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Transitions in Molecular Systems

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A representation of the multi-dimensional FC factor at different rotations between the normal coordinates.

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Contents

Preface

The analysis of electronic relaxation processes, especially of radiationless transitions in molecular systems, has rapidly evolved in the last few decades and today plays a central role in almost all investigations of molecular physics and spectroscopy. The development of lasers has significantly contributed to this evolution. The purpose of this book is to give a self-contained and unified presentation of this development, with applications to molecular and solid-state physics. It is primarily intended for graduate students in theoretical physics and chemistry, who are beginning their research careers, although it is hoped that any physicist and chemist working with lasers, molecular spectroscopy, and solid-state physics will also find it useful. The greatest possible emphasis has been placed on clarity, and to this end, presentation is often made in strict mathematical detail. I hope that the reader will thus be able to rederive many of the formulas presented without much difficulty. Some basic understanding of symmetry principles in solid state and molecular physics may be helpful for the reader.

The book consists of eight chapters and several appendices. In Chapter 1, the different basis sets used to classify molecular eigenstates and to study molecular dynamics, including molecular vibrations, are discussed within the context of the Duschinsky mixing effect. This mixing caused by the normal coordinate rotation has been elucidated further in following chapters.

In Chapter 2, the treatment of radiationless transition probability is presented on the basis of Green's function formulation for the transition amplitude, in which the states of interest are selected by suitable projection operators. A discussion of the proper basis set for describing electronic relaxation processes in large molecules is given for each of the cases treated.

Chapter 3 provides a detailed description of radiationless processes in a statistical large molecule embedded in an inert medium. In this chapter, we are for the first time able to express the vibrational overlap between the electronic states under consideration in terms of intramolecular distributions in the full harmonic approximation taking into account the effects of vibrational frequency distortion, potential surface displacement, and the Duschinsky rotation.

Chapter 4 deals in greater detail with the symmetry properties, the evaluation and presentation of the intramolecular distributions for arbitrary vibrational degrees of freedom.

An important example of the utility and power of the aforementioned intramolecular distributions is presented in Chapter 5. This chapter, which is of a more advanced nature, is entirely devoted to the investigation of the nuclear dependence of the electronic matrix element for radiationless transitions. It leads the reader, employing a class of integrals found in Appendix D, to a fix-point theorem for determining the q-centroid at which the electronic matrix element is to be evaluated. It is not recommended that the reader uninterruptedly attempt to master all of these derivations that lead to the proofs of the fundamental theorems. Instead, this chapter or a part of it, may be bypassed on the first reading, proceeding to the less complex following chapters and referring back, as necessary.

Chapter 6 deals with the time evolution of radiative decaying states of polyatomic molecules with special emphasis on radiative decay in internal conversion. The decay of a manifold of closely spaced coupled states is handled by the Green's function formalism, where the matrix elements are displayed in an energy representation that involves either the Born–Oppenheimer or the molecular eigenstate basis set. The features of radiationless transitions in large, medium-sized, and small molecules are elucidated, deriving general expressions for the radiative decay times and for the fluorescence quantum yields.

Chapter 7 introduces the reader to solutions of many selected problems in molecular physics. In particular, the following important problems are studied in detail: the fluorescence spectrum of *p*-terphenyl crystal, the vibrational fine structure of the spin-allowed absorption band of *trans*-$[\mathrm{Co(CN)_2}(tn)_2]\mathrm{Cl3H_2O}$, and transport phenomena of electronic excitation in pentacene-doped molecular crystals. It is followed by an analysis of phosphorescence and radiationless transition in aromatic molecules with nonbonding electrons as well as predissociation of the $^2\mathrm{B}_2$ state of $\mathrm{H_2O^+}$ by nonadiabatic interaction via conical intersection.

Finally, Chapter 8 deals with the evaluation of multidimensional Franck–Condon integrals. As an illustration of the complexity of the latter upon the normal mode rotation, a study of sequential two photon processes is presented.

At the beginning of each chapter, there is a brief summary of what the reader will find in the particular chapter. These summaries provide a detailed survey of the subject matter covered in this book. No attempt was made to provide all-inclusive references. References are not prioritized and are presented as supplementary reading for students.

Some people have made important contributions to this book at various stages of its development. In particular, I would like to mention here my scientific colleagues G. Olbrich, C. Kryschi, D. Gherban, A. Urushiyama, J. Degen, Th. Ledwig, and P.H. Cribb. In addition, I wish to express my deep appreciation to G. Moss for suggested improvements to text readability and to G. Pauli for preparing most of the graphics, which form an essential part of the presentation.

December 2008 *Hans J. Kupka*
Düsseldorf, Germany

1
Introduction

In this chapter we shall provide a brief overview of a number of different basis sets to classify molecular eigenstates and study molecular dynamics. The basic procedure is described in Section 1.1, where the solution of the Schrödinger equation for the molecular system is given by separating the electronic motion from the nuclear motion in the molecule. This procedure, called the adiabatic description, represents the basis set that most often describes the initially excited states in large molecules. Alternatively, Section 1.1.3 introduces the crude Born–Oppenheimer (BO) basis, and Section 1.1.4 gives a description of the Herzberg–Teller adiabatic approximation. Sections 1.2 and 1.3 are devoted to the vibrational wavefunctions and their normal coordinates as well as to the Duschinsky effect. Section 1.4 concludes the chapter with a mathematical analysis of two strongly coupled adiabatic states, one of the fundamental and difficult problems of physics. The analysis is performed by using a diabatic basis set, and as an application a formal and compact solution is derived for the predissociation of a triatomic molecule via a conical intersection.

We assume that the reader is familiar with the basic notions of quantum theory. However, to make our study reasonably self-contained, we have included some of the derivations in the appendices.

1.1
The Adiabatic Description of Molecules

1.1.1
Preliminaries

In the treatment of electronic states in large molecules, one usually neglects the details concerning the rotation and translation motions and rather concentrates on the dynamics of the electronic and vibrational motions. The starting point for the description of these motions in a molecule consisting of electrons and K nuclei is the complete Hamiltonian H of the molecule. To write down the Hamiltonian, the origin of the molecular coordinate system is placed at the center of mass. It is assumed that the positions of the K nuclei will deviate only by small amounts from some reference configuration. The molecules with large amplitude motions, such as internal rotations, are therefore explicitly excluded. The nuclear inertia tensor is then approximated by the inertia tensor of the reference configuration and the axes of the internal coordinate system are directed along the principal axes of this reference inertia tensor. If now the center of mass motion is removed, the nuclear motion can be described by a vector of $3K-6$ dimensions for a (nonlinear) system with K atoms. The latter are normally taken as linear combinations of mass-weighted vectors describing the displacements from the reference configuration [1–3]. With this approximation and, for the sake of simplicity, taking only the electrostatic Coulomb interaction, the vibronic Hamiltonian can be written as

$$H = T_e(\mathbf{r}) + T_N(\mathbf{q}) + U(\mathbf{r}, \mathbf{q}). \tag{1.1}$$

Here the vector $\mathbf{r} = (r_1, r_2, \ldots, r_n)$ where $r_i = (x_i, y_i, z_i)$ denotes collectively all electronic coordinates and the coordinates of the nuclei are specified by $\mathbf{q} = (q_1, q_2, \ldots, q_N)$, where $N = 3K-6$. In the following, we shall adopt the convention that the components of the vector $\mathbf{q}$ are labeled by Greek indices if they range from 1 to N, and the Latin ones denote the components of the electronic coordinates. The electronic kinetic energy operator $T_e(\mathbf{r})$ and the nuclear kinetic operator $T_N(\mathbf{q})$ are presented in a diagonal form:

$$T_e(\mathbf{r}) = -\sum_i \left(\frac{\hbar^2}{2m}\right)\left(\frac{\partial^2}{\partial r_i^2}\right) \tag{1.2}$$

and

$$T_N(\mathbf{q}) = -\sum_\mu \left(\frac{\hbar^2}{2}\right)\left(\frac{\partial^2}{\partial q_\mu^2}\right), \tag{1.3}$$

where m is the mass of the electron and q_μ are mass-weighted (dimensioned) nuclear coordinates given by

$$\mathbf{R} = \mathbf{R}_0 + M^{-1/2}\mathbf{A}\mathbf{q},$$

where $\mathbf{R}$ and $\mathbf{R}_0$ are $(3K-6)$-dimensional column vectors of the instantaneous and equilibrium Cartesian coordinates, respectively, associated with the nonzero frequency normal modes. M is the $(3K-6) \times (3K-6)$ mass-weighted matrix, $\mathbf{A}$ is the orthogonal transformation that diagonalizes the mass-weighted Cartesian force constant matrix, and $\mathbf{q}$ is the dimensioned normal coordinate vector. $U(\mathbf{r}, \mathbf{q})$ in Equation 1.1 is the total (internal) potential energy and includes all the electron–electron, nucleus–nucleus, and electron–nucleus interactions. In spite of the approximation already made, the exact molecular vibronic eigenstates $\Psi(\mathbf{r}, \mathbf{q})$ in a stationary state satisfy the time-independent Schrödinger equation

$$[T_e(\mathbf{r}) + T_N(\mathbf{q}) + U(\mathbf{r}, \mathbf{q})]\,\Psi(\mathbf{r}, \mathbf{q}) = E\,\Psi(\mathbf{r}, \mathbf{q}). \tag{1.4}$$

Serious approximations become necessary when one tries to solve Equation 1.4. One of these solutions is the adiabatic separation, which will be outlined below. This outline will serve as a guide to the possible classifications of molecular states and as an aid to the solution of specific quantum mechanical problems.

