CONTRIBUTORS TO THIS VOLUME

M. V. BASILEVSKY
I. B. BERSUKER
RAMON CARBÓ
LLORENÇ DOMINGO
MIKLÓS KERTÉSZ
JOSEP-JORDI PERIS
V. Z. POLINGER
V. M. RYABOY

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PER-OLOV LÖWDIN

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UPPSALA UNIVERSITY
UPPSALA, SWEDEN
AND
QUANTUM THEORY PROJECT
UNIVERSITY OF FLORIDA
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CONTRIBUTORS

Numbers in parentheses indicate the pages on which the authors' contributions begin.

M. V. BASILEVSKY (1), Karpov Institute of Physical Chemistry, Moscow B-120, USSR

I. B. BERSUKER (85), Institute of Chemistry, Academy of Sciences, MoSSR, Kishinev 277028, USSR

RAMON CARBÓ (215), Secció de Quimica Quántica, Departament de Quimica Orgánica, Institut Quimic de Sarriá, Barcelona-17, Spain

LLORENÇ DOMINGO (215), Secció de Quimica Quántica, Departament de Quimica Orgánica, Institut Quimic de Sarriá, Barcelona-17, Spain

MIKLÓS KERTÉSZ* (161), Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, Hungary

JOSEP-JORDI PERIS (215), Secció de Quimica Quántica, Departament de Quimica Orgánica, Institut Quimic De Sarriá, Barcelona-17, Spain

V. Z. POLINGER (85), Institute of Chemistry, Academy of Sciences, MoSSR, Kishinev 277028, USSR

V. M. RYABOY (1), Karpov Institute of Physical Chemistry, Moscow B-120, USSR

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*Present address: Department of Chemistry, Cornell University, Ithaca, New York 14853.

PREFACE

In investigating the highly different phenomena in nature, scientists have always tried to find some fundamental principles that can explain the variety from a basic unity. Today they have not only shown that all the various kinds of matter are built up from a rather limited number of atoms, but also that these atoms are constituted of a few basic elements of building blocks. It seems possible to understand the innermost structure of matter and its behavior in terms of a few elementary particles: electrons, protons, neutrons, photons, etc., and their interactions. Since these particles obey not the laws of classical physics but the rules of modern quantum theory of wave mechanics established in 1925, there has developed a new field of "quantum science" which deals with the explanation of nature on this ground.

Quantum chemistry deals particularly with the electronic structure of atoms, molecules, and crystalline matter and describes it in terms of electronic wave patterns. It uses physical and chemical insight, sophisticated mathematics, and high-speed computers to solve the wave equations and achieve its results. Its goals are great, but perhaps the new field can better boast of its conceptual framework than of its numerical accomplishments. It provides a unification of the natural sciences that was previously inconceivable, and the modern development of cellular biology shows that the life sciences are now, in turn, using the same basis. "Quantum biology" is a new field which describes the life processes and the functioning of the cell on a molecular and submolecular level.

Quantum chemistry is hence a rapidly developing field which falls between the historically established areas of mathematics, physics, chemistry, and biology. As a result there is a wide diversity of backgrounds among those interested in quantum chemistry. Since the results of the research are reported in periodicals of many different types, it has become increasingly difficult for both the expert and the nonexpert to follow the rapid development in this new borderline area.

The purpose of this serial publication is to try to present a survey of the current development of quantum chemistry as it is seen by a number of the internationally leading research workers in various countries. The authors have been invited to give their personal points of view of the subject freely and without severe space limitations. No attempts have been made to avoid overlap—on the contrary, it has seemed desirable to have certain important research areas reviewed from different points of view. The response from the authors has been so encouraging that a sixteenth volume is now being prepared.

The Editor would like to thank the authors for their contributions, which give an interesting picture of the current status of selected parts of quantum chemistry. The topics in this volume cover studies of the quantum theory of linear triatomic reactions, vibronic interactions and the Jahn–Teller effect, the electronic structure of polymers, and the use of unitary transformations in self-consistent field theory. Some of the articles emphasize studies in fundamental quantum theory and quantum statistics, and others applications to comparatively complicated systems.

It is our hope that the collection of surveys of various parts of quantum chemistry and its advances presented here will prove to be valuable and stimulating, not only to the active research workers but also to the scientists in neighboring fields of physics, chemistry, and biology who are turning to the elementary particles and their behavior to explain the details and innermost structure of their experimental phenomena.

PER-OLOV LÖWDIN

Quantum Dynamics of Linear Triatomic Reactions

M. V. BASILEVSKY and V. M. RYABOY
Karpov Institute of Physical Chemistry
Moscow, USSR

I. Introduction

The field of dynamics of triatomic exchange reactions has intensively developed over the last decade. The main results were summarized in

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several reviews (Truhlar and Wyatt, 1976; Connor, 1979; Bernstein, 1979; Wyatt, 1979, 1980; Light, 1979). Accurate quantum mechanical three-dimensional (3D) calculations are now available. Therefore, from a computational point of view, one could conclude that this field of research was exhausted to a considerable extent.

We have another point of view in the present survey. A linear collision of an atom and a diatomic molecule resulting in a rearrangement of chemical bonds is the simplest example of a chemical reaction. In the dynamical context a linear triatomic system presents an ideally pure model of interaction and interconversion between the translational and vibrational motions during a chemical process. Being an excellent nontrivial test for a mathematical technique aimed at solving dynamical problems, it is also sufficiently realistic to be considered as a source of useful and visual physical concepts. If the latter aspect prevails, the computational details become of secondary importance. Both general mathematical formulations and simplified models are interesting not by themselves but in connection with the perspective of their extention onto more complicated chemical objects.

A general qualitative approach in chemical dynamics is based on a fruitful intuitive idea of a reaction coordinate. Its mathematical formulation (Hofacker, 1963; Marcus, 1966, 1968; Basilevsky, 1977; Miller *et al.*, 1980) introduces special curvilinear coordinates describing a continuous transformation of a chemical system from an initial (reactant) to a final (product) state. Unfortunately, an exact version of this theory becomes considerably complicated in the case of a large curvature of the reaction coordinate.

If we disregard this complication, the dynamical treatment of polyatomic systems may be reduced, similar to the triatomic case, to a study of interactions between the translational motion along a reaction coordinate and transversal vibrational motions. When vibrational amplitudes are small, one neglects coupling of the above-mentioned motions with the overall rotation of a system. This simplification, well known in the theory of molecular vibrations (Eckart, 1935; Louk and Galbraith, 1976), is equally valid for treating a one-parameter evolution of a system of harmonic oscillators, which is a natural description of the motion of a polyatomic system along a reaction coordinate (Basilevsky, 1977). By this reasoning, a linear (1D) triatomic model deserves individual discussion.

One of the two aims of this article is the systematic presentation of 1D matrix theory of the reactive scattering in linear triatomic systems. Starting from the construction of curvilinear coordinates with a specially prepared translational degree of freedom, we proceed by averaging the overall translational–vibrational Hamiltonian over the vibrational coordinate.

Scattering solutions of the so-obtained 1D matrix Schrödinger equation are the main subject of the subsequent study. In its complete formulation this theory provides an exact solution of a dynamical problem for a given vibrational basis. We consider also its simplified qualitative versions. The main formal results can be extended onto systems with several vibrational modes.

In discussions of alternative formulations of general dynamical theory, we do not present them systematically but refer the reader to the reviews and original papers which contain the complete accounts.

Another aim of the present article is to discuss from a common position numerous results of dynamical calculations. We extract information from both quantal and classical treatments irrespective of the computational method used. Considering that as a collection of empirical observations, we attempt to give interpretations based on the 1D matrix theory. The reader will thus obtain a complete summary of the recent results of dynamical computations; however, their discussion and the presentation of the underlying theoretical background may be rather subjective.

