Hans J. Kupka

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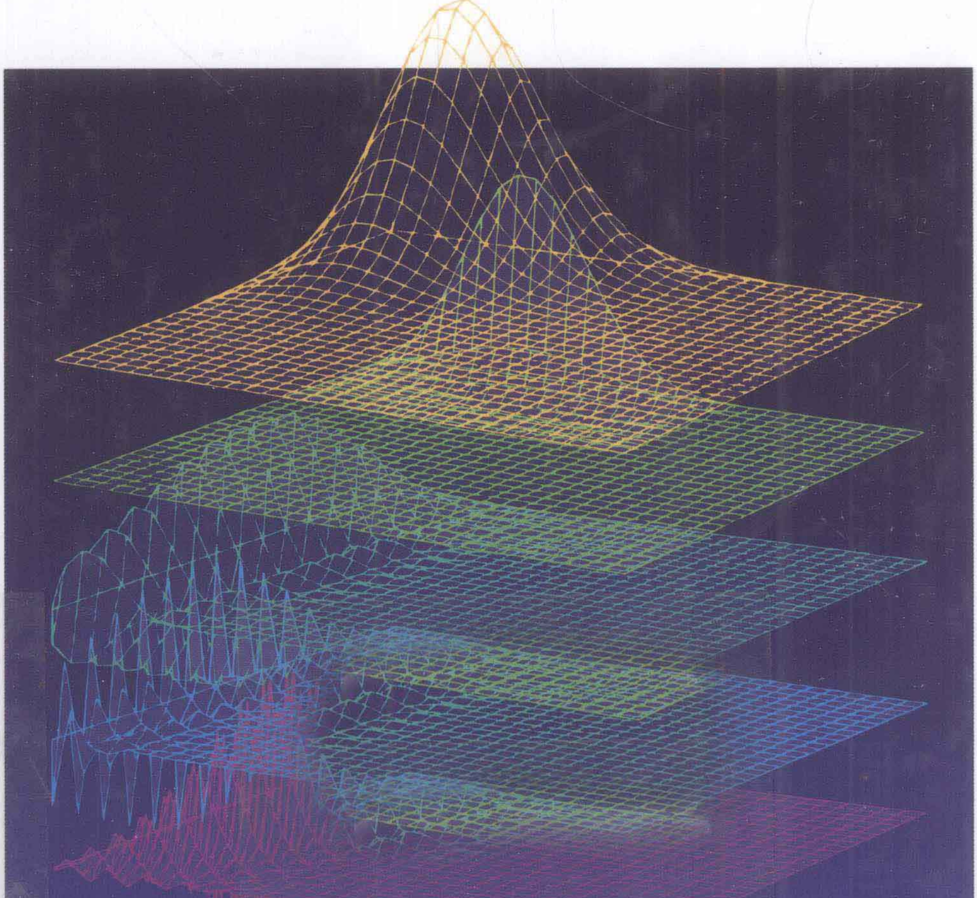
Transitions in Molecular Systems



Hans J. Kupka

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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.

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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 $^2B_2$ 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.

December 2008
Düsseldorf, Germany

Hans J. Kupka

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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 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

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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

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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

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

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]):

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

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

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

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

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

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

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

where $E_{a\mathrm{v}}$ is the eigenvalue for the vth 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]:

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

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

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

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 $E_{av}-E_{bv'}$, 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]:

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

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 $\chi_{b\mathrm{v}}(\mathbf{q})$:

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

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

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

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:

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

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 $\chi_{a\mathrm{v}}^{\mathrm{CA}}$ 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)

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