1.1.2
The Born–Oppenheimer Approximation

The first step of the adiabatic description is the Born–Oppenheimer approximation, according to which

> the nuclear kinetic energy is neglected, and
> the nuclear configuration is fixed at the position **R**.

The adiabatic approximation is based on the fact that typical electronic velocities are much greater than typical nuclear (ionic) velocities. (The significant electronic velocity is $v = 10^8$ cm/s, whereas typical nuclear velocities are at most of order 10^5 cm/s.) One therefore assumes that, because the nuclei have much lower velocities than the electrons, at any moment the electrons will be in their ground state for that particular instantaneous nuclear configuration.

Under circumstances where $T_{\mathrm{N}}(\mathbf{q}) = 0$, and at particular arrangement of the ion cores, we can separate electronic and nuclear motions. This can be accomplished by selecting some basis set of electronic wavefunctions $\varphi_a(\mathbf{r};\mathbf{q})$, which satisfy the partial Schrödinger equation

$$[T_{\mathrm{e}}(\mathbf{r}) + U(\mathbf{r},\mathbf{q})]\,\varphi_a(\mathbf{r};\mathbf{q}) = E_a(\mathbf{q})\,\varphi_a(\mathbf{r};\mathbf{q}), \tag{1.5}$$

where $E_a(\mathbf{q})$ corresponds to the electronic energy at this fixed nuclear configuration. The configuration $\mathbf{q}$ is chosen arbitrarily, but for the solution of Equation 1.5 it must be fixed. In other words, the electronic wavefunction $\varphi_a(\mathbf{r};\mathbf{q})$ depends on the electronic coordinate $\mathbf{r}$ and parametrically on the nuclear coordinates. For any value of $\mathbf{q}$, the φ_a are assumed to be orthonormal and complete (i.e., span the subspace defined by the electronic coordinates $\mathbf{r}$). They are also assumed to vary in a continuous manner with $\mathbf{q}$. The total (molecular) wavefunction $\Psi(\mathbf{r},\mathbf{q})$ can be expanded in terms of the electronic basis function [4, 5]

$$\Psi_{\mathrm{v}}(\mathbf{r},\mathbf{q}) = \sum_b \varphi_b(\mathbf{r};\mathbf{q})\chi_{b\mathrm{v}}(\mathbf{q}), \tag{1.6}$$

where the nuclear wavefunctions $\chi_{b\mathrm{v}}(\mathbf{q})$ are initially treated as coefficients in the series (1.6). These coefficients are selected such that Equation 1.4 is satisfied. We have to substitute Equation 1.6 for $\Psi(\mathbf{r},\mathbf{q})$ in Equation 1.4. Remarking that

$$\frac{\partial^2(\varphi_b\chi_{b\mathrm{v}})}{\partial q_\mu^2} = \left(\frac{\partial^2\varphi_b}{\partial q_\mu^2}\right)\chi_{b\mathrm{v}} + 2\frac{\partial\varphi_b}{\partial q_\mu}\frac{\partial\chi_{b\mathrm{v}}}{\partial q_\mu} + \varphi_b\left(\frac{\partial^2\chi_{b\mathrm{v}}}{\partial q_\mu^2}\right) \tag{1.7}$$

and

$$\frac{\partial^2(\varphi_b\chi_{b\mathrm{v}})}{\partial r_i^2} = \chi_{b\mathrm{v}}\left(\frac{\partial^2\varphi_b}{\partial r_i^2}\right),$$

we find according to Equation 1.6 that

$$H\sum_b \varphi_b\chi_{b\nu} = \sum_b \Bigg\{ E_b(\mathbf{q})\varphi_b(\mathbf{r};\mathbf{q})\chi_{b\nu}(\mathbf{q}) + T_{\mathrm{N}}(\mathbf{q})\varphi_b(\mathbf{r};\mathbf{q})\chi_{b\nu}(\mathbf{q}) \\ -2\sum_\mu \left(\frac{\hbar^2}{2}\right)\frac{\partial\varphi_b(\mathbf{r};\mathbf{q})}{\partial q_\mu}\frac{\partial\chi_{b\nu}(q)}{\partial q_\mu} + \varphi_b(\mathbf{r};\mathbf{q})T_{\mathrm{N}}(\mathbf{q})\chi_{b\nu}(\mathbf{q})\Bigg\} \\ = E\sum_b \varphi_b(\mathbf{r};\mathbf{q})\chi_{b\nu}(\mathbf{q}).$$

In deducing this result, we have used Equation 1.5 and the fact that the wavefunction φ_b is an eigenfunction of Equation 1.5. Multiplying from the left by φ_a^* and integrating over the electronic coordinates, we obtain the usual set of coupled equations for the χ_{av} [4, 5] (see also Ref. [6] with modifications given by McLachlan [7] and Kolos [8]):

$$[T_{\mathrm{N}}(\mathbf{q}) + E_a(\mathbf{q}) + \langle\varphi_a|T_{\mathrm{N}}|\varphi_a\rangle - E]\chi_{a\nu}(\mathbf{q}) \\ + \sum_{b\neq a}\left\{\langle\varphi_a|T_{\mathrm{N}}(\mathbf{q})|\varphi_b\rangle_r - 2\sum_\mu(\hbar^2/2)\langle\varphi_a|\partial/\partial q_\mu|\varphi_b\rangle_r\partial/\partial q_\mu\right\}\chi_{b\nu}(\mathbf{q}) = 0. \tag{1.8a}$$

The restriction $b \neq a$ in Equation 1.8a is a consequence of the orthonormality of the φ_b, $\langle\varphi_b|\varphi_a\rangle_r = \delta_{ab}$. Here and in Equation 1.8a, angle brackets indicate integration over the electronic coordinates only. To avoid confusion resulting from numerous subscripts, it is often convenient to adopt a matrix notation, writing Equation 1.8a as

$$[T_{\mathrm{N}}(\mathbf{q}) + E_a(\mathbf{q}) + \langle\varphi_a|T_{\mathrm{N}}(\mathbf{q})|\varphi_a\rangle - E]\chi_{a\nu} = \sum_{b\neq a} X_{ab}\chi_{b\nu}, \tag{1.8b}$$

where $X_{ab} = -\langle\varphi_a\big|[T_{\mathrm{N}},\varphi_b]\rangle_r$ and $[A, B] = AB - BA$. The adiabatic approximation (or BO adiabatic approximation in the nomenclature of Ballhausen and Hansen) is obtained by neglecting the coupling term in Equation 1.8a (the expression in the curly brackets). The molecular wavefunction now reduces to the simple product

$$\Psi_{a\nu}(\mathbf{r},\mathbf{q}) = \varphi_a(\mathbf{r};\mathbf{q})\chi_{a\nu}(\mathbf{q}) \tag{1.9}$$

and the corresponding equation for the nuclear function $\chi_{a\nu}(\mathbf{q})$ in this approximation has the form

$$[T_{\mathrm{N}}(\mathbf{q}) + E_a(\mathbf{q})]\chi_{a\nu}(q) = E_{av}\chi_{a\nu}(\mathbf{q}), \tag{1.10}$$

where $E_{a\nu}$ is the eigenvalue for the νth vibrational level in the ath electronic state. Thus, from Equations 1.5 and 1.10, we see that, in the BO approximation, the nuclei move in an effective potential $E_a(\mathbf{q})$ generated by the electron distribution, while the electron distribution is a function of the nuclear configuration $\mathbf{q}$. $E_a(\mathbf{q})$ is designated as the adiabatic potential surface of φ_a. The additional diagonal term $\langle\varphi_a|T_{\mathrm{N}}(q)|\varphi_a\rangle_r$ in Equation 1.8 is omitted in the BO approximation, as we have done in Equation 1.10. Alternatively, if this term (designated as the adiabatic correction to the potential energy surface) is taken into account, we speak of the Born–Huang approximation [5].