A systematic formulation of the matrix theory of chemical dynamics seems to us especially pertinent in a volume devoted to the recent developments of quantum chemistry. The matrix representation of a stationary Schrödinger equation for molecular electrons is a traditional and powerful mathematical tool of quantum chemistry. In chemical dynamics we also deal with the matrix representation of a Schrödinger equation associated with an evolution of a system of atomic nuclei along the reaction coordinate. Its solution reduces to iteratively repeating standard algebraic procedures (matrix multiplications, inversions, and diagonalizations) which are usual in regular quantum chemical calculations. Quantum chemistry, considered a theory of stable molecular systems, and chemical dynamics, the theory of their mutual transformations, are related not only by the common subject of research but also by a close resemblance of their mathematical techniques.

II. The Description of a Linear Exchange Reaction in Different Coordinate Systems

Potential energy surfaces (PES) of the reactions under discussion have two specific features. First, there always exists a pair of asymptotic regions—the reactant and the product regions—where the complete motion of a system reduces to a relative translation of an atom and a diatomic embodying small vibrations. Second, there exists an intermediate region where the two chemical bonds of a linear triatomic system change simultaneously. Although present in any triatomic system, this latter region is dynamically important only in those systems undergoing a chemical rearrangement. The identification of translational and vibrational degrees of freedom is rather arbitrary there because at any choice they interact intensively and that cannot be eliminated. We shall use the term "rearrangement" or "interaction" zone for that region, depending on which aspect (structural or dynamical) should be emphasized.

In a dynamical study it is important to choose coordinates that enable us first to separate the variables in asymptotic regions in both kinetic and potential energies, and second to present a unique and physically visual description of the rearrangement zone. It is not a simple task to combine these advantages into the framework of a single coordinate system.

One coordinate is always translational. The respective motion is free in at least one of the asymptotic directions. Let us call the other (transversal) coordinate "vibrational". Wave functions of a 1D vibrational Hamiltonian present a natural basis set for the expansion of a complete two-variable wave function. That corresponds to the simplest visual model of a chemical reaction proceeding as a translation of an oscillator with variable parameters. Usually, some refinement is necessary for the consideration of a pair of oscillators (reactant and product) interacting during their simultaneous translational motion. That is a satisfactory model when the PES sections along a vibrational coordinate represent a pair of distinctly separated potential wells. If that is really the case, we deal with a "good" vibrational coordinate.

Two different approaches are possible. The first one suggests relatively simple coordinate systems, generating simple expressions of kinetic energy but complicated vibrational potentials. So the basis functions are available only by means of numerical integration. The second approach uses sophisticated curvilinear coordinate systems, specially conformed to reproduce the shape of a PES. Now the vibrational coordinate becomes good, and simple analytical basis functions are available. The price for that is a complicated expression for kinetic energy.

Further on we shall call "physical" the first type of coordinates (they have come from nuclear physics) and "chemical" the second type (they use a chemical idea of reaction coordinate). When solving the Schrödinger equation in physical coordinates one has to evaluate matrix elements of simple operators with complicated basis functions; however, basis functions are simple in chemical coordinates but the operators for which matrix elements are to be calculated are complicated.

A. Kinetic Energy

The kinetic energy operator (Laplasian) is defined in general curvilinear coordinates as (Sokolnikoff, 1951):

$$T = \frac{1}{2}\frac{\partial}{\partial q^i} J g^{ij} \frac{\partial}{\partial q^j}$$
$$J = [\det\|g^{ij}\|]^{-1/2} = [\det\|g_{ij}\|]^{1/2} \tag{1}$$

Here g_{ij}, g^{ij}, and J are the covariant and contravariant metric tensors and the Jacobian, respectively. The summation over repeating indices is implied. The matrices of the metric tensors obey the relation

$$\|g^{ij}\| = \|g_{ij}\|^{-1} = J^{-2}\begin{pmatrix} g_{22} & -g_{12} \\ -g_{21} & g_{11} \end{pmatrix} \tag{2}$$

A coordinate change $(q^{i'}) \rightarrow (q^i)$ generates the standard transformation

$$g_{ij} = \frac{\partial q^{i'}}{\partial q^i}\frac{\partial q^{j'}}{\partial q^j} g_{i'j'}$$

A practical prescription for calculating the metric tensor immediately follows by specifying $q^{i'}$ as Cartesian coordinates $x^{i'}(g_{i'j'} = \delta_{i'j'})$:

$$g_{ij} = \sum_k (\partial x^k/\partial q^i)(\partial x^k/\partial q^j) \tag{3}$$

Thereby

$$J = \det\|\partial x^k/\partial q^i\| \tag{4}$$

Note that the operator representation (1) of the kinetic energy is valid only in a special case: when the wave function λ, operated by T, embodies an absolute scalar. That is to say, $\lambda(q^i) = \lambda(q^{i'})$ after a coordinate change. Otherwise, the expression for T becomes more complicated.

B. Simple Coordinate Systems

1. *Cartesian Coordinates*

The mass-weighed Jacobi coordinates shown in Fig. 1 are Cartesian for a linear three-atomic system

$$\mathrm{A + BC \rightarrow AB + C}$$

If we omit the mass-dependent scale factors, the two sets $(x^{(1)}, z^{(1)})$ and $(x^{(2)}, z^{(2)})$ represent the following variables:

$x^{(1)}$ the distance between A and the center of mass of BC
$x^{(2)}$ the distance between C and the center of mass of AB
$z^{(1)}$ the distance between B and C
$z^{(2)}$ the distance between A and B

The asymptotic directions of the reactant and the product valleys coincide with $x^{(1)}$ and $x^{(2)}$ axes, respectively, and a PES is confined between these

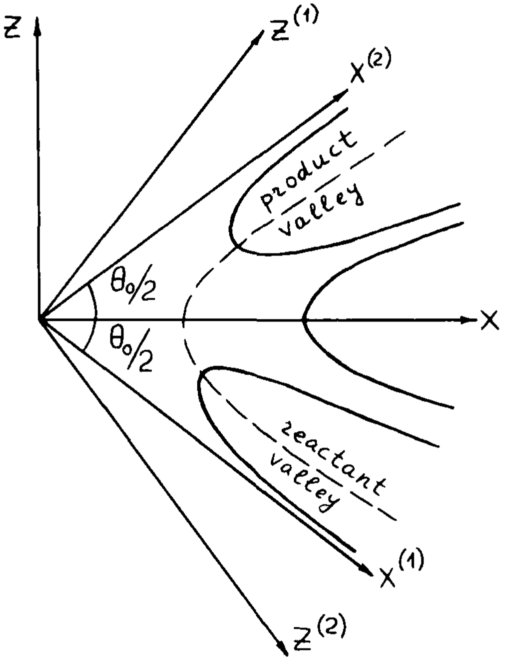


Fig. 1. Mass-weighted Jacobi coordinates.

axes. Therefore, the angle θ_0 determined by the masses of particles m_A, m_B, m_C, is an important characteristic of a system

$$\theta_0 = \arctan \left[\frac{(m_A + m_B + m_C)m_B}{m_A m_C} \right]^{1/2} \tag{5}$$

The metric tensor is represented by a unit matrix. The treatment of the potential energy is illustrated by using the $(x^{(1)}, z^{(1)})$ set:

$$V(x^{(1)}, z^{(1)}) = V_1(x^{(1)}) + V_2(x^{(1)}, z^{(1)})$$

We take a repulsive curve for V_1, the PES cross section along the line $z^{(1)} = z_0^{(1)}$ (an equilibrium bond length of BC; see Fig. 2a). The variables asymptotically separate in the reactant valley: $V_2(x^{(1)}, z^{(1)}) = V_2(z^{(1)})$ when $x^{(1)}$ is large and $z^{(1)}$ is small (see Fig. 2b). The $x^{(1)}$ dependence of $V^{(2)}$ is seen to be stronger the less the $x^{(1)}$ value. In the rearrangement zone (both $x^{(1)}$ and $z^{(1)}$ are small) the potential V_2 at fixed $x^{(1)}$ is neither a usual (harmonic or Morse-like) curve, nor a double-well curve. For instance, it may have the shape shown in Fig. 2c. Finally, the variables $(x^{(1)}, z^{(1)})$ do not asymptotically separate in the product valley.

