nonsymmetric species, such as NaKRb. The latter were taken by Longuet-Higgins [7] as test cases to resolve a controversy over the “noncrossing rule” in polyatomics.

The next significant development in the history of the geometric phase is due to Mead and Truhlar [10]. The early workers [1–3] concentrated mainly on the spectroscopic consequences of localized non-adiabatic coupling between the upper and lower adiabatic electronic eigenstates, while one now speaks of the geometric phase associated with a well-separated lower adiabatic surface, such that the nuclear motions revolve around the intersection point Q_0, without passing close to it. Longuet-Higgins et al. [2] treat this situation in a linear coupling approximation, but Mead and Truhlar [10] were the first to provide a systematic formulation. Any treatment must recognize that the nature of the nuclear wave function is necessarily affected by the electronic sign change, since the total wave function must be a single-valued function of Q. This means either that the boundary conditions on the nuclear wave function must incorporate a compensating sign change for circuits around Q_0 or that the real adiabatic eigenstates, $|x_\pm\rangle$, must be defined with compensating phase factors, such that

$$|n_\pm\rangle = e^{i\psi_\pm(Q)}|x_\pm\rangle$$

is single valued around Q_0. Ham [11] analyses the ordering of vibronic eigenvalues in the presence of geometric phase from the former standpoint, while Mead and Truhlar [10] adopt the latter formulation, which leads to a *vector potential* contribution to the nuclear kinetic energy, dependent on the form of the chosen phase factor $\psi(Q)$. Residual arbitrariness in the choice of $\psi_\pm(Q)$, subject to the single valuedness of $|n_\pm\rangle$, must cancel out in any consistent treatment of the nuclear dynamics.

Berry [8] set the theory in a wider context, by defining a "gauge invariant" geometric phase, which is specific to the system in question and to the geometry of the chosen encircling path, but is also independent of the above residual arbitrariness. The resulting integrated geometric phase applies to quite general situations, provided there is a single isolated point of degeneracy. The degeneracy need not be twofold, nor need the encircling path lie in the plane containing Q_0, as demonstrated by Berry's [8] explicit treatment of angular momentum precession, with arbitrary $2J + 1$ degeneracy, in a slowly rotating magnetic field.

Macroscopic physical manifestations of the above adiabatic geometric phase may be found in the Aharonov–Bohm effect [12] and in nuclear magnetic resonance (NMR) systems subject to slowly rotating magnetic fields [13]. Their observation in molecular systems is less straightforward. Books have been written about the multisurface dynamics of Jahn–Teller systems [14,15], but effects attributable to the geometric phase on the lowest adiabatic potential surface are quite elusive. One example is an observed energy level dependence on the square of a half-odd quantum number, j, in Na_3 [16,17], as first predicted by Longuet-Higgins et al. [2]. It depends, however, on the assumption of strictly linear Jahn–Teller coupling, because j is conserved only in the absence of corrugations on the lower surface arising from the inclusion of quadratic and higher Jahn–Teller coupling terms (see Sections V.A and V.C). The strongest general prediction, for C_3 point groups, is that geometric phase causes a systematic inversion in the vibronic tunneling splitting associated with the above corrugations [11]; thus the levels of the lowest vibronic triplet are predicted in the order $E(E) < E(A)$, an order that is successively reversed and restored in the higher triplets. The possible observation of similar geometric phase related effects in molecular scattering situations is discussed in several of the following chapters.