From numerical calculations of the low-lying electronic states of $H_2{}^+$ and H_2, it is known that this correction is invariably small [9, 10] and can usually be neglected.

The approximate wavefunctions of the adiabatic approximation are characterized by the following off-diagonal matrix elements between different electronic states [11]:

$$(\langle\Psi_{a\mathrm{v}}|H|\Psi_{a\mathrm{v}'}\rangle_r)_q = E_{a\mathrm{v}}\delta_{\mathrm{vv}'} \tag{1.11}$$

(i.e., the adiabatic basis set is diagonal within the same electronic configuration) and

$$\begin{aligned}\left(\langle\Psi_{a\mathrm{v}}|H|\Psi_{b\mathrm{v}'}\rangle_r\right)_{\mathbf{q}} &= \left(\chi_{a\mathrm{v}}\langle\varphi_a|T_{\mathrm{N}}|\varphi_b\rangle_r\chi_{b\mathrm{v}'}\right)_{\mathbf{q}}\\ &\quad -\hbar^2\sum_{\mu}\left(\chi_{a\mathrm{v}}\langle\varphi_a|\partial/\partial q_\mu|\varphi_b\rangle_r\partial\chi_{b\mathrm{v}'}/\partial q_\mu\right)_{\mathbf{q}}.\end{aligned} \tag{1.12}$$

In Equation 1.12, we have indicated convenient abbreviations for the two integrals: $\langle|\,|\rangle$ for the integral over electronic coordinates and $(|\,|)$ for the integral over nuclear coordinates. Equation 1.12 represents the so-called Born–Oppenheimer coupling, which promotes transitions between potential energy surfaces via the nuclear kinetic energy operator. If these terms in the basis defined by Equation 1.9 are small relative to the separation of vibronic states $E_{a\mathrm{v}}-E_{b\mathrm{v}'}$, the BO approximation will give a very good approximation and will lead to tremendous simplification. In the case of close lying vibronic states belonging to different electronic configurations $E_{a\mathrm{v}} \approx E_{b\mathrm{v}'}$, the adiabatic approximation can fail. The interaction of nuclear vibrations with the electronic motion in molecules gives rise to interesting effects that have been attributed to linear and quadratic terms in the nuclear displacements from the equilibrium configuration. Linear vibronic coupling terms lead to vibrational borrowing, an effect that appears most clearly with forbidden electronic transitions made allowed through the simultaneous excitation of certain asymmetric vibrations. The other physical situations associated with linear displacements along certain asymmetric normal coordinates lead to the *Jahn–Teller* [12–25] and the *pseudo-Jahn–Teller* effects (see Appendix K). The effect of quadratic nuclear displacement terms is manifested in the *Renner effect* [26]. Although the study of these effects is of considerable interest, their observation is limited to systems of high symmetry that have degenerate or nearly degenerate electronic states.

Going back to expression (1.12) for the coupling term, we shall now elucidate the situation that occurs when the potential energy surfaces belonging to different electronic states cross. This is easily obtained on introducing the following expressions [27]:

$$[E_b(\mathbf{q})-E_a(\mathbf{q})]\langle\varphi_a|\partial/\partial q_\mu|\varphi_b\rangle = \langle\varphi_a|\partial U/\partial q_\mu|\varphi_b\rangle \tag{1.13}$$

and

$$[E_b(\mathbf{q})-E_b(\mathbf{q})]\left\langle\varphi_a\middle|\partial^2/\partial q_\mu^2\middle|\varphi_b\right\rangle = \left\langle\varphi_a\middle|\partial^2 U/\partial q_\mu^2\middle|\varphi_b\right\rangle + 2\langle\varphi_a|(\partial U/\partial q_\mu)\partial/\partial q_\mu|\varphi_b\rangle. \tag{1.14}$$

In the region where the two potential energy surfaces do not cross, $E_a(\mathbf{q}) \neq E_b(\mathbf{q})$, Equation 1.13 may obviously be rewritten as

$$\langle\varphi_a|\partial/\partial q_\mu|\varphi_b\rangle = \langle\varphi_a|\partial U/\partial q_\mu|\varphi_b\rangle/[E_b(\mathbf{q})-E_a(\mathbf{q})] \tag{1.15}$$

and relation (1.15) is well behaved. At the surface intersections $E_a(\mathbf{q}) = E_b(\mathbf{q})$, relation (1.15) is not as such without further ado valid. To see this, we differentiate the general expression (1.13) with respect to q_μ and then evaluate the result at the surface intersection to yield

$$\langle\varphi_a|\partial/\partial q_\mu|\varphi_b\rangle = \left[\partial\langle\varphi_a|\partial U/\partial q_\mu|\varphi_b\rangle/\partial q_\mu\right]/\left[\partial E_b/\partial q_\mu - \partial E_a/\partial q_\mu\right], \tag{1.16}$$

where we have assumed, for simplicity, that the intersection surface results from the variation of a single coordinate q_μ and that $(\partial E_b/\partial q_\mu)_c \neq (\partial E_a/\partial q_\mu)_c$ at the intersection point c. This means that $\langle\varphi_a|\partial/\partial q_\mu|\varphi_b\rangle$ is well behaved over the whole range of values of q_μ. Indeed, Equation 1.16 can be rederived directly from Equation 1.15 by applying l'Hospital's rule. Expression (1.15) should likewise be well behaved (nonsingular) in the more general case of multidimensional surface intersections, where q_μ in Equation 1.16 denotes the coordinate normal to the intersection surface defined by $E_a(\mathbf{q}) = E_b(\mathbf{q})$. The property of $\langle\varphi_a|\partial^2/\partial q_\mu^2|\varphi_b\rangle$ and its nonsingularity clearly follow in a completely analogous way.

The behavior of $\langle\varphi_a|\partial/\partial q_\mu|\varphi_b\rangle$ and $\langle\varphi_a|\partial^2/\partial q_\mu^2|\varphi_b\rangle$ has been examined in Ref. [28] for $H_2{}^+$ as a function of the internuclear distance R. Both these quantities were shown to vary smoothly with R. Subsequently, Nitzan and Jortner [29] have used Equation 1.15 in the whole range of values of q_μ, including the region of the intersection of the adiabatic surfaces by assuming the principal value for $[E_a(\mathbf{q}) - E_b(\mathbf{q})]^{-1}$ at the intersection point. This leads to a finite but peaked value of (1.15) at the surface intersection. A representative example of a similar situation will be shown in Sections 1.6 and 7.6, where the nonadiabatic coupling (1.15) near the conical intersection between states ${}^2B_2$ and ${}^2A_1$ of H_2O^+ is shown.

1.1.3
The Crude Born–Oppenheimer Basis Set

In this and the following sections, we will discuss ways of selecting the basis function φ_a by separating the nuclear and electronic motions in a manner different from that in the previous section. In the present approach, the electronic Hamiltonian is assumed to be

$$H_{\text{elec}} = T_e(\mathbf{r}) + U(\mathbf{r}, \mathbf{q}_0) + \Delta U(\mathbf{r}, \mathbf{q}), \tag{1.17}$$

where $\mathbf{q}_0$ is a reference configuration and $\Delta U = U(\mathbf{r}, \mathbf{q}) - U(\mathbf{r}, \mathbf{q}_0)$ is taken as a perturbation. In what follows, we will first briefly discuss the crude approximation and then the improvement of the crude BO basis set by using the Herzberg–Teller approximation. In addition to its practical utility, the Herzberg–Teller approximation provides an instructive way of viewing the (improved) crude BO basis complementary to that of the adiabatic basis derived in Section 1.1, permitting a reconciliation between the apparently contradictory features of both the crude BO basis set and the BO adiabatic basis set. The situation we have in mind occurs in the case of widely separated electronic states, which when mixed with each other give rise to vibronically induced allowed electronic transitions [30, 31] (see, for example, the mixing of odd parity states with the even parity states of transition metal complexes).