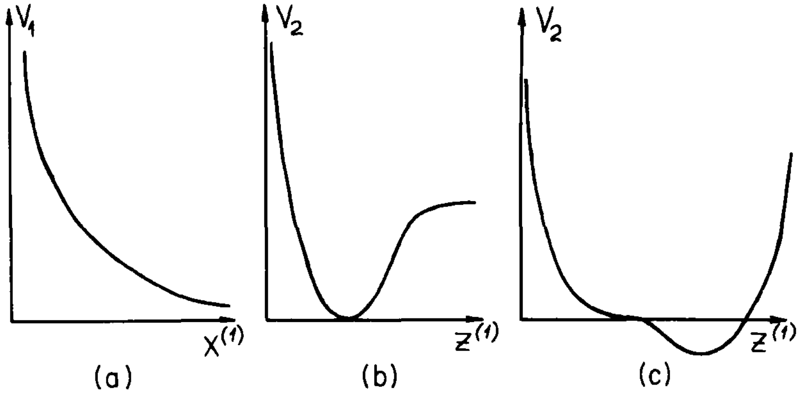


Fig. 2. The potential energy surface cuts for A + BC → AB + C system in Jacobi coordinates. Here, $x^{(1)}_{\text{reactant}}$ and $x^{(1)}_{\text{product}}$ are the values of the $x^{(1)}$ coordinate in the asymptotic reactant and product regions: (a) $z^{(1)} = z^{(1)}_0$, (b) $x^{(1)} = x^{(1)}_{\text{reactant}}$, (c) $x^{(1)} = x^{(1)}_{\text{product}}$.

Hence $x^{(1)}$ is a good translational coordinate and $z^{(1)}$ is a good vibrational coordinate in the reactant valley. It is not so in the rearrangement zone and especially not in the product valley.

Similarly, the coordinates $(x^{(2)}, z^{(2)})$ are well suited to treat the product valley but are unsuitable for the rearrangement zone and the reactant valley.

One more set of Cartesian coordinates is (x, z), see Fig. 1, where the x axis is a bisector of angle θ_0.

2. *Natural Reaction Coordinates*

The natural reaction coordinates (NRC) (Marcus, 1966) specify a position of representative point P (Fig. 3) by the translational variable s and the vibrational variable v: $P = P(s, v)$. The s coordinate is defined as an arc length of the reference curve C, measured from a certain point $s = 0$ to the projection of P on the curve. The v coordinate orthogonal to s is the shortest distance from P to the curve.

Further on we always use the minimum energy path as a reference curve. It coincides with the valley bottoms in the asymptotic regions and passes through the saddle point in the rearrangement zone. The symmetry of this curve, as shown in Fig. 3, is not necessary. We accept that point $s = 0$ lies on the bisector of angle θ_0.

An important characteristic of the reference curve is its curvature $K(s)$ defined as (Pogorelov, 1969)

$$K(s) = d\alpha/ds \qquad (6)$$

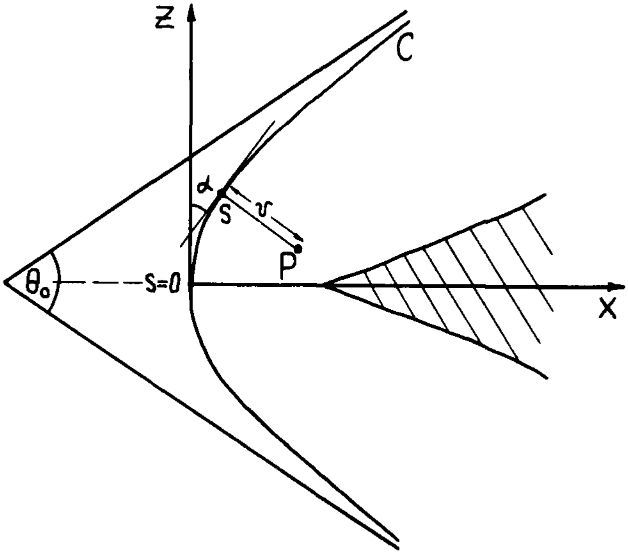


Fig. 3. Natural reaction coordinates (NRC). The multivalued region is dashed.

Here angle α is measured between the Cartesian axis z and the tangent vector to C in the clockwise direction (Fig. 3):

$$\alpha(s) = \int_0^s K(s)\, ds \tag{7}$$

The normalization condition is

$$\int_{-\infty}^{\infty} K(s)\, ds = \pi - \theta_0 \tag{8}$$

Finally, we write the metric tensor and the Jacobian:

$$\|g^{ij}\| = \begin{pmatrix} J^{-2} & 0 \\ 0 & 1 \end{pmatrix}, \qquad J = 1 + K(s)v = J^{\mathrm{NRC}} \tag{9}$$

On defining the potential energy as

$$V(s, v) = V_1(s) + V_2(s, v)$$

we take for $V_1(s)$ the cross section of a PES along the reference curve. Then $V_2(s, v)$ represents vibrational potentials of the respective molecules in the asymptotic regions and the variables separate. Suppose that PES sections for s is a constant represent single-well curves also in the rearrangement zone. Then s and v are good coordinates everywhere in the vicinity of the reference curve.

The latter restriction is important. It follows from the fact that the Jacobian vanishes at the points forming a pair of evolutes, the curves $v = \bar{v}(s) = -K^{-1}(s)$. They join at the point of maximum curvature. For $v < \bar{v}(s)$, the respective points fall into a multivalued region (Light, 1971; Miller and Light, 1971), where several pairs (s, v) can be attributed to the same representative point. The NRC Hamiltonian becomes invalid there. Hence the NRC are good coordinates only when a vibrational amplitude is small, the smallness parameter being $g = Kl$, where K is the maximum curvature and the length unit l is chosen as a classical amplitude for the vibrational ground state at the point where $K(s) = K$. The NRC are useful if $g \ll 1$, this condition meaning that the multivalued region is classically inaccessible, given a practically interesting energy of a system.

The maximum curvature value is related [although not uniquely, see Eq. (8)], to the angle θ_0 [Eq. (5)] and through that to the masses of particles. Hence, NRC are useful in studying reactions

$$\mathbf{L} + \mathbf{HH} \rightarrow \mathbf{LH} + \mathbf{H} \qquad (\theta_0 \gtrsim 80^\circ)$$

Here **L** and **H** denote light and heavy atoms, respectively. The condition $g \ll 1$ is usually obeyed (see, however, Section IV,C,4).

The opposite is true for reactions with different mass relations:

$$\mathbf{H} + \mathbf{LL} \rightarrow \mathbf{HL} + \mathbf{L} \qquad (\theta_0 \approx 45^\circ)$$

$$\mathbf{H} + \mathbf{LH} \rightarrow \mathbf{HL} + \mathbf{H} \qquad (\theta_0 \lesssim 15^\circ)$$

Now the characteristic parameter g is not small and NRC are not good coordinates.