Section II begins with a general discussion of conical intersections, including deductions from the point group and time-reversal symmetries, concerning connections between the nuclear coordinate dependencies of different electronic Hamiltonian matrix elements. Section III is concerned with the nature of electronic adiabatic eigenstates close to a conical intersection. The crucial result for later sections is that an $E \times \epsilon$ conical intersection gives rise to an adiabatic eigenvector sign change regardless of the size and shape of the encircling loop, provided that no other degenerate points are enclosed. Specifically, geometrical aspects of adiabatic eigenvector evolution are discussed in Section IV, along the lines of papers by Berry [8] and Aharonov et al. [18]. Different expressions for its evaluation are also outlined. Various aspects of the $E \times \epsilon$ Jahn–Teller problem, with linear and quadratic coupling, including and excluding spin–orbit coupling, are outlined in Section V. More general aspects of the nuclear dynamics on the lower potential sheet arising from a conical intersection are treated in Section VI, from two viewpoints. Section VI.A expounds Ham's general conclusions about the order of vibronic tunneling levels from a band theory standpoint [11], with sign-reversing boundary conditions on the nuclear wave functions. There is also an appendix for readers unfamiliar with Floquet theory arguments. By contrast, Section VI.B outlines the elements of Mead and Truhlar's theory [10], with normal boundary conditions on the nuclear wave function and a vector potential contribution to the nuclear kinetic energy, arising from the compensating phase factor $\psi(Q)$, which was discussed above. The relationship between the contributions of Aharonov et al. [18] and Mead and Truhlar [10] are described. Aspects of the symmetry with respect to nuclear spin exchange in the presence of geometric phase are also discussed. Section VII collects the main conclusions and draws attention to related early work on situations with greater complexity than the simple $E \times \epsilon$ problem.

II. CONICAL INTERSECTIONS

Molecular aspects of geometric phase are associated with *conical intersections* between electronic energy surfaces, $W(Q)$, where Q denotes the set of say k vibrational coordinates. In the simplest two-state case, the $W(Q)$ are eigensurfaces of the nuclear coordinate dependent Hermitian electronic Hamiltonian matrix,

$$H(Q) = \begin{pmatrix} H_{\mathrm{AA}}(Q) & H_{\mathrm{AB}}(Q) \\ H_{\mathrm{BA}}(Q) & H_{\mathrm{BB}}(Q) \end{pmatrix} \tag{1}$$

namely,

$$W_{\pm}(Q) = \frac{1}{2}[H_{\mathrm{AA}}(Q) + H_{\mathrm{BB}}(Q)] \pm \frac{1}{2}\sqrt{[H_{\mathrm{AA}}(Q) - H_{\mathrm{BB}}(Q)]^2 + 4|H_{\mathrm{AB}}(Q)|^2} \tag{2}$$

Strict degeneracy between the electronic energy surfaces therefore requires the existence of points Q_0 at which $H_{\mathrm{AA}}(Q) = H_{\mathrm{BB}}(Q)$ and $H_{\mathrm{AB}}(Q) = 0$. These two independent conditions will rarely occur by variation of a single coordinate Q [unless $H_{\mathrm{AB}}(Q) = 0$ by symmetry]—hence the diatomic "noncrossing rule." There is, however, no such prohibition in polyatomics. In the common case of a real representation, degeneracies can clearly lie on a surface of dimensionality $k - 2$, where k is the number of vibrations [6,7,19,20]. They are termed *conical* if $H_{\mathrm{AA}}(Q) - H_{\mathrm{BB}}(Q)$ and $H_{\mathrm{AB}}(Q)$ vanish linearly in Q. Such points are symmetry determined for Jahn–Teller systems [4], which include all electronically degenerate nonlinear polyatomics. They also occur as a result of bending at, say a $\Sigma - \Pi$ intersection in a linear molecule [6], and at more general configurations of nonsymmetrical species. For example, Longuet-Higgins [7] shows that Heitler–London theory for a system of three dissimilar H-like atoms, such as LiNaK, has a pair of doublet states with eigensurfaces governed by the Hamiltonian matrix

$$H = \begin{pmatrix} W - \alpha + \frac{1}{2}(\beta + \gamma) & \sqrt{\frac{3}{2}}(\beta - \gamma) \\ \sqrt{\frac{3}{2}}(\beta - \gamma) & W + \alpha - \frac{1}{2}(\beta + \gamma) \end{pmatrix} \tag{3}$$

where α, β, and γ are exchange integrals for the three interatomic bonds. A conical intersection therefore occurs at geometries such that $\alpha = \beta = \gamma$, which again implies two independent constraints.