In the crude adiabatic (CA) approximation [1, 32–40], the electronic wavefunctions $\varphi_a^{\mathrm{CA}}(\mathbf{r};\mathbf{q})$ defined at a specific nuclear configuration $\mathbf{q}_0$ satisfy the following Schrödinger equation:

$$[T_{\mathrm{e}}(\mathbf{r}) + U(\mathbf{r},\mathbf{q}_0)]\,\varphi_a^{\mathrm{CA}}(\mathbf{r};\mathbf{q}_0) = E_a^{\mathrm{CA}}\varphi_a^{\mathrm{CA}}(\mathbf{r};\mathbf{q}_0), \tag{1.18}$$

where E_a^{CA} is the ath eigenvalue and $\mathbf{q}_0$ implies all the nuclear coordinate positions of the reference configuration. Since these wavefunctions form a complete set (which span the Longuet–Higgins space), the eigenstate of the total Hamiltonian $\Psi_v(\mathbf{r},\mathbf{q})$ may be expanded (analogous to Equation 1.6) in terms of $\varphi_a^{\mathrm{CA}}(\mathbf{r};\mathbf{q}_0)$:

$$\Psi_{\mathrm{v}}(\mathbf{r},\mathbf{q}) = \sum_b \varphi_b^{\mathrm{CA}}(\mathbf{r};\mathbf{q}_0)\,\chi_{b\mathrm{v}}(\mathbf{q}). \tag{1.19}$$

As before, $\chi_{b\mathrm{v}}(\mathbf{q})$ are initially treated as expansion coefficients, which must be determined. Inserting Equation 1.19 in Equation 1.4 results in the usual infinite set of coupled equations for the $\chi_{b\mathrm{v}}(\mathbf{q})$:

$$\begin{aligned}&\left[T_{\mathrm{N}}(\mathbf{q}) + E_a^{\mathrm{CA}} + \left\langle\varphi_a^{\mathrm{CA}}(\mathbf{r};\mathbf{q}_0)\,|\Delta U|\,\varphi_a^{\mathrm{CA}}(\mathbf{r};\mathbf{q}_0)\right\rangle - E_t\right]\chi_{a\mathrm{v}}(\mathbf{q})\\ &\qquad + \sum_{b\neq a}\left\langle\varphi_a^{\mathrm{CA}}(\mathbf{r};\mathbf{q}_0)\,|\Delta U|\,\varphi_b^{\mathrm{CA}}(\mathbf{r};\mathbf{q}_0)\right\rangle\,\chi_{b\mathrm{v}'}(\mathbf{q}) = 0.\end{aligned} \tag{1.20}$$

The functions $\chi_{a\mathrm{v}}(\mathbf{q})$ are therefore determined by the set of coupled equations (1.20). The potential functions $\left\langle\varphi_a^{\mathrm{CA}}|\Delta U|\varphi_b^{\mathrm{CA}}\right\rangle$ are usually represented as power series expansions in the normal coordinates q_μ around q_0, where q_0 is usually chosen at the minimum of the ground state.

Provided that

$$\left\langle\varphi_a^{\mathrm{CA}}|\Delta U|\varphi_b^{\mathrm{CA}}\right\rangle = 0 \tag{1.21}$$

for $a \neq b$, Equation 1.19 is simply written as a product

$$\Psi_{a\mathrm{v}}^{\mathrm{CA}}(\mathbf{r},\mathbf{q}) = \varphi_a^{\mathrm{CA}}(\mathbf{r};\mathbf{q}_0)\chi_{a\mathrm{v}}^{\mathrm{CA}}(\mathbf{q}), \tag{1.22}$$

where the coefficient $\chi_{a\mathrm{v}}^{\mathrm{CA}}$ is the eigenstate of the following equation:

$$\left[T_{\mathrm{N}}(\mathbf{q}) + E_a^{\mathrm{CA}} + \left\langle\varphi_a^{\mathrm{CA}}|\Delta U|\varphi_b^{\mathrm{CA}}\right\rangle\right]\chi_{a\mathrm{v}}^{\mathrm{CA}}(\mathbf{q}) = E_{a\mathrm{v}}^{\mathrm{CA}}\chi_{a\mathrm{v}}^{\mathrm{CA}}(\mathbf{q}). \tag{1.23}$$

The diagonal matrix elements $\left\langle\varphi_a^{\mathrm{CA}}|\Delta U|\varphi_a^{\mathrm{CA}}\right\rangle$ are the effective potential energy surface that governs nuclear motion. From Equations 1.10 and 1.23, it is evident that the vibrational wavefunction $\chi_{a\mathrm{v}}^{\mathrm{CA}}$ differs from the adiabatic wavefunction $\chi_{a\mathrm{v}}^{\mathrm{BO}}$. As long as the basis set $\varphi_a^{\mathrm{CA}}(r;q_0)$ is complete in the electronic space, the CA basis is perfectly adequate (independent of the choice of $\mathbf{q}_0$). The two matrix representations 1.8 and (1.20) are merely two different representations of the same operator.

1.1.4
Correction of the Crude Adiabatic Approximation

The electronic wavefunction in the crude adiabatic approximation is defined according to Equation 1.18 at a specific nuclear configuration $\mathbf{q}_0$ and therefore it does not depend on the nuclear coordinates $\{q_\mu\}$. To calculate corrections to this extreme case, we apply the Rayleigh–Schrödinger (RS) perturbation calculation, taking ΔU as perturbation operator. This leads to

$$\varphi_a(\mathbf{r},\mathbf{q}) = \varphi_a^{\mathrm{CA}}(\mathbf{r}) + \sum_{b\neq a} \varphi_b^{\mathrm{CA}}(\mathbf{r}) c_{ba}(\mathbf{q}), \tag{1.24a}$$

where

$$c_{ba}(\mathbf{q}) = \frac{\langle \varphi_b^{\mathrm{CA}}(\mathbf{r})|\Delta U|\varphi_a^{\mathrm{CA}}(\mathbf{r})\rangle}{E_a^{\mathrm{CA}} - E_b^{\mathrm{CA}}} + \sum_{c\neq a,b} \frac{\langle \varphi_b^{\mathrm{CA}}(\mathbf{r})|\Delta U|\varphi_c^{\mathrm{CA}}(\mathbf{r})\rangle \langle \varphi_c^{\mathrm{CA}}(\mathbf{r})|\Delta U|\varphi_a^{\mathrm{CA}}(\mathbf{r})\rangle}{\left(E_a^{\mathrm{CA}} - E_b^{\mathrm{CA}}\right)\left(E_a^{\mathrm{CA}} - E_c^{\mathrm{CA}}\right)} \tag{1.25}$$

and

$$E_{a,b}^{\mathrm{CA}} = E_{a,b}(\mathbf{q}_0).$$

The same procedure gives for the eigenvalues (in second order)

$$E_a(\mathbf{q}) = E_a^{\mathrm{CA}} + (\Delta U)_{aa} + \sum_{b\neq a} \frac{(\Delta U)_{ab}(\Delta U)_{ba}}{E_a^{\mathrm{CA}} - E_b^{\mathrm{CA}}}, \tag{1.26}$$

where

$$(\Delta U)_{ab} = \langle \varphi_a^{\mathrm{CA}}(\mathbf{r})|\Delta U|\varphi_b^{\mathrm{CA}}(\mathbf{r})\rangle. \tag{1.27}$$

Expansion of ΔU in the vicinity of $\mathbf{q}_0$ in terms of nuclear coordinates $\{q_\mu\}$ gives

$$\Delta U = \sum_\mu \left(\frac{\partial U(\mathbf{q})}{\partial q_\mu}\right)_{\mathbf{q}_0} q_\mu + \frac{1}{2}\sum_{\mu,\nu} \left(\frac{\partial^2 U(\mathbf{q})}{\partial q_\mu \partial q_\nu}\right)_{\mathbf{q}_0} q_\mu q_\nu + \cdots. \tag{1.28}$$

After inserting (1.28) into (1.26), we have

$$E_a(\mathbf{q}) = E_a^{\mathrm{CA}} + \sum_\mu U_\mu^{aa} q_\mu + \frac{1}{2}\sum_{\mu,\nu} q_\mu q_\nu \left\{ U_{\mu,\nu}^{aa} + 2\sum_{b\neq a} \frac{U_\mu^{ab} U_\nu^{ba}}{E_a^{\mathrm{CA}} - E_b^{\mathrm{CA}}} \right\} \tag{1.29}$$

with

$$U_\mu^{ab} = \left\langle \varphi_a^{\mathrm{CA}}(\mathbf{r}) \middle| \left(\frac{\partial U(\mathbf{r},\mathbf{q})}{\partial q_\mu}\right)_{\mathbf{q}_0} \middle| \varphi_b^{\mathrm{CA}}(\mathbf{r}) \right\rangle \tag{1.30}$$

and quadratic terms in q_μ:

$$U_{\mu\nu}^{ab} = \left\langle \varphi_a^{\mathrm{CA}}(\mathbf{r}) \middle| \frac{\partial^2 U(\mathbf{r},\mathbf{q})}{\partial q_\mu \partial q_\nu} \middle| \varphi_b^{\mathrm{CA}}(\mathbf{r}) \right\rangle. \tag{1.31}$$