3. *Polar Coordinates. The Definition of Chemical and Physical Coordinates*

The polar coordinates shown in Fig. 4a (Kuppermann, 1970; Connor *et al.*, 1975; Light and Walker, 1976) are often convenient for describing the rearrangement zone. The angular variable θ (times a factor having the length dimension) is a translational coordinate, whereas the radial variable r is a vibrational coordinate. The potential energy is often represented as a "rotated Morse function" (Connor *et al.*, 1975). The origin $\rho = 0$ is placed to the right from the reference curve in the classically inaccessible region; the deeper the shift, the less angle θ_0. That allows a unique description of the rearrangement zone for the reactions **L** + **HH** and **H** + **LL** (for instance, $F + H_2$; $\theta_0 = 46.3^\circ$). This construction fails to be valid for the reactions **H** + **LH** because one has to shift the origin so far to the right that the rotating radius intersects the PES valley at a very acute

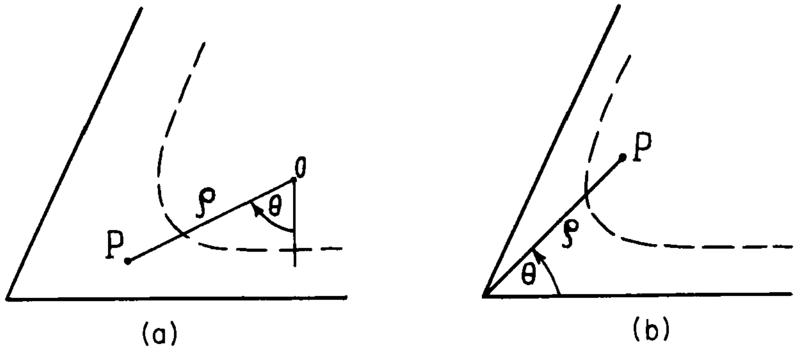


Fig. 4. The polar coordinate systems for describing the rearrangement region. The dotted curves represent the minimum energy path.

angle in the rearrangement region. That is why the respective oscillators corresponding to the PES sections along the radii greatly differ from the real ones, namely, those orthogonal to the reference curve. Their frequencies are unrealistically small, which promotes strong nonadiabatic coupling and results in poor convergence of basis expansions.

The reactions **H** + **LH** are most conveniently treated in terms of other polar coordinates (Fig. 4b) (Kuppermann *et al.*, 1980; Romelt, 1980; Hauk *et al.*, 1980). Now the PES sections $V(\rho, \theta)$ (ρ = const) along the vibrational coordinate θ change their shapes, displaying a single-well potential in the rearrangement zone (small ρ) and gradually becoming double-well curves while passing to the asymptotic regions (large ρ). Therefore, if one reckons on dealing with normal oscillator basis functions, then θ is a bad vibrational coordinate in the intermediate range of ρ. However, a good convergence of a basis expansion is assured, when one uses exact eigenfunctions of vibrational potential irrespective of what form they have. The difficulty is transferred to a numerical calculation of basis functions and to the following calculation of matrix elements with them. The appropriate technique has been developed recently (Kuppermann *et al.*, 1980; Römelt, 1980, 1982; Hauk *et al.*, 1980).

As the terminology proposed in the introduction to this section suggests, the coordinates in Fig. 4a are chemical ones. They represent a chemical rearrangement as a translational motion. The alternative coordinates in Fig. 4b, representing it as a vibration, are physical ones. According to this classification, all Cartesian coordinates (Fig. 1) are physical, whereas NRC are typical chemical coordinates.

The simplest physical skewed coordinates $(x^{(1)}, z^{(1)})$ or $(x^{(2)}, z^{(2)})$

(Fig. 1) were used by Diester (1971). Their drawback is that $z^{(1)}$ is a bad vibrational coordinate for the upper half-plane, the same being true for $z^{(2)}$ in the lower half-plane.

The analytical treatment of polar coordinates is quite simple. For instance, for the physical coordinates

$$\rho = [x^{(1)2} + z^{(1)2}]^{1/2}, \qquad 0 \leq \theta = \arctan[z^{(1)}/x^{(1)}] \leq \theta_0$$

The metric tensor and the Jacobian are

$$g^{ij} = \begin{pmatrix} 1 & 0 \\ 0 & \rho^{-2} \end{pmatrix}, \qquad J = \rho$$

C. Combined Coordinates

1. *General Description of Combined Coordinates*

The above-considered non-Cartesian physical coordinates are not suitable for separating variables in asymptotic regions. Now we construct the coordinates free of this deficiency. They resemble NRC in the asymptotic regions and are easily transformed into them, but the NRC separate just in those regions. Moreover, they are unique in the rearrangement zone, this trait being common to physical coordinates. We shall use the term "combined" for these new coordinates (CC).

The translational coordinate r is measured along the Cartesian axis x; $r > 0$. The origin position may be varied. In any case, a family of coordinate net curves $\Gamma(r)$ is defined for $r > 0$ (Fig. 5). The value of r is determined by the point of their intersection with the x axis. The vibrational coordinate y is measured along the net curves as their arc length from the x axis to a representative point $P(r, y)$. It is positive in the upper half-plane ($z > 0$) and negative in the lower one ($z < 0$).

The curves $\Gamma(r)$ are determined by the field of their directions $\gamma(r, y)$. The angle γ is measured in the anticlockwise direction from the positive z half-axis to the tangent vector of $\Gamma(r)$ at a respective point. The curvature of the coordinate curves obeys the relations

$$\kappa(r, y) = d\gamma/dy, \qquad \gamma(r, y) = \int_0^y \kappa(r, y)\, dy \tag{10}$$

We want y to be a good vibrational coordinate in asymptotic regions defined by the condition $r \gg r_1$. There the asymptotic valleys are directed along the branches of the reference curve C, which are almost rectilinear, becoming true straight lines at $r \to \infty$. We denote the points where the $\Gamma(r)$ curves intersect these branches as $s^{(1)}$ (in the reactant

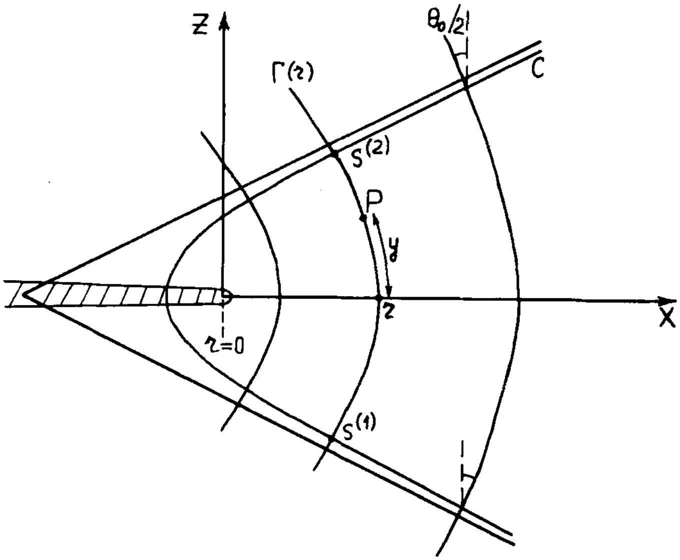


Fig. 5. The combined coordinate system (CC); C is the reference curve of NRC; $\Gamma(r)$ is the set of coordinate curves of CC.

region) and as $s^{(2)}$ (in the product region): $s^{(1)} = s^{(1)}(r, y)$; $s^{(2)} = s^{(2)}(r, y)$. Now y becomes a good coordinate and the variables separate if

$$\partial\gamma/\partial y \approx 0, \qquad \gamma(r, s^{(1)}) \approx -\gamma(r, s^{(2)}) \approx \theta_0/2 \tag{11}$$

(for y near $s^{(1)}$ or $s^{(2)}$). It is understood that these equalities become exact when $r \to \infty$.

