Hans Kupka

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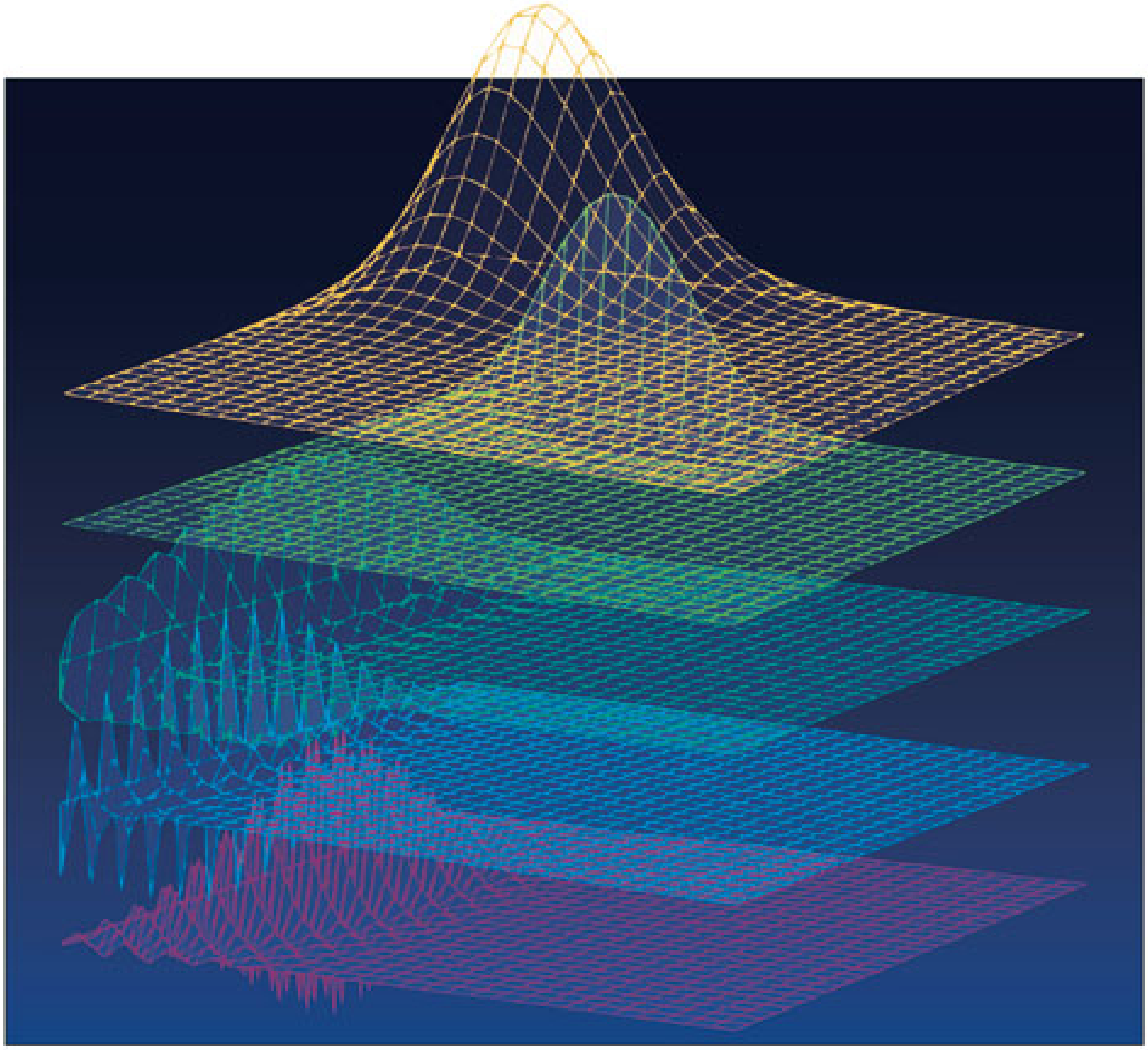
Transitions in Molecular Systems



Contents

Preface

1 Introduction

- 1.1 The Adiabatic Description of Molecules
- 1.2 Normal Coordinates and Duschinsky Effect
- 1.3 The Vibrational Wavefunctions
- 1.4 The Diabatic Electronic Basis for Molecular Systems

2 Formal Decay Theory of Coupled Unstable States

- 2.1 The Time Evolution of an Excited State
- 2.2 The Choice of the Zero-Order Basis Set