In writing Equation 1.29, we have taken into account the linear terms from Equation 1.28 in second order and quadratic terms in $\mathbf{q}$ in first order. Correspondingly, the coefficients $c_{ba}(\mathbf{q})$ in (1.25) are expressed as (in second order)

$$c_{ba}(\mathbf{q}) = \sum_{\mu} \frac{U_{\mu}^{ba}}{E_a^{\mathrm{CA}} - E_b^{\mathrm{CA}}} q_{\mu} + \sum_{\mu,\nu} \left[\frac{1}{2} \frac{U_{\mu\nu}^{ba}}{E_a^{\mathrm{CA}} - E_b^{\mathrm{CA}}} + \sum_{c \neq a} \frac{U_{\mu}^{bc} U_{\nu}^{ca}}{\left(E_a^{\mathrm{CA}} - E_b^{\mathrm{CA}}\right)\left(E_a^{\mathrm{CA}} - E_c^{\mathrm{CA}}\right)} \right] q_{\mu} q_{\nu}. \tag{1.32}$$

The correction of the CA approximation performed above is known as "vibronic coupling" and the wavefunction (1.24a) is sometimes designated as the Herzberg–Teller approximation. In this approximation, the corrected molecular eigenfunction can be written as

$$\Psi_{a\nu}(\mathbf{r},\mathbf{q}) = \left[\varphi_a^{\mathrm{CA}}(\mathbf{r}) + \sum_{b \neq a} \varphi_b^{\mathrm{CA}}(\mathbf{r}) c_{ba}(\mathbf{q}) \right] \chi_{a\nu}^{\mathrm{BO}}(\mathbf{q}) \tag{1.33}$$

and is still (of product form) adiabatic. Ballhausen and Hansen [1] have introduced the term Herzberg–Teller adiabatic approximation to emphasize the adiabatic nature of Equation 1.33 [40].

An obvious generalization of Equation 1.24a results if we choose

$$\varphi_a(\mathbf{r};\mathbf{q}) = \sum_b \varphi_b^{\mathrm{CA}}(\mathbf{r}) \bar{c}_{ba}(\mathbf{q}) \tag{1.24b}$$

for an adiabatic electronic wavefunction $\varphi_a(\mathbf{r};\mathbf{q})$. Upon substituting Equation 1.24b into Equation 1.6, we obtain

$$\Psi_{\nu}(\mathbf{r},\mathbf{q}) = \sum_c \varphi_c^{\mathrm{CA}}(\mathbf{r}) \sum_b \bar{c}_{cb}(\mathbf{q}) \chi_{b\nu}^{\mathrm{BO}}(\mathbf{q}), \tag{1.34}$$

which can be compared with Equation 1.19 to yield the relation

$$\chi_{c\nu}^{\mathrm{CA}}(\mathbf{q}) = \sum_b \bar{c}_{cb}(\mathbf{q}) \chi_{b\nu}^{\mathrm{BO}}(\mathbf{q}) \tag{1.35}$$

between the vibrational wavefunction in the CA approximation and the vibrational wavefunction in the BO approximation.

The classic cases of the Herzberg–Teller mechanism relate to coupling between two electronic states of different symmetry. An important example of this case occurs when electric dipole transitions of one of the two states are forbidden (e.g., the Laporte-forbidden d–d and f–f transitions). In this case, the forbidden transition may acquire absorption intensity by Herzberg–Teller mixing with an allowed transition via a nontotally symmetric mode of appropriate symmetry (the irreducible representation of the active mode must be contained in the direct product of the irreducible representations for the two states coupled by the Herzberg–Teller mechanism). We shall illustrate our results in Chapter 7 by evaluating the vibronic induced d–d transitions in transition metal complexes.

1.2
Normal Coordinates and Duschinsky Effect

Let us now return to Equation 1.29 for the potential energy surface of the *a*th electronic state and reformulate it in a more suitable (canonical) form:

$$E_a(\mathbf{q}) = E_a(\mathbf{q}_0) + \sum_{\mu} l^a_{\mu} q_{\mu} + \frac{1}{2}\sum_{\mu,\nu} f^a_{\mu\nu} q_{\mu} q_{\nu} = E^0_a + (\mathbf{l}^a)^t \mathbf{q} + \frac{1}{2}\mathbf{q}^t \mathbf{F}^a \mathbf{q}, \tag{1.36}$$

with

$$l^a_{\mu} = U^{aa}_{\mu}$$

and

$$f^a_{\mu\nu} = U^{aa}_{\mu\nu} + 2\sum_{b \neq a} \frac{U^{ab}_{\mu} U^{ba}_{\nu}}{E^{\mathrm{CA}}_a - E^{\mathrm{CA}}_b}. \tag{1.37}$$

In Equation 1.36, the boldface letters $\mathbf{q}$ and $\mathbf{F}$ are column vector and square matrix, respectively. The superscript t indicates matrix transposition. Apart from the linear terms in q_{μ}, the potential of the ath electronic state contains in the harmonic approximation pure and mixed quadratic terms. The linear terms $l_{\mu} \neq 0$, especially for total symmetric vibrational modes μ (see Equations 1.30 and 1.37) is closely related to the geometrical displacement associated with the electronic transition between the electronic ground state and the ath electronic state. The pure quadratic force constant coefficients $f^a_{\mu\mu}$ describe the curvature of the potential energy surface of the ath electronic state along the axes of the nuclear coordinate system, whereas the mixed quadratic terms $f^a_{\mu\nu} (\mu \neq \nu)$ are responsible for the mixing of vibrational coordinates (modes) upon electronic excitation (see later). Therefore, our first goal is to transform them from the expression of $E_a(\mathbf{q})$. Since $\mathbf{F}^a$ is a real and symmetric square matrix, it can be diagonalized by the following transformation:

$$\mathbf{q}^a = \mathbf{A}^a \mathbf{q} + \mathbf{k}^a, \tag{1.38}$$

where $\mathbf{A}^a$ is an orthogonal matrix that diagonalizes the mass-weighted force constant matrix $\mathbf{F}$. Applying Equation 1.38 on the electronic ground state $a = 0$ and noting that $(\mathbf{AB})^t = \mathbf{B}^t \mathbf{A}^t$ for any two matrices, we have

$$\begin{aligned}
E_0(\mathbf{q}) &= E_0(\mathbf{q}_0) + (\mathbf{l}^0)^t (\mathbf{A}^0)^{-1} \mathbf{q}^0 - (\mathbf{l}^0)^t (\mathbf{A}^0)^{-1} \mathbf{k}^0 \\
&\quad + \frac{1}{2}[(\mathbf{A}^0)^{-1}(\mathbf{q}^0 - \mathbf{k}^0)]^t \, \mathbf{F}^0 [(\mathbf{A}^0)^{-1}(\mathbf{q}^0 - \mathbf{k}^0)] \\
&= E_0(\mathbf{q}_0) + (l^0)^t (\mathbf{A}^0)^{-1} \mathbf{q}^0 + \frac{1}{2}(\mathbf{q}^0)^t \mathbf{A}^0 \mathbf{F}^0 (\mathbf{A}^0)^{-1} \mathbf{q}^0 - \frac{1}{2}(\mathbf{q}^0)^t \mathbf{A}^0 \mathbf{F}^0 (\mathbf{A}^0)^{-1} \mathbf{k}^0 \\
&\quad - \frac{1}{2}(\mathbf{k}^0)^t \mathbf{A}^0 \mathbf{F}^0 (\mathbf{A}^0)^{-1} \mathbf{q}^0 - (\mathbf{l}^0)^t (\mathbf{A}^0)^{-1} \mathbf{k}^0 + \frac{1}{2}(\mathbf{k}^0)^t \mathbf{A}^0 \mathbf{F}^0 (\mathbf{A}^0)^{-1} \mathbf{k}^0 \\
&= E_0(\mathbf{q}_0) + ((\mathbf{l}^0)^t (\mathbf{A}^0)^{-1} - (\mathbf{k}^0)^t \mathbf{A}^0 \mathbf{F}^0 (\mathbf{A}^0)^{-1}) \mathbf{q}^0 + \frac{1}{2}(\mathbf{q}^0)^t \mathbf{A}^0 \mathbf{F}^0 (\mathbf{A}^0)^{-1} \mathbf{q}^0 \\
&\quad - (\mathbf{l}^0)^t (\mathbf{A}^0)^{-1} \mathbf{k}^0 + \frac{1}{2}(\mathbf{k}^0)^t \mathbf{A}^0 \mathbf{F}^0 (\mathbf{A}^0)^{-1} \mathbf{k}^0.
\end{aligned} \tag{1.39}$$