So the coordinate net curves become straight lines orthogonal to the regerence curve C in the vicinity of that curve. They remain curvilinear near $y = 0$, but that region is classically inaccessible for $r \gg r_1$.

The normalization of the curvature $\kappa(r, y)$ follows from Eq. (11):

$$\int_{-\infty}^{\infty} \kappa(r, y)\, dy = \pi f(r), \qquad f(r) \to \theta_0/\pi \quad \text{for} \quad r \to \infty \tag{12}$$

2. *Chemical and Physical Combined Coordinates*

We now discuss some properties of the net curves $\Gamma(r)$ near the origin $r = 0$ and consider two alternative descriptions.

a. Chemical CC: The point $r = 0$ is located to the right of the rearrangement zone. These coordinates are shown in Fig. 5. In order to cover the region close to the abscissa half-axis to the left from the point $r = 0$, one has to accept

$$\kappa(r, y) = \pi\delta(y) \qquad \text{for} \quad r \to 0 \tag{13}$$

where δ is the Dirac function. Equations (11) and (13) are the main relations defining chemical CC. Their further specification is less important. One may state, by a simplicity argument, that the curves $\Gamma(r)$ are everywhere convex, symmetrical with respect to the x axis, and that their curvature $\kappa(r, 0) = \kappa_0(r)$ is a maximum for r fixed

$$\begin{gathered} 0 \leq \kappa(r, y) \leq \kappa(r, 0) = \kappa_0(r) \\ \partial\kappa/\partial y = 0, \qquad \gamma(r, y) = 0 \qquad \text{for} \quad y = 0 \end{gathered} \tag{14}$$

The following detailing of function $f(r)$ agrees with

$$1 \geq f(r) \geq \theta/\pi, \qquad \partial f/\partial r < 0 \tag{15}$$

The left-hand side of this inequality follows from Eq. (13). These are chemical coordinates, since the transition from reactants to products in the rearrangement zone proceeds as a translational motion. Note that a natural scale of lengths is drastically distorted near the origin, the point $r = 0$, $y = 0$. The kinetic energy has a singularity at that point. That is why basis expansions are expected to diverge for $r < \epsilon$ (the dashed region in Fig. 5). The value of ϵ can be decreased by shifting the origin point in a classically inaccessible region. (The elimination of the dashed region does not influence a dynamical calculation if ϵ is sufficiently small). The latter remark imposes a restriction on applying chemical CC, which resembles a similar situation with the chemical polar coordinates.

b. Physical CC: The point $r = 0$ is located to the left of the rearrangement zone. The natural scale of lengths is not seriously distorted in these coordinates. The chemical rearrangement is now treated as a vibrational motion; y is not a good vibrational coordinate in the rearrangement region because the respective PES sections resemble very greatly those of the physical polar coordinates. The only important distinction from the latter coordinates, fixed by conditions of Eq. (11), enables an accurate treatment of asymptotic regions. The region close to $r = 0$, is physically insignificant, and there is no need of detailing the properties of the curves $\Gamma(r)$ there.

3. *Calculation of the Metric Tensor in Curvilinear Coordinates*

The calculation is based on Eq. (3). As a preliminary stage, it is necessary to express Cartesian coordinates (x, z) in terms of curvilinear ones (Pogorelov, 1969):

$$\begin{aligned} \text{NRC:}\quad x(s, v) &= \int_0^s \sin\alpha\, ds - v\cos\alpha + \text{const} \\ z(s, v) &= \int_0^s \cos\alpha\, ds + v\sin\alpha \\ \text{CC:}\quad x(r, y) &= r - \int_0^y \sin\gamma\, d\gamma \\ z(r, y) &= \int_0^y \cos\gamma\, d\gamma \end{aligned}$$

[For the definitions of angles α and γ, see Eqs. (7) and (10).] The derivatives for the NRC case are

$$\left(\frac{\partial x}{\partial s}\right)_v = \left(1 + v\frac{d\alpha}{ds}\right)\sin\alpha = (1 + Kv)\sin\alpha, \qquad \left(\frac{\partial x}{\partial v}\right)_s = -\cos\alpha$$

$$\left(\frac{\partial z}{\partial s}\right)_v = \left(1 + v\frac{d\alpha}{ds}\right)\cos\alpha = (1 + Kv)\cos\alpha, \qquad \left(\frac{\partial z}{\partial v}\right)_s = \sin\alpha$$

The substitution of these expressions in Eq. (3) gives the metric tensor (9).

The derivatives for the CC case are

$$\begin{aligned} (\partial x/\partial r)_y &= 1 - \int_0^y \cos\gamma(\partial\gamma/\partial r)_y\, dy, \qquad (\partial x/\partial y)_r = -\sin\gamma \\ (\partial z/\partial r)_y &= -\int_0^y \sin\gamma(\partial\gamma/\partial r)_y\, dv, \qquad (\partial z/\partial y)_r = \cos\gamma \end{aligned} \tag{16}$$

Analytical integration is not possible in general. The matrix elements g_{ij}^{CC} are

$$\begin{gathered} g_{rr} = (\partial x/\partial r)_y^2 + (\partial z/\partial r)_y^2, \qquad g_{yy} = (\partial x/\partial y)_r^2 + (\partial z/\partial y)_r^2 = 1 \\ g_{ry} = g_{yr} = (\partial x/\partial r)_y(\partial x/\partial y)_r + (\partial z/\partial r)_y(\partial z/\partial y)_r \end{gathered} \tag{17}$$

This metric tensor equals unity on the x axis: $g_{rr} = g_{yy} = 1$, $g_{ry} = 0$ for $y = 0$.

The Jacobian of CC is

$$\begin{aligned} J^{CC} &= \left(\frac{\partial x}{\partial r}\right)_y \left(\frac{\partial z}{\partial y}\right)_r - \left(\frac{\partial x}{\partial y}\right)_r \left(\frac{\partial z}{\partial r}\right)_y \\ &= \cos\gamma\left[1 - \int_0^y \cos\gamma\left(\frac{\partial\gamma}{\partial r}\right)_y dy\right] - \sin\gamma\int_0^y \sin\gamma\left(\frac{\partial\gamma}{\partial r}\right)_y dy \end{aligned} \tag{18}$$

This expression is positive if $\partial\gamma/\partial r < 0$ for $y > 0$ and if $\partial\gamma/\partial r > 0$ for $y < 0$. The inequalities are verified for particular CC sets (Basilevsky and Ryaboy, 1980a,b; Basilevsky *et al.*, 1982a) by adding an extra condition $[\partial\kappa_0(r)/\partial r] < 0$, which means that the curvature maximum decreases with the increase of r.

4. *The Relation between NRC and CC in Asymptotic Regions*

The respective transformation is useful because NRC are specially suited for treating asymptotic regions. It is easily accomplished because only the first of conditions (11) is needed. The r dependence of γ may be retained, so the NRC translational coordinate is allowed to be curvilinear, although it is supposed that the multivalued region can be neglected.