Aspects of the Jahn–Teller symmetry argument will be relevant in later sections. Suppose that the electronic states are n-fold degenerate, with symmetry Γ_e at some symmetrical nuclear configuration Q_0. The fundamental question concerns the symmetry of the nuclear coordinates that can split the degeneracy linearly in $Q - Q_0$, in other words those that appear linearly in Taylor series for the n^2 matrix elements $\langle A|H|B\rangle$. Since the bras $\langle A|$ and kets $|B\rangle$ both transform as Γ_e and H are totally symmetric, it would appear at first sight that the Jahn–Teller active modes must have symmetry $\Gamma_Q = \Gamma_e \times \Gamma_e$. There are, however, further restrictions, dependent on whether the number of electrons is even or odd. The following argument [4,5] uses the symmetry of the electronic states under the time-reversal operator $\hat{T}$ to establish general relations between the various matrix elements. The essential properties are that $\hat{T}$ commutes with the Hamiltonian

$$\hat{H}\hat{T} = \hat{T}\hat{H}; \tag{4}$$

that any state $|A\rangle$ has a time-reverse $\hat{T}|A\rangle$, such that

$$\langle \hat{T}\beta|\hat{T}\alpha\rangle = \langle\beta|\alpha\rangle^*; \tag{5}$$

and that states with even and odd electrons are symmetric and antisymmetric under $\hat{T}^2$, respectively. It therefore follows that

$$\begin{aligned}\langle A|H|\hat{T}B\rangle &= \langle \hat{T}A|\hat{T}H\hat{T}B\rangle^* = \langle \hat{T}A|H|\hat{T}^2\beta\rangle^* = \pm\langle B|H|\hat{T}A\rangle \\ &= \frac{1}{2}\left(\langle A|H|\hat{T}B\rangle \pm \langle B|H|\hat{T}A\rangle\right)\end{aligned} \tag{6}$$

where the upper and lower signs apply for even and odd electron systems, respectively.

Suppose now that $|A\rangle$ and $|B\rangle$ belong to an electronic representation Γ_e. Since H is totally symmetric, Eq. (6) implies that the matrix elements $\langle A|H|\hat{T}B\rangle$ belong to the representation of symmetrized or anti-symmetrized products of the bras $\{\langle A|\}$ with the kets $\{|\hat{T}A\rangle\}$. However, the set $\{|\hat{T}A\rangle\}$ is, however, simply a reordering of the set $\{|A\rangle\}$. Hence, the symmetry of the matrix elements in the even- and odd-electron cases is given, respectively, by the symmetrized $[\Gamma_e \times \Gamma_e]$ and antisymmetrized $\{\Gamma_e \times \Gamma_e\}$ parts of the direct product of Γ_e with itself. A final consideration is that coordinates belonging to the totally symmetric representation, Γ_0, cannot break any symmetry determined degeneracy. The symmetries of the Jahn–Teller active modes are therefore given by

$$\begin{aligned}&\Gamma_Q \subset [\Gamma_e \times \Gamma_e] - \Gamma_0 \qquad \text{for even electron systems} \\ &\Gamma_Q \subset \{\Gamma_e \times \Gamma_e\} - \Gamma_0 \qquad \text{for odd electron systems}\end{aligned}$$

This is the central Jahn–Teller [4,5] result. Three important riders should be noted. First, $\Gamma_Q = 0$ for spin-degenerate systems, because $\{\Gamma_e \times \Gamma_e\} = \Gamma_0$. This is a particular example of the fact that Kramer's degeneracies, arising from spin alone can only be broken by magnetic fields, in the presence of which H and $\hat{T}$ no longer commute. Second, a detailed study of the molecular point groups reveals that all degenerate nonlinear polyatomics, except those with Kramer's degeneracy, have at least one vibrational coordinate covered by the above rules. Finally, no linear polyatom has such coordinates. Hence, there are no symmetry determined conical intersections in linear molecules. The leading vibronic coupling terms are quadratic in the nuclear coordinates, giving rise to a Renner–Teller [9] rather than a Jahn–Teller effect.