In deriving (1.39), we have made use of the relation $\mathbf{A}^{-1} = \mathbf{A}^t$ for $\mathbf{A}$ being orthogonal. (The inverse of the matrix is its transpose $\mathbf{A}^t \mathbf{A} = \mathbf{E}$.) The linear term in $\mathbf{q}$ in

Equation 1.39 vanishes, if

$$(\mathbf{l}^0)^t(\mathbf{A}^0)^{-1} - (\mathbf{k}^0)^t\mathbf{A}^0\mathbf{F}^0(\mathbf{A}^0)^{-1} = 0$$

and hence

$$(\mathbf{l}^0)^t(\mathbf{A}^0)^{-1}\mathbf{k}^0 = (\mathbf{k}^0)^t\mathbf{A}^0\mathbf{F}^0(\mathbf{A}^0)^{-1}\mathbf{k}^0. \tag{1.40}$$

Inserting (1.40) into (1.39) yields

$$E_0(\mathbf{q}) = E_0(\mathbf{q}_0) + \frac{1}{2}(\mathbf{q}^0)^t\Lambda^0\mathbf{q}^0 - \frac{1}{2}(\mathbf{k}^0)^t\Lambda^0\mathbf{k}^0, \tag{1.41}$$

where $\Lambda^0 = \mathbf{A}^0\mathbf{F}^0(\mathbf{A}^0)^{-1} = \mathrm{diag}\,(\lambda_1^0, \lambda_2^0, \ldots, \lambda_N^0)$ is composed of diagonal elements λ_μ, which arises from the nonzero frequency normal modes. Thus, Equation 1.41 represents the potential surface of the ground electronic state in the diagonal (canonical) form in mass-weighted ground-state normal coordinates. The last term in Equation 1.41 is a constant and can be included in $E_0(\mathbf{q}_0)$. Thus, the transformation (1.38) that diagonalizes the potential energy for the nuclear motion is determined uniquely by the coefficients l_μ^0 and $f_{\mu\nu}^0$ of the respective electronic state.

Equation 1.41 pertains to the normal coordinates in the ground electronic state; an analogous expression holds for any electronic state a, where again $\Lambda^a = \mathbf{A}^a\mathbf{F}^a(\mathbf{A}^a)^{-1} = \mathrm{diag}\,(\lambda_1^a, \lambda_2^a, \ldots, \lambda_N^a)$ and $\mathbf{A}^a$ is the transformation matrix to mass-weighted coordinates, defined by

$$\mathbf{q}^a = \mathbf{A}^a\mathbf{q} + \mathbf{k}^a. \tag{1.42}$$

It can be proved that

$$E_a = E_a^0 + \frac{1}{2}(\mathbf{q}^a)^t\Lambda^a\mathbf{q}^a. \tag{1.43}$$

Combining (1.42) for $a \neq 0$ and (1.38) leads to

$$\mathbf{q}^a = \mathbf{A}^a(\mathbf{A}^0)^{-1}\mathbf{q}^0 + \mathbf{k}^a - \mathbf{A}^a(\mathbf{A}^0)^{-1}\mathbf{k}^0,$$

which we abbreviate to

$$\mathbf{q}^a = \mathbf{W}\mathbf{q}^0 + \mathbf{k}^{0a}, \tag{1.44}$$

where $\mathbf{W} = \mathbf{A}^a(\mathbf{A}^0)^{-1}$ thus formed is known as the Duschinsky rotation matrix associated with the $0 \to a$ electronic transition and $\mathbf{k}^{0a}$ is related to the geometrical displacement vector between these states. (To simplify notation, we shall henceforth drop the $0a$ superscript on **k**.)

According to Equation 1.44, the normal coordinates of an excited electronic state $\mathbf{q}^a$ relative to those of the ground electronic state $\mathbf{q}^0$ are rotated (rotation matrix **W**) and displaced by the vector **k**. This rotation is called the Duschinsky rotation or Duschinsky mixing effect [41–44] (of the vibrational modes among each other). This mixing effect is subject to symmetry rules of the molecular symmetry group. Since in the most common instances vibrational modes of the same symmetry are mixed with each other (Equations 1.29–1.31 and 1.37), the matrix **W** assumes the quasi-diagonal form indicated below:

$$\mathbf{W} = \begin{vmatrix} ///// & & & \\ & //// & 0 & \\ & 0 & /// & \\ & & & // \end{vmatrix},$$

where the elements outside the shaded area are zero, since they correspond to modes of different symmetry. Simple symmetry arguments show that $U^{aa}_{\mu\nu} \neq 0$ if $q_\mu\, q_\nu$ transform as the totally symmetric transformation and $U^{ab}_{\mu}\, U^{ba}_{\nu} \neq 0$ if $q_\mu\, q_\nu$ transform as the direct product of φ_a and φ_b. Rotations of normal coordinates in an excited electronic state relative to the ground-state normal coordinate space can therefore be expected for such a molecule if it possesses at least two different modes transforming as the same irreducible representation [41]. Cross-terms, and hence rotations in totally symmetric modes, are generated by the $U^{aa}_{\mu\nu}$ term in Equation 1.29, whereas rotations in the nontotally symmetric modes are generated by the terms in the summation over $b \neq a$. As we shall see, this feature plays a crucial role in the derivation of transition probabilities. Vibrational modes of the same symmetry species assigned to the same shading fields in the matrix **W** cannot be represented as single separable modes and are said to be mixed or nonseparable modes.

A very thorough survey of the Duschinsky effect is given in Refs [45–57]. A 8 × 8 Duschinsky matrix **W** has been determined by quantum mechanical calculation of the potential energy surfaces to interpret the vibronic structure of the $^1B_u \leftarrow {}^1A_g$ transition of *trans,trans*-1,3,5,7-octatetraene in alkane matrices at 4.2 K [45]. The mixed modes are of a_{1g} symmetry. Supersonic jet excitation and single vibronic level dispersed fluorescence spectra of α- and β-methyl naphthalene (S_1 state) presented in Ref. [46] reveal that mode mixing of the ground-state normal coordinates and energy redistribution appear to be active in the S_1 state. The vibronic spectra and related phenomena such as fluorescence–absorption mirror symmetry breakdown are found in azulene and certain azaazulenes [47–49]. On the basis of an analysis of vibronic spectra and calculation of normal vibrations, a complete assignment of the vibrational frequencies of *s*-tetrazine-d_0 and *s*-tetrazine-d_8 in the $^1B_{3u}$ excited state is given in Ref. [50]. In this connection, the rotation matrix **W** calculated from the data on the intensities of the vibronic band is used to estimate the force field in the excited electronic state. In Ref. [51], a Duschinsky effect that results from two nontotally symmetric vibrations involved in the vibronic coupling in the S_1-S_0 systems of benzonitrile and phenyl acetylene is reported. An *ab initio* calculation of multidimensional FC (MFC) factors used to analyze the vibronic spectrum of ethylene corresponding to the π–π^* excitation was presented in Ref. [52] taking into account 12 normal coordinates of ethylene among which 4 totally symmetric modes are mixed. Recently, in a study of the photoelectron spectra of H_2O^+ ($\tilde{B}^2B_2$) and D_2O^+, Jia-Lin Chang has calculated MFC integrals including the Duschinsky effect. He found that the photoelectron spectra were mainly composed of ω_2 progressions and combination bands of ω_1 and ω_2 vibrations [53]. The idea that the Duschinsky effect plays a crucial role in the identification of band structures is also confirmed by the vibrational assignment for the $\tilde{A}^1B_2$-$\tilde{X}^1A_1$ transition in tropolone. This molecule possesses an intramolecular hydrogen bond and the hydroxyl proton tunnels from one oxygen atom to the other. Spectroscopic studies indicate that tropolone exhibits a double minimum energy potential along the tunneling coordinate and tunneling doublings have been detected in many vibronic bands in the absorption and laser excitation spectra [54–56]. However, the band structure is exceedingly complex and some of the complexity in the vibrational bands around the 0–0 band is due to strong Duschinsky mixing involving the two lowest b_1 modes ω_{25} and ω_{26}.

The importance of determining the potential energy surfaces of molecular states is clear. The shape of these BO surfaces of the molecular states is intimately involved in the electronic transitions between vibronic states belonging to crossing BO surfaces. This was applied by Paluso *et al.* to the dynamics of electronic transfer in neutral mixed valence monoradicals, using the diabatic representation (as will be illustrated in Section 1.4) and by considering a significant Duschinsky effect [57]. Generally, a significant Duschinsky effect might be expected when the change in equilibrium geometry upon excitation has components of large and comparable magnitude along two or more totally symmetric (ground-state) coordinates. This point will be clarified in detail in Chapter 3 and also in our subsequent consideration, where the Duschinsky effect will play an important role.