Using the fact that γ is independent of y, we can perform integrations in Eq. (16) analytically. The following formulas are helpful:

$$\partial\gamma/\partial r = (\partial\gamma/\partial s)(\partial s/\partial r) = -(\partial s/\partial r)(\partial\alpha/\partial s) = -K\xi^{-1} \tag{19}$$

From a geometric argument we obtain

$$-\xi = -\partial r/\partial s = \pm(1 - K|y_0|)/\cos\gamma \tag{20}$$

The signs + and − are taken for reactants and products, respectively; $y_0 = y_0(r)$ is the coordinate, where the net curve $\Gamma(r)$ intersects the reference curve C. Noting that

$$y - y_0 = \pm v \tag{21}$$

we obtain the explicit formulas

$$\|g_{rv}^{\mathrm{CC}}\| = \begin{pmatrix} \xi^{-2}(1 + Kv)^2 + \sin^2\gamma & -\sin\gamma \\ -\sin\gamma & 1 \end{pmatrix}$$

$$J^{\mathrm{CC}} = \xi^{-1}(1 + Kv)$$

Now the NRC metric tensor appears as a result of the coordinate transformation (Section II,A). We calculate the derivatives

$$\partial s/\partial r = \xi^{-1}, \qquad \partial s/\partial y = 0, \qquad \partial v/\partial r = \pm(-\sin\gamma), \qquad \partial v/\partial y = \pm 1$$

and return to Eq. (9). For the ratio of Jacobians we obtain

$$\pm J^{\mathrm{NRC}}/J^{\mathrm{CC}} = -\xi \tag{22}$$

The transformation $r \leftrightarrow s$ becomes one-dimensional because s is independent of y. So $\partial s/\partial r = ds/dr$ and ξ is also independent of y. According to Eq. (21), the NRC and CC vibrational variables become the same, a single discrepancy being different positions of their origins. The two results represented by Eqs. (21) and (22) are of particular importance for the asymptotic transformation of the solutions of the Schrödinger equation (Section III,B,2).

D. Commentary

Section I,B,1. Cartesian coordinates were described in detail by Marcus (1966) and Glasstone *et al.* (1941).

Section I,B.2. The general idea of NRC is due to Hofacker (1963). Marcus (1966) elaborated the particular NRC system presented in Section II. Miller and Light (1971) suggested a method of overcoming the difficulty associated with their multivaluedness; it was thoroughly discussed by Light (1971).

Section I,B,3. The similar polar coordinates were originally applied in nuclear physics (Delves, 1959, 1960).

Sections I,C,1 and I,C,2. The details of transformations may be found in the papers by Basilevsky and Ryaboy (1980a,b). The practical validity of CC depends on the possibility of obtaining an analytical metric tensor. A special function $\gamma(y)$ must be invented, so that integrals in Eq. (16) could be evaluated analytically. Such coordinates were described by Basilevsky *et al.* (1982a).

Section I,C,4. The connection between CC and the Cartesian coordinates, either $(x^{(1)}, z^{(1)})$ in the reactant region or $(x^{(2)}, z^{(2)})$ in the product region is derived quite similarly. The asymptotic descriptions by NRC and by Cartesian coordinates coincide. The only difference is that in the latter case the duplication of signs is eliminated in Eqs. (20) and (21) [see also Eqs. (48) and (60) in following sections]. So one can do without NRC even in asymptotic regions. However, we consider NRC an important qualitative concept necessary for an understanding of chemical dynamics. That is the reason for their detailed description here.

III. One-Dimensional Matrix Hamiltonian

Averaging the original two-variable Schrödinger equation over the vibrational coordinate yields a one-dimensional translational equation of motion. The averaging procedure is often regarded as a technical one. However, it deserves some discussion when curvilinear coordinates are used. We shall treat a one-dimensional matrix Hamiltonian H as a model Hamiltonian for the reactive scattering problem. It is understood to possess certain symmetry properties, namely, those providing exact conservation of the probability flux for any size of the vibrational basis set.

The symmetry of the matrix operator H arises as a consequence of the self-conjugation property of the original two-variable Hamiltonian $\mathcal{H}$. It can be achieved only if the averaging procedure, necessary for obtaining H, follows certain a prescription. Otherwise, the symmetry will be disturbed, and the conservation law will hold approximately only for several solutions, corresponding to the channels with the lowest energy. Although the accuracy of the flux conservation for a fixed restricted number of solutions can be increased by increasing the size of basis expansions, still a calculation with broken symmetry leaves a feeling of discomfort. Besides that, the dynamical calculation becomes practically more efficient, when the symmetrical Hamiltonian is applied.

A. Averaging the Hamiltonian over the Vibrational Coordinate

1. *One-Dimensional Equation of Motion*

We start with a two-variable Schrödinger equation

$$(\mathcal{H} - E)\lambda = 0, \qquad \mathcal{H} = T + V \tag{23}$$

Equation (1) gives a nonsymmetrical kinetic energy operator. We perform its symmetrization by means of the substitution

$$\lambda = J^{-1/2}\psi \tag{24}$$

That gives a symmetrized Schrödinger equation

$$\begin{gathered}(\mathcal{H}^{\text{symm}} - E)\psi = 0 \\ \mathcal{H}^{\text{symm}} = J^{1/2}\mathcal{H}J^{-1/2} = J^{1/2}TJ^{-1/2} + V\end{gathered} \tag{25}$$

An explicit evaluation of the quantity $J^{1/2}TJ^{-1/2}$ requires cumbersome manipulation which can be facilitated by using the covariant differentiation technique (Basilevsky and Ryaboy, 1980b). The one-dimensional representation is obtained after performing a standard expansion of the wave function ψ over vibrational basis functions φ_n. We shall use the following special notation for column and row vectors:

$$(\cdot\cdot\cdot) \equiv \langle\langle \cdot\cdot\cdot|, \qquad \begin{pmatrix}\cdot\\\cdot\\\cdot\end{pmatrix} \equiv |\cdot\cdot\cdot\rangle\rangle$$

The row of basis functions, written as $\langle\langle\varphi|$, satisfies the vibrational Schrödinger equation

$$h\langle\langle\varphi| = \langle\langle\varphi|\epsilon \tag{26}$$

Here h is a vibrational Hamiltonian (it depends parametrically on the translational coordinate) and ϵ is a diagonal matrix of its eigenvalues.

The basis expansion is

$$\psi_\alpha = \langle\langle\varphi|\chi\rangle\rangle, \qquad \langle\langle\psi| = \langle\langle\varphi|X \tag{27}$$

The column vector $|\chi\rangle\rangle \equiv |\chi^{(\alpha)}\rangle\rangle$ represents a translational wave function in the basis $\langle\langle\varphi|$. The complete set of vectors $|\chi^{(\alpha)}\rangle\rangle$ is collected in matrix X. (The completeness is meant within a given basis manifold. We always consider truncated basis sets and deal with matrices X of a finite dimension).

Averaging Eq. (25) produces a one-dimensional matrix Schrödinger equation:

$$H(E)X \equiv AX'' + BX' + CX = 0 \tag{28}$$

The matrix operator $H(E)$ is the result of averaging the operator $(\mathscr{H}^{\text{symm}} - E)$; the prime is the differentiation with respect to the translational variable.

The benefit resulting from the transformation (24) is revealed already in the averaging procedure. Wave functions $\lambda \equiv \lambda_\alpha(E|q^i)$ (the channel index α labels a set of quantum numbers specifying a given state) satisfy the usual orthonormalization property

$$\int \lambda^*_{\alpha'}(E'|q^i)\lambda_\alpha(E|q^i)J\,dq^1\,dq^2 = \delta(E - E')\,\delta_{\alpha\alpha'} \tag{29}$$

The volume element in curvilinear coordinates is $J\,dq^1\,dq^2$. For the functions $\psi \equiv \psi_\alpha(E|q^i)$ we find

$$\int \psi^*_{\alpha'}(E'|q^i)\psi_\alpha(E|q^i)\,dq^1\,dq^2 = \delta(E - E')\,\delta_{\alpha\alpha'}$$

So these functions are orthonormalized with a unit weight. The symmetrization allows us to evaluate all integrals as if the coordinates q^i were Cartesian. Averaging in (28) reduces to a simple integration over a vibrational variable q^2:

$$H(E) = \int |\varphi\rangle\rangle(\mathscr{H}^{\text{symm}} - E)\langle\langle\varphi|dq^2$$