The symmetry argument actually goes beyond the above determination of the symmetries of Jahn–Teller active modes, the coefficients of the matrix element expansions in different coordinates are also symmetry determined. Consider, for simplicity, an electronic state of symmetry E in an even-electron molecule with a single threefold axis of symmetry, and choose a representation in which two complex electronic components, $|e_\pm\rangle = 1/\sqrt{2}(|e_\mathrm{A}\rangle \pm i|e_\mathrm{B}\rangle)$, and two degenerate complex nuclear coordinate combinations $Q_\pm = re^{\pm i\phi}$ each have character $\tau^{\pm 1}$ under the C_3 operation, where $\tau = e^{2\pi i/3}$. The bras $\langle e_\pm|$ have character $\tau^{\mp 1}$. Since the Hamiltonian operator is totally symmetric, the diagonal matrix elements $\langle e_\pm|H|e_\pm\rangle$ are totally symmetric, while the characters of the off-diagonal elements $\langle e_\mp|H|e_\pm\rangle$ are $\tau^{\pm 2}$. Since $\tau^3 = 1$, it follows that an expansion of the complex Hamiltonian matrix to quadratic terms in $Q_\pm$ takes the form

$$H = \begin{pmatrix} 0 & kQ_- + lQ_+^2 \\ kQ_+ + lQ_-^2 & 0 \end{pmatrix} \tag{7}$$

The corresponding expression in the real basis $(|e_\mathrm{A}\rangle, |e_\mathrm{B}\rangle)$ is

$$H = \begin{pmatrix} kr\cos\phi + lr^2\cos 2\phi & kr\sin\phi - lr^2\sin 2\phi \\ kr\sin\phi - lr^2\sin 2\phi & -kr\cos\phi - lr^2\cos 2\phi \end{pmatrix} \tag{8}$$

after substitution for (Q_+, Q_-) in terms of (r, ϕ). Equation (8) defines what is known as the $E \times \epsilon$ Jahn–Teller problem, which is discussed in Section V.

More general situations have also been considered. For example, Mead [21] considers cases involving degeneracy between two Kramers doublets involving four electronic components $|\alpha\rangle$, $|\alpha'\rangle$, $|\beta\rangle$, and $|\beta'\rangle$. Equations (4) and (5), coupled with antisymmetry under $\hat{T}^2$ lead to the following identities between the various matrix elements

$$\langle\alpha|\hat{H}|\alpha\rangle = \langle\hat{T}\alpha|\hat{T}\hat{H}|\alpha\rangle^* = \langle\hat{T}\alpha|\hat{H}|\hat{T}\alpha\rangle^* = \langle\alpha'|\hat{H}|\alpha'\rangle^* = \langle\alpha'|\hat{H}|\alpha'\rangle \tag{9}$$

$$\langle\alpha|\hat{H}|\alpha'\rangle = \langle\alpha|\hat{H}|\hat{T}\alpha\rangle = \langle\hat{T}\alpha|\hat{T}\hat{H}|\hat{T}\alpha\rangle^* = \langle\hat{T}\alpha|\hat{H}|\hat{T}^2\alpha\rangle^* = -\langle\alpha'|\hat{H}|\alpha\rangle^* \tag{10}$$

$$\langle\alpha|\hat{H}|\beta\rangle = \langle\hat{T}\alpha|\hat{T}\hat{H}|\beta\rangle^* = \langle\hat{T}\alpha|\hat{H}|\hat{T}\beta\rangle^* = \langle\alpha'|\hat{H}|\beta'\rangle^* \tag{11}$$

$$\langle\alpha|\hat{H}|\beta'\rangle = \langle\hat{T}\alpha|\hat{T}\hat{H}|\beta'\rangle^* = \langle\hat{T}\alpha|\hat{H}|\hat{T}\beta'\rangle^* = -\langle\alpha'|\hat{H}|\beta\rangle^* \tag{12}$$

The conclusion is therefore that the 4 × 4 Hamiltonian matrix, which is assumed to have zero trace, takes the form

$$H(Q) = \begin{pmatrix} w(Q) & 0 & u(Q) & v(Q) \\ 0 & w(Q) & -v^*(Q) & u^*(Q) \\ u^*(Q) & -v(Q) & -w(Q) & 0 \\ v^*(Q) & u(Q) & 0 & -w(Q) \end{pmatrix} \tag{13}$$

where $w(Q)$ is real. Consequently, there are five independent conditions for a strict conical intersection between two Kramers doublets, although $v(Q)$ may, for example, vanish in model situations (see Section V.B). Moreover, there is no certainty that the intersection will lie in a dynamically accessible region of the coordinate space.