1.3
The Vibrational Wavefunctions

The introduction of mass-weighted normal coordinates $\{q_\mu\}$ obtained by diagonalizing the mass-weighted force constant matrix $\mathbf{F}$ in the respective electronic states allows us to solve Equation 1.10 for the vibrational wavefunctions in these states in a very convenient manner. Indeed, writing the kinetic operator (1.3) in mass-weighted coordinates q_μ and taking the diagonalized form (1.43) of the potential energy surface $E_a(\mathbf{q}^a)$, Equation 1.10 is written as

$$\left[-\left(\frac{\hbar^2}{2}\right)\sum_\mu \frac{\partial^2}{\partial q_\mu^{a^2}} + \frac{1}{2}\sum_\mu \lambda_\mu^a q_\mu^{a^2}\right]\chi_{av}(\mathbf{q}^a) = E_{av}\chi_{av}(\mathbf{q}^a), \tag{1.45}$$

where the superscript a denotes the respective electronic state to which χ_{av} is assigned. In our formulation of Equation 1.45, we have made use of the fact that the kinetic energy operator remains invariant under the transformation (1.44). The Hamiltonian of the nuclear motion in Equation 1.45 separates now into parts, each of which is represented by an individual harmonic oscillator H_μ with

$$H_\mu = -\left(\frac{\hbar^2}{2}\right)\frac{\partial^2}{\partial q_\mu^{a^2}} + \frac{1}{2}\lambda_\mu^a q_\mu^{a^2}. \tag{1.46}$$

For local stable molecules, $\lambda_\mu^a > 0$ ($\mu = 1, 2, \ldots, N$), and we can set $\lambda_\mu^a = \omega_\mu^{a2}$, where ω_μ^a is the vibrational frequency of the μth oscillator. The eigenfunctions and eigenvalues of (1.46) are known and given by

$$H_\mu \chi_{an_\mu}\left(\beta_\mu^{a^{1/2}} q_\mu^a\right) = E_{an_\mu} \chi_{an_\mu}\left(\beta_\mu^{a^{1/2}} q_\mu^a\right), \tag{1.47}$$

where

$$E_{an_\mu} = \hbar\omega_\mu^a (n_\mu + 1/2), \quad n_\mu = 0, 1, 2, \ldots \tag{1.48}$$

and

$$\chi_{an_\mu}\left(\beta_\mu^{a^{1/2}} q_\mu^a\right) = \left(\frac{\beta_\mu^{a^{1/2}}}{\sqrt{\pi} 2^{n_\mu} n_\mu!}\right)^{1/2} \exp\left(-\frac{1}{2}\beta_\mu^a q_\mu^{a^2}\right) H_{n_\mu}\left(\beta_\mu^{a^{1/2}} q_\mu^a\right). \tag{1.49}$$

Here H_{n_μ} is the Hermite polynomial of the degree n_μ:

$$H_n(x) = \sum_{k=0} \frac{(-1)^k n!}{k!(n-2k)!} (2x)^{n-2k}$$

and $\beta_\mu^a = (\omega_\mu^a/\hbar)$. The q_μ^a's are dimensioned mass-weighted normal coordinates and the transformation to dimensionless normal coordinates is accomplished by the corresponding frequency factors of the vibrational modes μ in the electronic state a, $\beta_\mu^{a^{1/2}} = (\omega_\mu^a/\hbar)^{1/2}$. The eigenfunction and eigenvalue of the total Hamiltonian $\sum_\mu H_\mu$ are

$$\chi_{an_1 n_2 \ldots n_N}(q_1^a, q_2^a, \ldots, q_N^a) = \chi_{an_1}\left(\beta_\mu^{a^{1/2}} q_1^a\right) \chi_{an_2}\left(\beta_\mu^{a^{1/2}} q_2^a\right) \cdots \chi_{an_N}\left(\beta_\mu^{a^{1/2}} q_N^a\right)$$

and

$$E_{an_1 n_2 \ldots n_N} = E_{an_1} + E_{an_2} + \cdots + E_{an_N}, \tag{1.50}$$

where the vibrational quantum numbers $n_1, n_2, \ldots, n_N$ assume in mutual independence of one another the values $n_\mu = 0, 1, 2, \ldots$.

1.4

The Diabatic Electronic Basis for Molecular Systems

1.4.1

Preliminaries

The Born–Oppenheimer adiabatic approximation derived in Section 1.1 is very useful in classifying molecular eigenstates and calculating molecular dynamics. As long as adiabatic potential energy surfaces remain well separated, it is generally a good approximation to consider the nuclear motion to be confined to one such surface. When two or more surfaces intersect or pass close to one another, it becomes necessary to consider more than one surface in the calculation of nonradiative transition probabilities. When more than one surface must be considered, the adiabatic function is not necessarily more advantageous than various possible linear combinations of these functions. In particular, if the combination is taken over a small number of electronic states presumed to be of interest for a particular problem, they can be chosen by means of a proper transformation such that the nuclear derivative coupling terms (e.g., in Equation 1.12) vanish with respect to the new basis functions. The coupling for the new so-called diabatic basis occurs then as a potential operator.

Consider an example in which only two adiabatic states (say φ_1 and φ_2) are strongly coupled and assume that the coupling involving the other states can be safely neglected. In this case, the nuclear derivative coupling term in Equation 1.12 is given by the components

$$g_\mu = \langle \varphi_2 | \partial/\partial q_\mu | \varphi_1 \rangle \tag{1.51}$$

of a nuclear momentum vector $\mathbf{g}(\mathbf{q}) = (\nabla_q)_{21}$. Here ∇_q stands for the vectorial operator $\nabla_q = (\partial/\partial q_1, \partial/\partial q_2, \ldots, \partial/\partial q_N)$. In this two-state approximation, it is convenient to consider as an alternative a diabatic basis set (ϕ_1, ϕ_2) defined by the condition [58–65]

$$\langle \phi_2 | \nabla_q | \phi_1 \rangle = 0. \tag{1.52}$$

In the diabatic representation, the nuclear coupling is eliminated or drastically reduced. The new diabatic states (ϕ_1, ϕ_2) are thereby allowed to move along with the nuclei [7, 65]. They are not the fixed functions considered in Section 1.2 and referred to as crude adiabatic. Hence, they will be denoted by $\phi_i(\mathbf{r}, \mathbf{q})$ to emphasize the fact that $\nabla\phi_i \neq 0$. In this two-state approximation, it is always possible to transform the pair of adiabatic functions (φ_1, φ_2) by a q-dependent orthogonal transformation [7, 63, 65]:

$$\begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} = \begin{pmatrix} \cos\theta(\mathbf{q}) & \sin\theta(\mathbf{q}) \\ -\sin\theta(\mathbf{q}) & \cos\theta(\mathbf{q}) \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}. \tag{1.53}$$

Substituting Equation 1.53 into Equation 1.52 now leads to

$$g(\mathbf{q}) = \nabla_q \theta(\mathbf{q}) + \langle \phi_2 | \nabla_q | \phi_2 \rangle. \tag{1.54}$$

Note that Equation 1.54 is a vector equation. Thus, condition (1.52) implies that there should exist an angle θ such that

$$g(\mathbf{q}) = \nabla_q \theta(\mathbf{q}). \tag{1.55}$$

As discussed in Ref. [63], this can only be the case if

$$\operatorname{curl} g(\mathbf{q}) = 0, \tag{1.56}$$

which means that if q_μ and q_ν are two of the nuclear coordinates, we can have a solution only if

$$\frac{\partial}{\partial q_\mu} g_\nu - \frac{\partial}{\partial q_\nu} g_\mu = 0. \tag{1.57}$$

As proved in Ref. [63], this follows trivially for a polyatomic molecule if one adopts as diabatic functions a set of q-independent functions for which $\nabla\phi_i = 0$. This can be seen if we use Equation 1.53 to prove another very useful result [66, 67]:

$$|\nabla\phi_1\rangle = (g(\mathbf{q}) - \nabla\theta)|\phi_2\rangle + \sum_a [\cos\theta\,\langle\varphi_a|\nabla\varphi_1\rangle - \sin\theta\,\langle\varphi_a|\nabla\varphi_2\rangle]|\varphi_a\rangle, \quad (1.58)$$

which follows from the fact that $(\nabla_q)_{21} = -(\nabla_q)_{12}$. Here φ_a are adiabatic eigenfunctions of H_{el} other than φ_1 and φ_2. This is a most remarkable fact. It asserts that there can be no solution if $\nabla\phi_1 \neq 0$. Then, one must be either $(\mathbf{g} - \nabla\theta) \neq 0$ or $\langle\varphi_a|\nabla|\varphi_i\rangle \neq 0$ $(i = 1, 2)$, or both of them. In the first case, this is in striking contrast to the concept of a strictly diabatic basis (see Equation 1.55). In the second case, there is an interaction with the other (higher) electronic states. The possibility remains, however, that it might be possible to eliminate the largest part of the coupling through transformation, so that the remainder can be neglected and Equation 1.55 can be replaced by the less stringent condition:

$$\langle\phi_2|\nabla_q|\phi_1\rangle \approx 0. \quad (1.59)$$

A particularly nice discussion to this subject can be found in Refs [7, 60, 63, 68, 69].