2. *Translational NRC Hamiltonian*

The NRC Hamiltonian obtained after symmetrization is

$$\mathscr{H}^{\text{symm}} = -\frac{\hbar^2}{2\mu}\left[\frac{\partial}{\partial s}\,J^{-2}\,\frac{\partial}{\partial s} + \frac{\partial^2}{\partial v^2}\right] + V_1(s) + V_2(s, v) + V_3(s, v)$$

The transformation (24) has added an extra term to the potential:

$$V_3(s, v) = -\frac{\hbar^2}{2\mu}\left\{\tfrac{1}{4}J^{-2}K^2 + J^{-1/2}\,\frac{\partial}{\partial s}\left[J^{-1}\,\frac{\partial}{\partial s}\,(J^{-1/2})\right]\right\}$$

For the simplest model we accept that the vibrational potential $V_2(s, v)$ is harmonic. That specifies Eq. (26) as follows:

$$\begin{gathered} h = -(\hbar^2/2\mu)(d^2/dv^2) + \tfrac{1}{2}\omega^2 v^2 \\ \epsilon_n = (n + \tfrac{1}{2})\hbar\omega, \qquad \omega \equiv \omega(s), \qquad n = 0, 1, 2, \ldots \end{gathered} \tag{30}$$

The averaged matrix operator is

$$H(E) = \int dv(|\varphi\rangle\rangle(\mathscr{H}^{\text{symm}} - E)\langle\langle\varphi|)$$

$$\int dv(|\varphi\rangle\rangle\langle\langle\varphi|) = I$$

The detailed transcription of Eq. (28) takes the form

$$\begin{aligned}
&G\frac{d^2}{ds^2}X + \left(\frac{dG}{ds} + Q\right)\frac{dX}{ds} + \left(D + M + \frac{1}{2}\frac{dQ}{ds}\right)X = 0 \\
&G = \int dv(|\varphi\rangle\rangle J^{-2}\langle\langle\varphi|) \\
&D = 2\mu\hbar^{-2}(EI - \epsilon) + \tfrac{1}{4}K^2G \\
&Q = \int dv\left(\left|\varphi\right\rangle\right\rangle J^{-2}\left\langle\left\langle\frac{d\varphi}{ds}\right| - \left|\frac{d\varphi}{ds}\right\rangle\right\rangle J^{-2}\left\langle\left\langle\varphi\right|\right) \qquad (31) \\
&M = \int dv\left[\left|\varphi\right\rangle\right\rangle J^{-1/2}\frac{d}{ds}\left(J^{-1}\frac{d}{ds}J^{-1/2}\right)\left\langle\left\langle\varphi\right|\right. \\
&\qquad + \frac{1}{2}\frac{d}{ds}\left(\left|\varphi\right\rangle\right\rangle J^{-2}\left\langle\left\langle\frac{d\varphi}{ds}\right| + \left|\frac{d\varphi}{ds}\right\rangle\right\rangle J^{-2}\left\langle\left\langle\varphi\right|\right) \\
&\qquad \left. - \left|\frac{d\varphi}{ds}\right\rangle\right\rangle J^{-2}\left\langle\left\langle\frac{d\varphi}{ds}\right|\right]
\end{aligned}$$

These matrices have certain symmetry properties important in the following treatment. Denoting the matrix transposal as a curly overbar, we find

$$G = \tilde{G}, \qquad D = \tilde{D}, \qquad M = \tilde{M}, \qquad Q = -\tilde{Q} \qquad (32)$$

We should not overlook the fact that the integrals in (31) diverge. Their singularities are generated by the zero of the Jacobian at the point $v = -K^{-1}$: $J^{-1} = (1 + Kv)^{-1}$, occurring on the boundary of multivalued region.

We eliminate that complication by a formal trick: Consider evaluation of matrix G, for example. In a complete basis set the following identities are true for a function $f(v)$:

$$\int |\varphi\rangle\rangle f(v)\langle\langle\varphi|dv = f(W), \qquad W = \int |\varphi\rangle\rangle v\langle\langle\varphi|dv$$

$$W_{kk+1} = (\hbar/2\mu\omega)^{1/2}(k+1)^{1/2}, \qquad W_{kk-1} = (\hbar/2\mu\omega)^{1/2}k^{1/2}$$

$$W_{kl} = 0 \qquad (l \neq k+1,\ k-1)$$

They enable one to calculate G as

$$G = (I + KW)^{-2} \qquad (33)$$

For a truncated basis this procedure is an approximation, but it is expected to converge together with expansion (27) when the basis increases.

Equation (33) is an essence of the NRC approximation, neglecting the multivalued region and the corresponding singularity. It seems to be reasonable in the case of low energy and small curvature, when the multivalued region is classically inaccessible at least for several lower vibrational states φ_n. An explicit criterion reads

$$Kl = K[\hbar/2\mu\omega]^{1/2} \ll 1 \tag{34}$$

Here $\sqrt{2}l$ is the classical vibrational amplitude for $n = 0$. When condition (34) is violated, the NRC calculation diverges as the basis increases [strictly speaking, Eq. (27) then represents an asymptotic expansion]. The remarkable signal is that the determinant of G, as calculated by Eq. (33), becomes negative. (The true matrix G must be positive definite.)

3. *Symmetrization and Averaging of the CC Hamiltonian*

Let us write the symmetrized CC Hamiltonian

$$\begin{aligned}\mathcal{H}^{\text{symm}} = &-\frac{\hbar^2}{2\mu}\left[\frac{\partial}{\partial r}J^{-2}\frac{\partial}{\partial r} - \left[\left(\frac{\partial}{\partial r}J^{-2}g_{ry}\frac{\partial}{\partial y}\right)\right.\right.\\ &\left.\left.+\frac{\partial}{\partial y}\left(J^{-2}g_{yr}\frac{\partial}{\partial r}\right)+\frac{\partial}{\partial y}\left(J^{-2}g_{rr}\frac{\partial}{\partial y}\right)\right]\right]\\ &+V_1(r)+V_2(r,y)+V_3(r,y)\end{aligned}$$

Here, $g_{yr} = g_{ry}$ and g_{rr} are the elements of the metric tensor (17). An extra potential term $V_3(r, y)$ arose due to the symmetrization. Its explicit expression is cumbersome (Basilevsky and Ryaboy, 1980b) and is not given here.

Now we recall vibrational potential:

$$V_2(r,y) = \begin{cases} V_2^{(1)}(y - y_0^{(1)}, r) & \text{for} \quad y < 0 \text{ (reactants)} \\ V_2^{(2)}(y - y_0^{(2)}, r) & \text{for} \quad y > 0 \text{ (products)} \end{cases} \tag{35}$$

So we have a pair of equations for basis functions:

$$h^{(1)}\langle\langle\varphi^{(1)}| = \langle\langle\varphi^{(1)}|\epsilon^{(1)}, \qquad h^{(2)}\langle\langle\varphi^{(2)}| = \langle\langle\varphi^{(2)}|\epsilon^{(2)} \tag{36}$$

The distinction of vibrational Hamiltonians $h^{(1)}$ and $h^{(2)}$ comes from Eq. (35).