3 Description of Radiationless Processes in Statistical Large Molecules

- 3.1 Evaluation of the Radiationless Transition Probability
- 3.2 The Generating Function for Intramolecular Distributions I_1 and I_2
- 3.3 Derivation of the Promoting Mode Factors $K_\eta(t)$ and $I_\eta(t)$
- 3.4 Radiationless Decay Rates of Initially Selected Vibronic States in Polyatomic

Molecules

4 Calculational Methods for Intramolecular Distributions I_1, I_2, and I_N

4.1 The One-Dimensional Distribution $I_1(0,n;a,b)$
4.2 The Distributions I1(m, n;a,b)
4.3 Calculation of the Multidimensional Distribution
4.4 General Case of N-Coupled Modes
4.5 Displaced Potential Surfaces
4.6 The Contribution of Medium Modes

5 The Nuclear Coordinate Dependence of Matrix Elements

5.1 The q-Centroid Approximation
5.2 Determination of the q-Centroid

6 Time-Resolved Spectroscopy

6.1 Formal Consideration
6.2 Evaluation of the Radiative Decay Probability of a Prepared State
6.3 The Sparse Intermediate Case
6.4 Radiative Decay in Internal Conversion by Introduction of Decay Rates for $\{\psi_1\}$
6.5 Dephasing and Relaxation in Molecular Systems

- 7 Miscellaneous Applications
  - 7.1 The Line Shape Function for Radiative Transitions
  - 7.2 On the Mechanism of Singlet–Triplet Interaction
  - 7.3 Comment on the Temperature Dependence of Radiationless Transition
  - 7.4 Effect of Deuteration on the Lifetimes of Electronic Excited States
  - 7.5 Theory and Experiment of Singlet Excitation Energy Transfer in Mixed Molecular Crystals
  - 7.6 Electronic Predissociation of the $^2B_2$ State of H_2O^+
- 8 Multidimensional Franck–Condon Factor
  - 8.1 Multidimensional Franck–Condon Factors and Duschinsky Mixing Effects
  - 8.2 Recursion Relations
  - 8.3 Some Numerical Results and Discussion
  - 8.4 Implementation of Theory and Results
  - 8.5 The One-Dimensional Franck–Condon Factor (N = 1)
- Appendices

Appendix A: Some Identities Related to Green's Function
- A.1 The Green's Function Technique
- A.2 Evaluation of the Diagonal Matrix Element of G_{ss}

Appendix B: The Coefficients of the Recurrence

Appendix C: The Coefficients of the Recurrence

Appendix D: Solution of a Class of Integrals

Appendix E: Quantization of the Radiation Field

Appendix F: The Molecular Eigenstates

Appendix G: The Effective Hamiltonian and Its Properties

Appendix H: The Mechanism of Nonradiative Energy Transfer
- H.1 Single-Step Resonance Energy Transfer
- H.2 Phonon-Assisted Energy Transfer

Appendix I: Evaluation of the Coefficients $b_{\mu\nu}$, $c_{\mu\nu}$, and b_{μ} in the Recurrence Equations 8.28 and 8.29
    I.1 Application

Appendix J: Evaluation of the Position Expectation Values of $\chi sm(q^s)$

Appendix K: Vibronic Coupling Between Two Electronic States: The Pseudo-Jahn–Teller Effect

Referenes

Index

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Cover Picture

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

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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*-$[Co(CN)_2(tn)_2]Cl3H_2O$, 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 $^2B_2$ state of 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.

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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 Schr€odinger 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

$$H = T_{\mathrm{e}}(\mathbf{r}) + T_{\mathrm{N}}(\mathbf{q}) + U(\mathbf{r}, \mathbf{q}). \quad (1.1)$$

Here the vector $\mathbf{r} = (r_1, r_2, . . . , r_n)$ 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 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(**r**) and the nuclear kinetic operator T_N(**q**) are presented in a diagonal form:

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

and

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

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

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

where **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 (3*K*–6) × (3*K*–6) mass-weighted matrix, A is the orthogonal transformation that diagonalizes the mass-weighted Cartesian force constant matrix, and **q** is the dimensioned normal coordinate vector. U(**r**, **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 Ψ(**r, q**) in a stationary state satisfy the time-independent Schrodinger equation

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

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 $T_N(\mathbf{q}) = 0$, 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