III. ADIABATIC EIGENSTATES NEAR A CONICAL INTERSECTION

Suppose that $|x_n(Q)\rangle$ is the adiabatic eigenstate of the Hamiltonian $H(q;Q)$, dependent on internal variables q (the electronic coordinates in molecular contexts), and parameterized by external coordinates Q (the nuclear coordinates). Since $|x_n(Q)\rangle$ must satisfy

$$H(q;Q)|x_n(Q)\rangle = E_n(Q)|x_n(Q)\rangle \qquad \langle x_m|x_n\rangle = \delta_{mn} \tag{14}$$

it follows by the Hellman–Feynman theorem that

$$[H(q;Q) - E_n(Q)]\nabla_Q|x_n(Q)\rangle = [\nabla_Q E_n - \nabla_Q H]|x_n(Q)\rangle \tag{15}$$

Thus, on expanding

$$\nabla_Q|x_n(Q)\rangle = \sum_m |x_m(Q)\rangle\langle x_m|\nabla_Q|x_n\rangle \tag{16}$$

the off-diagonal matrix elements of ∇_Q may be derived from Eq. (15) in the form

$$\langle x_m|\nabla_Q|x_n\rangle = \frac{\langle x_m|\nabla_Q H|x_n\rangle}{E_n(Q) - E_m(Q)} \tag{17}$$

The adiabatic approximation involves neglect of these off-diagonal terms, on the basis that $|E_n(Q) - E_m(Q)| \gg |\langle x_m|\nabla_Q H|x_n\rangle|$. The diagonal elements $\langle x_n|\nabla_Q|x_n\rangle$ are undetermined by this argument, but the gradient of the normalization integral, $\langle x_n|x_n\rangle = 1$, shows that

$$\nabla_Q\langle x_n|x_n\rangle = \langle x_n|\nabla_Q x_n\rangle + \langle\nabla_Q x_n|x_n\rangle = \langle x_n|\nabla_Q x_n\rangle + \langle x_n|\nabla_Q x_n\rangle^* = 0 \tag{18}$$

Consequently,

$$\langle x_n|\nabla_Q x_n\rangle = -\langle x_n|\nabla_Q x_n\rangle^* \tag{19}$$

from which $\langle x_n|\nabla_Q x_n\rangle = 0$, for real $|x_n\rangle$.

Equations (16)–(20) show that the real adiabatic eigenstates are everywhere smooth and continuously differentiable functions of Q, except at degenerate points, such that $E_n(Q) - E_m(Q) = 0$, where, of course, the $|x_n\rangle$ are undefined. There is, however, no requirement that the $|x_n\rangle$ should be real, even for a real Hamiltonian, because the solutions of Eq. (14) contain an arbitrary Q dependent phase term, $e^{i\psi(Q)}$ say. Second, as we shall now see, the choice that $|x_n\rangle$ is real raises a different type of problem. Consider, for example, the model Hamiltonian in Eq. (8), with $l = 0$;

$$H = \begin{pmatrix} kr\cos\phi & kr\sin\phi \\ kr\sin\phi & -kr\cos\phi \end{pmatrix} \tag{20}$$

with a degeneracy at $r = 0$ and real eigenvectors

$$|x_+\rangle = \begin{pmatrix} \cos\frac{\phi}{2} \\ \sin\frac{\phi}{2} \end{pmatrix} \qquad |x_-\rangle = \begin{pmatrix} -\sin\frac{\phi}{2} \\ \cos\frac{\phi}{2} \end{pmatrix} \tag{21}$$

It is readily verified that

$$\langle x_+|\frac{\partial}{\partial\phi}|x_+\rangle = \langle x_-|\frac{\partial}{\partial\phi}|x_-\rangle = 0 \tag{22}$$

but the new problem is that

$$|x_\pm(\phi + 2\pi)\rangle = -|x_\pm(\phi)\rangle \tag{23}$$

which means that $|x_\pm(\phi)\rangle$ is double valued with respect to encirclement of the degeneracy at $r = 0$. In the molecular context, the assumption of a real adiabatic electronic eigenstate therefore requires boundary conditions such that the associated nuclear wave function also changes sign on any path around the origin, because the total wave function itself must be single valued. A more convenient alternative, for practical calculations, is often to add a phase modification, such that the modified eigenstates, $|n_\pm\rangle$, are single valued [2,10].