Let us now return to Equation 1.55. The angle $\theta(\mathbf{q})$, which depends on N internal nuclear coordinates, can be obtained by a multidimensional integration of the coupling matrix element g_μ [62]. For example, in a two-dimensional configuration space (q_x, q_y), one has

$$\theta(q_x, q_y) = \theta(q_{x0}, q_{y0}) + \int_{q_{x0}}^{q_x} g_x(x, q_{y0})\mathrm{d}x + \int_{q_{y0}}^{q_y} g_y(q_{x0}, y)\mathrm{d}y. \quad (1.60)$$

In the case where g is an irrotational vector and θ a single-valued function, the value of θ should be independent of the integration path.

We shall return in Chapter 7 to a more extensive discussion of applications of the approximation just described. Now we consider the coupling between two electronic states, the potential energy surfaces of which cross in one point.

1.4.2
Conical Intersection Between the States $\tilde{B}\,^2B_2/^2A'$ and $\tilde{A}\,^2A_1/^2A'$ of H_2O^+

The method we have described for studying unimolecular decay of electronically excited molecules may be applied to a variety of problems. These include, for example, the study of properties of conical and Jahn–Teller intersections. Illustrative calculations are presented for the H_2O^+ ion, whose dissociation mechanisms are controlled by a conical intersection between the states $^2B_2$ and $^2A_1$ (C_{2v}), the potential energy surfaces of which have been calculated in Refs [70, 71]. A schematic view of these surfaces is given in Figure 1.1. The coordinates (r, α) are defined as follows: coordinate r is the asymmetric stretch $r = R_1 - R_2$, where R_1 and R_2 are the two OH bond lengths and α is the valence angle between R_1 and R_2. When the two OH bond lengths are equal ($r = 0$; C_{2v} point group) and $q = 1/2(R_1 + R_2)$, the symmetric stretching coordinate is equal to 1.15 Å, the states $\tilde{A}$ and $\tilde{B}$ belong to the $^2A_1$ and $^2B_2$ representations. Their potential energy surfaces cross at $\alpha_c = 71.6°$ [70] and the energy at the conical intersection is equal to 74.4385 hartree. The minimum of the

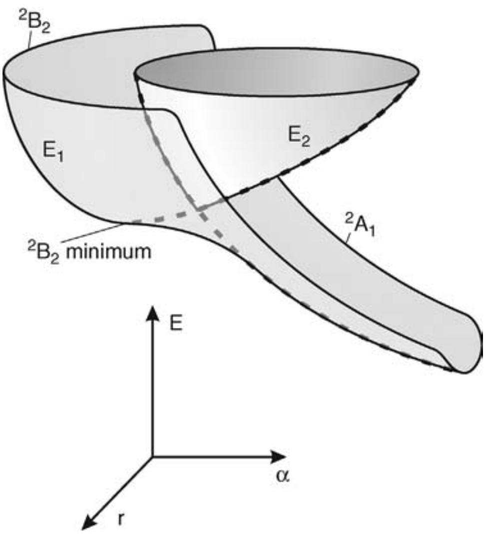

Figure 1.1 The actual form of the $\tilde{B}^2B_2$ and $\tilde{A}^2A_1$ potential surfaces of H_2O^+ in the adiabatic representation. The upper adiabatic potential energy surface E_2 consists of parts of the surfaces of the states $^2B_2$ and $^2A_1$. (After Ref. [35].)

potential function of the state $^2B_2$ lies at an absolute energy of −75.4435 hartree and the $^2B_2$ state equilibrium conformation has an H−O−H bond angle of 55.7°. When the antisymmetric stretching coordinate r differs from zero, that is, when the two OH bond lengths are unequal, both electronic states then belong to the $^2A'$ representation of the C_s point group and therefore the corresponding potential energy surfaces repel each other. As a result, a region of strong nonadiabatic interaction is centered around the apex of the double cone. It is important to note that the two interacting states $\tilde{A}$ and $\tilde{B}$ are well separated in energy from the remaining states. If it did, one is dealing here with a two-state conical intersection problem (with the second term in Equation 1.58 having been omitted).

The *ab initio* calculations at the SCF level of the nonadiabatic coupling matrix element $g_\alpha = \partial\theta/\partial\alpha$ for different cross sections $r =$ constant have shown [70] that g_α has a Lorentzian shape with a unique maximum centered at the crossing between the two surfaces (e.g., at $\alpha_c = 71.6°$). Along the direction r, the function g_r exhibits again a unique maximum and a Lorentzian shape, although the two contributions g_r^{MO} and g_r^{CI} sometimes add and sometimes subtract. The resulting $g_r = g_r^{\mathrm{MO}} + g_r^{\mathrm{CI}}$ is therefore found to be positive at values of α smaller than α_c and negative for α larger than α_c, where α_c denotes the value of the valence angle at the apex of the cone. The closer the cross section lies to the apex of the cone, the narrower the g-function becomes. In the case, where the cross section passes through the apex of the cone, the linear model (which will be encountered later) predicts that the g-function should become a Dirac delta function with an area close to the theoretical value of $\pi/2$ [70, 73–76].

Adiabatic surfaces are defined as the eigenvalues of the electronic Hamiltonian (see Equation 1.5). In the diabatic representation defined above, the potential energy surfaces are defined by the diagonal elements H_{11} and H_{22}. They can cross freely and are coupled by an off-diagonal matrix element H_{12}. Adiabatic surfaces are related to diabatic matrix elements H_{ii} by the equation

$$E_i(\mathbf{q}) = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}\left[(H_{11} - H_{22})^2 + 4H_{12}^2\right]^{1/2}, \quad i = 1, 2. \tag{1.61}$$

This expression is the equation of a double cone with expansion of the H_{ij} functions around the apex and retention of first-order terms only. The linear approximation will be discussed later in this section.

The unitary transformation (1.53) (of the Hamiltonian matrix in the diabatic basis (ϕ_1, ϕ_2)) leading to $E_i(\mathbf{q})$ is determined by the angle

$$\theta = \frac{1}{2}\arctan\{2H_{12}/(H_{11} - H_{22})\}, \tag{1.62}$$

which depends on three internal nuclear coordinates $\theta = \theta(q, r, \alpha)$. Furthermore, one has from (1.55)

$$g_\mu = \partial\theta/\partial q_\mu, \tag{1.63}$$

with $g_\mu = \langle \varphi_2 | \partial/\partial q_\mu | \varphi_1 \rangle$ or equivalently (see Equation 1.60)

$$\theta(r, \alpha) = \int_{r_0}^{r} \mathrm{d}r g_r(r, \alpha) + \int_{\alpha_0}^{\alpha} \mathrm{d}\alpha\, g_\alpha(r_0, \alpha) \tag{1.64}$$

if we restrict ourselves to an integration at fixed value of q (the symmetric stretching coordinate). In the case of H_2O^+, $q = 1.15$ Å, that is, the value of q at the apex of the cone. The integration in Equation 1.64 of the *ab initio* calculated g_μ matrix elements can be performed numerically. Before giving a more quantitative discussion, we first note that Equation 1.64 defines generally a multivalued function (i.e., $\theta(\mathbf{q})$ is of modulus π). This behavior of θ is a result of the singularities of the functions g_α and g_r at $\alpha = 71.6^\circ$ and $r = 0$ (the apex of the cone). This problem is better understood within the framework of the linear model of the conical intersection, which will be dealt with later.

Once the angle θ is known as a function of the internal coordinates, it is not difficult to obtain the diabatic energies H_{11} and H_{22} and the coupling matrix element H_{12} by inverting the orthogonal transformation (1.53). A schematic view of the diabatic surfaces H_{11} and H_{22} is given in Figure 1.2.

1.4.3
The Linear Model for Conical Intersection

The linear model of a conical intersection [58, 66, 77–79] is obtained by neglecting terms of order higher than one in the expansion of the matrix elements H_{ij} around the apex of the cone ($r = 0$, $\alpha_c = 71.6^\circ$):

$$H_{11} - H_{22} = F_\alpha(\alpha - \alpha_c), \tag{1.65}$$