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

where E_a(q) corresponds to the electronic energy at this fixed nuclear configuration. The configuration 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 r and parametrically on the nuclear coordinates. For any value of **q**, the φ_a are assumed to be orthonormal and complete (i.e., span the subspace defined by the electronic coordinates **r**). They are also assumed to vary in a continuous manner with **q**. The total (molecular) wavefunction $\Psi(\mathbf{r}, \mathbf{q})$ can be expanded in terms of the electronic basis function [4, 5]

$$\Psi_{v}(\mathbf{r}, \mathbf{q}) = \sum_{b} \varphi_{b}(\mathbf{r}; \mathbf{q}) \chi_{bv}(\mathbf{q}), \tag{1.6}$$

where the nuclear wavefunctions $\chi_{bv}(\mathbf{q})$ 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

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

and

$$\frac{\partial^{2}(\varphi_{b}\chi_{bv})}{\partial r_{i}^{2}} = \chi_{bv}\left(\frac{\partial^{2}\varphi_{b}}{\partial r_{i}^{2}}\right),$$

we find according to Equation 1.6 that

$$\begin{aligned} H\sum_{b}\varphi_{b}\chi_{bv} &= \sum_{b}\Bigg\{E_{b}(\mathbf{q})\varphi_{b}(\mathbf{r};\mathbf{q})\chi_{bv}(\mathbf{q}) + T_{\mathrm{N}}(\mathbf{q})\varphi_{b}(\mathbf{r};\mathbf{q})\chi_{bv}(\mathbf{q}) \\ &\qquad -2\sum_{\mu}\left(\frac{\hbar^{2}}{2}\right)\frac{\partial\varphi_{b}(\mathbf{r};\mathbf{q})}{\partial q_{\mu}}\frac{\partial\chi_{bv}(q)}{\partial q_{\mu}} + \varphi_{b}(\mathbf{r};\mathbf{q})T_{\mathrm{N}}(\mathbf{q})\chi_{bv}(\mathbf{q})\Bigg\} \\ &= E\sum_{b}\varphi_{b}(\mathbf{r};\mathbf{q})\chi_{bv}(\mathbf{q}). \end{aligned}$$

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]):

$$\begin{aligned} &[T_{\mathrm{N}}(\mathbf{q}) + E_{a}(\mathbf{q}) + \langle\varphi_{a}|T_{\mathrm{N}}|\varphi_{a}\rangle - E]\chi_{av}(\mathbf{q}) \\ &\quad + \sum_{b\neq a}\left\{\langle\varphi_{a}|T_{\mathrm{N}}(\mathbf{q})|\varphi_{b}\rangle_{r} - 2\sum_{\mu}(\hbar^{2}/2)\langle\varphi_{a}|\partial/\partial q_{\mu}|\varphi_{b}\rangle_{r}\partial/\partial q_{\mu}\right\}\chi_{bv}(\mathbf{q}) = 0. \end{aligned} \tag{1.8a}$$

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

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

where X_{ab}, $= -\langle\varphi_a|[T_N,\varphi_b]\rangle_r$ 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

$$\Psi_{av}(\mathbf{r},\mathbf{q})=\varphi_a(\mathbf{r};\mathbf{q})\chi_{av}(\mathbf{q}) \quad (1.9)$$

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

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

where E_{av} is the eigenvalue for the nth 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 (q) generated by the electron distribution, while the electron distribution is a function of the nuclear configuration **q**. $E_a(\mathbf{q})$ is designated as the adiabatic potential surface of φ_a. The additional diagonal term $\langle\varphi_a|[T_N,(q)\varphi_a]\rangle_r$ 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]:

$$\left(\langle \Psi_{av} | H | \Psi_{av'} \rangle_r\right)_q = E_{av}\delta_{vv'} \tag{1.11}$$

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

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

In Equation 1.12, we have indicated convenient abbreviations for the two integrals: ⟨||⟩ 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 $E_{av}-E_{bv'}$, 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 $E_{av}\approx E_{bv'}$ 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]:

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

and

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

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

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

and relation (1.15) is well behaved. At the surface intersections $E_a(\mathbf{q}) \neq E_b(\mathbf{q})$, 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

(1.16) $\langle \varphi_a | \partial/\partial q_\mu | \varphi_b \rangle = [\partial\langle \varphi_a | \partial U/\partial q_\mu | \varphi_b \rangle/\partial q_\mu] / [\partial E_b/\partial q_\mu - \partial E_a/\partial q_\mu],$

where we have assumed, for simplicity, that the intersection surface results from the variation of a single coordinate q_μ, and that $(\partial E_b/\partial q_\mu)_c \equiv (\partial E_a/\partial_\mu)_c$ at the intersection point *c.* This means that $\langle \varphi_a | \partial^2/\partial q_\mu^2 | \varphi_b \rangle$ 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 (non-singular) 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 $\langle \varphi | \partial / \partial q_\mu | \varphi_b \rangle$ 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

$$H_{\mathrm{elec}} = T_{\mathrm{e}}(\mathbf{r}) + U(\mathbf{r}, \mathbf{q}_0) + \Delta U(\mathbf{r}, \mathbf{q}), \quad (1.17)$$