$$|n_+\rangle = e^{i\psi(Q)}\begin{pmatrix} \cos\frac{\phi}{2} \\ \sin\frac{\phi}{2} \end{pmatrix} \qquad |n_-\rangle = e^{i\psi(Q)}\begin{pmatrix} -\sin\frac{\phi}{2} \\ \cos\frac{\phi}{2} \end{pmatrix} \tag{24}$$

with $\psi(Q_f) - \psi(Q_i) = \pm\pi$. The simplest choice in the present context is $\psi(Q) = \phi/2$ but any phase factor, $e^{i\psi(\phi)}$, that changes sign around a circuit of ϕ is equally acceptable. Nevertheless, the geometric phase defined in Section IV and the associated vector potential theory outlined in Section VI.B are gauge invariant (i.e., independent of this phase ambiguity).

We should also notice explicitly that [22]

$$\langle x_- | \nabla_Q | x_+ \rangle = \frac{\mathbf{e}_\phi}{2r} \tag{25}$$

where $\mathbf{e}_\phi$ is a unit vector in the direction of increasing ϕ. Equation (25) shows that the non-adiabatic coupling diverges at the conical intersection point, which is of course a manifestation of the fact that $|x_\pm\rangle$ are undefined at an exact degeneracy. It is readily verified that $\langle n_- | \nabla_Q | n_+ \rangle$ and $\langle n_+ | \nabla_Q | n_+ \rangle$ also diverge in a similar way.

In turn, this leads to an important conclusion, for the general discussion, that the above sign change, for real eigenstates such that $\langle x_\pm(Q + \delta Q) | x_\pm(Q) \rangle \to 1$ as $\delta Q \to 0$, arises solely from the electronic degeneracy—not from the linearity of Eq. (20), because the adiabatic eigenstates were seen above to be smooth continuously differentiable functions of the nuclear coordinates Q, except at the conical intersection Q_0, where the divergence occurs. To reverse a famous argument of Longuet-Higgins [7], suppose that a sign change were observed for an arbitrarily small path C around Q_0, on which the linear approximation (20) is valid, but not around some larger loop L, which excludes other degeneracies. Now, imagine a continuous expansion and deformation that takes C into L, parameterized by a monotonically increasing parameter λ. There must be some point λ_0, at which $|x_-(Q)\rangle$, say, is sign reversing on $C(\lambda_0)$ but sign preserving on $C(\lambda_0 + d\lambda)$. In other words, the change from sign reversing to sign preservation on the larger loop requires the smoothly continuous function $|x_-(Q)\rangle$ to undergo a discontinuous change at λ_0—a logical impossibility.

Longuet-Higgins [7] actually uses the argument in reverse to infer the logical existence of conical intersections, from the observation of sign changes around arbitrary loops, a test that is now widely used to detect the existence of conical intersections between ab initio potential energy surfaces [23]. A generalization of the Longuet-Higgins argument to the case of a spin–orbit coupled doublet has been given by Stone [24]. As discussed above [see Eq. (13)] the Hamiltonian matrix is then intrinsically complex, and there are no real adiabatic eigenstates. Nevertheless one can still find "parallel transported" states $|x_\pm\rangle$, with vanishing diagonal elements, as in Eq. (22), which acquire a variable phase change, according to the radius of the encircling loop. The conical intersection is now removed by spin–orbit coupling, but it's influence is still apparent in simple sign changes of $|x_\pm\rangle$ around very large loops. The difference from the Longuet-Higgins case is that the phase change falls to zero on very small circles around the maximum on the lower adiabatic surface. This situation is further discussed in Section V.B.