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 vibroni-cally 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 q_0 satisfy the following Schrodin-ger equation:

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

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 $\varphi_a^{\mathrm{CA}}(\mathbf{r};\mathbf{q}_0)$:

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

As before, $\chi_{bv}(\mathbf{q})$ 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 $\chi_{bv}(\mathbf{q})$

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

The functions $\chi_{bv}(\mathbf{q})$ are therefore determined by the set of coupled equations (1.20). The potential functions $\langle\varphi_a^{\mathrm{CA}}|\Delta U|\varphi_b^{\mathrm{CA}}\rangle$

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

(1.21) $\langle \varphi_a^{\mathrm{CA}} | \Delta U | \varphi_b^{\mathrm{CA}} \rangle = 0$

for a ≠ b, Equation 1.19 is simply written as a product

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

where the coefficient χ_{av}^{CA} is the eigenstate of the following equation:

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

The diagonal matrix elements $\langle \varphi_a^{\mathrm{CA}} | \Delta U | \varphi_a^{\mathrm{CA}} \rangle$ are the effective potential energy surface that governs nuclear motion. From Equations 1.10 and 1.23, it is evident that the vibrational wavefunction χ_{av}^{CA} differs from the adiabatic wavefunction χ_{av}^{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-Schrodinger (RS) perturbation calculation, taking ΔU as perturbation operator. This leads to

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

where

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

and

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

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

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

where

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

Expansion of ΔU in the vicinity of q_0 in terms of nuclear coordinates $\{q_\mu\}$ gives

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

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

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

with

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

and quadratic terms in q_μ:

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

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

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

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

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

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

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

which can be compared with Equation 1.19 to yield the relation

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

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 ath electronic state and reformulate it in a more suitable (canonical) form:

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

with

$$l_{\mu}^{a} = U_{\mu}^{aa}$$

and

$$f_{\mu\nu}^{a} = U_{\mu\nu}^{aa} + 2\sum_{b\neq a} \frac{U_{\mu}^{ab} U_{\nu}^{ba}}{E_a^{\mathrm{CA}} - E_b^{\mathrm{CA}}}. \tag{1.37}$$

In Equation 1.36, the boldface letters **q** and **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 *a*th 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 *a*th electronic state. The pure quadratic force constant coefficients $f_{\mu\mu}^{a}$ 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:

(1.38) $$\mathrm{q}^a = \mathrm{A}^a\mathrm{q} + \mathrm{k}^a,$$

where $\mathbf{A}^a$ is an orthogonal matrix that diagonalizes the mass-weighted force constant matrix **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

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

(1.39)

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

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

and hence

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

Inserting (1.40) into (1.39) yields

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

where $\Lambda^0 = \mathrm{A}^0\mathrm{F}^0(\mathrm{A}^0)^{-1} = \mathrm{diag}\,(\lambda_1^0, \lambda_2^0, \ldots, \lambda_N^0)$ 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 $E_0(q_0)$. 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 $\Lambda^a = \mathbf{A}^a\mathbf{F}^a(\mathrm{A}^a)^{-1} = \mathrm{diag}\,(\lambda_1^a, \lambda_2^a, \ldots, \lambda_N^a)$ and $\mathbf{A}^a$ is the transformation matrix to mass-weighted coordinates, defined by

(1.42) $\mathrm{q}^a = \mathrm{A}^a\mathrm{q} + \mathrm{k}^a.$

It can be proved that

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

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

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

which we abbreviate to

(1.44) $\mathrm{q}^a = \mathrm{W}\mathrm{q}^0 + \mathrm{k}^{0a},$

where $\mathrm{W} = \mathrm{A}^a(\mathrm{A}^0)^{-1}$ thus formed is known as the Duschinsky rotation matrix associated with the 0 → *a* electronic transition and k^{0a} is related to the geometrical displacement vector between these states. (To simplify notation, we shall henceforth drop the 0*a* 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 (S1 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 v2 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 $\tilde{A}^1B_2$-$\tilde{X}^1A_1$