Longuet-Higgins [7] also reinforces the discussion by the following qualitative demonstration of a cyclic sign change for the LiNaK like system subject to Eq. (3), in which rows and columns are labeled by the basis functions

$$\begin{aligned} {}^2\Psi_1 &= \frac{1}{\sqrt{2}}(\psi_B - \psi_C) \\ {}^2\Psi_2 &= \frac{1}{\sqrt{6}}(-2\psi_A + \psi_B + \psi_C) \end{aligned} \tag{26}$$

where $\psi_A = (\bar{a}bc)$, and so on, with the β spin on atom A. Thus ${}^2\Psi_1$ may be recognized as the Heitler–London ground state of BC in the "reactant" $A + BC$ geometry, at which $\beta = \gamma = 0$. Second, there is also a "transition state" geometry B–A–C at which $\alpha < \beta = \gamma$, where the lower eigenstate goes over to ${}^2\Psi_2$. The table below follows changes in the ground-state wave function as the system proceeds through various permutations of the three possible reactant and transition state geometries, subject to the constraint that the overlap from one step to the next is positive.

Geometry	Ground-State Wave Function
A + BC	$\frac{1}{\sqrt{2}}(\psi_B - \psi_C)$
A–B–C	$\frac{1}{\sqrt{6}}(2\psi_B - \psi_A - \psi_C)$
AB + C	$\frac{1}{\sqrt{2}}(\psi_B - \psi_A)$
B–A–C	$\frac{1}{\sqrt{6}}(-2\psi_A + \psi_B + \psi_C)$
B + AC	$\frac{1}{\sqrt{2}}(-\psi_A + \psi_C)$
B–C–A	$\frac{1}{\sqrt{6}}(-\psi_A - \psi_B + 2\psi_C)$
BC + A	$\frac{1}{\sqrt{2}}(-\psi_B + \psi_C)$

Comparison between the first and last lines of the table shows that the sign of the ground-state wave function has been reversed, which implies the existence of a conical intersection somewhere inside the loop described by the table.

IV. GEOMETRIC PHASE

While the presence of sign changes in the adiabatic eigenstates at a conical intersection was well known in the early Jahn–Teller literature, much of the discussion centered on solutions of the coupled equations arising from nonadiabatic coupling between the two or more nuclear components of the wave function in a spectroscopic context. Mead and Truhlar [10] were the first to focus on the consequences for both scattering and spectroscopy on a single adiabatic electronic energy surface, influenced by, but well separated from a conical intersection (see Section VI). Berry [8], who coined the term *geometric phase*, set the argument in a more general context. Given the existence of an infinity of phase modified adiabatic eigenstates of any given problem, the questions at issue are

1. Whether there are any physical invariants of the system, independent of phase modifications.
2. How such invariants can be computed.

Berry [8] starts by assuming the existence of a *single-valued* adiabatic eigenstate $|n(Q)\rangle$, such as that in Eq. (24), subject to

$$H(Q)|n(Q)\rangle = E_n(Q)|n(Q)\rangle \qquad \langle m|n\rangle = \delta_{nm} \tag{27}$$

Solutions of the time-dependent Schrödinger equation

$$i\hbar\frac{d|\Psi(Q(t))\rangle}{dt} = H(Q(t))|\Psi(Q(t))\rangle \tag{28}$$

are sought then in the form

$$|\Psi(Q(t))\rangle = |n(Q(t))\rangle e^{i\gamma(t)-(i/\hbar)\int E_n(Q(t))dt} \qquad \gamma(0) = 0 \tag{29}$$

as the system is taken slowly round a time dependent path $Q(t)$. It readily follows from Eq. (28) and (29) that

$$\nabla_{\mathbf{Q}}|n(Q)\rangle \cdot \dot{\mathbf{Q}} + i\frac{d\gamma}{dt}|n(Q)\rangle = 0 \tag{30}$$

from which it follows by integrating around a closed path C in parameter space that

$$\gamma_C = \gamma(T) - \gamma(0) = i\oint_C \langle n|\nabla_{\mathbf{Q}}n\rangle \cdot \dot{\mathbf{Q}}\,dt = i\oint_C \langle n|\nabla_{\mathbf{Q}}n\rangle \cdot \mathbf{dQ} \tag{31}$$

It should be noted, by taking the gradient of the normalization identity that

$$\langle n|\nabla_{\mathbf{Q}}n\rangle = -\langle\nabla_{\mathbf{Q}}n|n\rangle = -\langle n|\nabla_{\mathbf{Q}}n\rangle^{*}. \tag{32}$$