According to Eqs. (35) and (36), the functions $\varphi_n^{(1)}$ and $\varphi_n^{(2)}$ are defined on the half-axes $y < 0$ and $y > 0$, respectively. It is expedient to extend them onto the whole y range in some naturally continuous manner. Then the basis functions will be continuously defined for all y. One is required to add an extra term to the Hamiltonian in order to compensate for a change of the true potential (35), namely,

$$V_2(r, y) = \bar{V}_2(r, y) + [V_2(r, y) - \bar{V}_2(r, y)]$$

where $\bar{V}_2(r, y)$ is a sum of two potentials (35) spread over the whole y axis. The so-determined basis functions fail to be orthogonal

$$\int \varphi_i^{(1)}\varphi_j^{(1)}\, dy = \int \varphi_i^{(2)}\varphi_j^{(2)}\, dy = \delta_{ij}, \qquad \int \varphi_i^{(1)}\varphi_j^{(2)}\, dy = \sigma_{1i,2j} \tag{37}$$

In the overall ("double") basis

$$\langle\langle\varphi| \equiv (\varphi^{(1)}, \varphi^{(2)}) \tag{38}$$

the expressions (37) define the matrix of overlap integrals σ. The translational matrix Hamiltonian equals

$$\begin{aligned} H(E) &= \int dy(|\varphi\rangle\rangle \mathcal{H}^{\text{symm}}\langle\langle\varphi|) - E\sigma \\ &= A(d^2/dr^2) + B(d/dr) + C, \qquad \int dy(|\varphi\rangle\rangle\langle\langle\varphi|) = \sigma \end{aligned} \tag{39}$$

We again omit the explicit expression. [It has been obtained for a slightly different matrix Hamiltonian, changing stepwise on the cut formed by the r axis (see Section III,D)]. To proceed further we need only indicate the symmetry properties [similar to those in Eq. (32)] inherent in the matrix coefficients

$$A = \tilde{A}, \qquad B = A' + b, \qquad b = -\tilde{b}, \qquad C = \tfrac{1}{2}b' + c, \qquad c = \tilde{c} \tag{40}$$

If one neglects interactions between the reactant and product channels, then the basis set becomes orthonormal and the matrix Hamiltonian takes the block form

$$H(E) = \begin{array}{c} \left(\begin{array}{c|c} H^{(1)}(E) & 0 \\ \hline 0 & H^{(2)}(E) \end{array}\right) \\ \begin{array}{cc} \underbrace{\phantom{H^{(1)}}}_{\text{reactant channels}} & \underbrace{\phantom{H^{(2)}}}_{\text{product channels}} \end{array} \end{array} \begin{array}{l} \left.\vphantom{H^{(1)}}\right\}\text{reactant channels} \\ \left.\vphantom{H^{(2)}}\right\}\text{product channels} \\ \end{array} \tag{41}$$

The calculation of the matrices $H^{(1)}(E)$ and $H^{(2)}(E)$ involves only the basis functions of reactants or products, respectively. This factorization occurs in the region where the NRC approximation is valid.

4. *The Basis-Set Transformations*

The self-conjugation property of the original Hamiltonian $\mathcal{H}$ is transferred onto the translational Hamiltonian $H(E)$ as the symmetry conditions (40). They prove to be invariant under transformations of the type

$$X = UY \tag{42}$$

where U is a square matrix and Y is a new unknown solution. By a comparison of Eqs. (42) and (27), we conclude that U can be regarded as a linear transformation of a basis set

$$\langle\langle\varphi_1| = \langle\langle\varphi|U \tag{43}$$

The equation for Y is

$$H_1(E)Y \equiv A_1Y'' + B_1Y' + C_1Y = 0 \tag{44}$$

and its matrix coefficients obey the same symmetry relations:

$$\begin{array}{lll} A_1 = \tilde{U}AU, & A_1 = \tilde{A}_1, & B_1 = A_1' + b_1 \\ b_1 = -\tilde{b}_1, & C_1 = \frac{1}{2}b_1' + c_1, & c_1 = \tilde{c}_1 \end{array} \tag{45}$$

The explicit expressions for the matrices b_1 and c_1 are available after trivial algebraic manipulations. If U is orthogonal ($\tilde{U}U = I$), then

$$\begin{aligned} b_1 &= \tilde{U}bU + \tilde{U}AU' - \tilde{U}'AU \\ c_1 &= \tilde{U}cU + \tfrac{1}{2}[(\tilde{U}bU' + \widetilde{\tilde{U}bU'}) \\ &\quad + (\tilde{U}AU')' + (\widetilde{\tilde{U}AU'})'] - \tilde{U}'AU' \end{aligned}$$

If U satisfies the equation

$$AU' = -\tfrac{1}{2}bU \tag{46}$$

then $b_1 = 0$ and $c_1 = \tilde{U}(-\frac{1}{4}bA^{-1}b)U + \tilde{U}cU$. The latter transformation is of practical importance because it enables one to completely eliminate the first-derivative term in Eq. (28); see Section V,A,2.

B. Natural (N) and Double ($2N$) Representations

1. *Definitions*

Let us accept a convention that the numbers of channels of reactants and products are the same, each being equal to N, and that they do not change along the translational coordinate. (This restriction is not at all necessary. Its violation complicates the notation but does not modify the following reasoning.) We shall call "double" (or $2N$) that representation of the one-dimensional matrix Hamiltonian using the double basis (38). The natural representation, considered above in a relation with the NRC, will be also called the N representation.

The translational coordinate has a lower bound in the double representation ($0 < r < \infty$), but it changes within infinite limits in the natural representation ($-\infty < s < \infty$). We shall refer to the basis functions $\varphi_i^{(1)}$ and $\varphi_i^{(2)}$ as vibrational states of reactants and products, respectively, no matter what their position is on the translational coordinate. The most important peculiarity of the double representation is the presence of the nonvanishing matrix elements between the reactant and the product states. Therefore, coupling occurs between the reactant and product channels in the interaction zone. The coupling is absent in the natural representation as a formal result of the elimination of the multivaluedness of the NRC. That is why only the double representation is able to provide a complete description of the reactive scattering in the interaction zone, but only an incomplete model description is available in terms of the natural representation.

On the other hand, the coupling between the reactant and product channels vanishes in asymptotic regions. So the natural representation becomes accurate there. Moreover, it is most convenient to describe the asymptotic regions. Therefore it is desirable to reveal a connection between the two representations in the region where both of them are acceptable.

2. *The Relation between Double and Natural Representations in Asymptotic Regions*

Two equivalent forms of a general solution of the translational equation (28) can be written if both representations are true:

$$X^{(N)}(s) = N\left\{ \overbrace{\begin{pmatrix} \qquad \end{pmatrix}}^{2N} \right. \tag{47a}$$

which is the natural representation, and

$$X^{(2N)}(r) = \begin{array}{r} N\left\{\vphantom{X^{(2N,1)}_{a}}\right. \\ N\left\{\vphantom{X^{(2N,2)}_{a}}\right. \end{array} \overbrace{\begin{pmatrix} X^{(2N,1)} \\ \hline X^{(2N,2)} \end{pmatrix}}^{2N} \begin{array}{l} \left.\vphantom{X^{(2N,1)}_{a}}\right\} \text{reactant channels} \\ \left.\vphantom{X^{(2N,2)}_{a}}\right\} \text{product channels} \end{array} \tag{47b}$$

which is the double representation.

The braces indicate the dimensions of the matrix blocks. The number of independent solutions in the natural representation (that is, the number of columns in matrix $X^{(N)}$) is twice as large as the basis dimension, because a second-order differential equation is dealt with. The number of independent solutions in the double representation is $4N$. However, as will be shown in the next section, half of them are unnecessary and should be omitted. We return to Fig. 5 and correlate a pair of values $s^{(1)}$ and $s^{(2)}$ with every value of the translational coordinate r. Then there arise a pair of equivalent expressions for the two-variable wave function λ_α satisfying the original equation (23):

$$\begin{aligned} \text{NRC:}\quad & \langle\langle\lambda| = [J^{\text{NRC}}(s^{(1)}, v)]^{-1/2}\langle\langle\varphi^{(1)}|X^{(N)}(s^{(1)}) \\ \text{CC:}\quad & \langle\langle\lambda| = [J^{\text{CC}}(r, y)]^{-1/2}\langle\langle\varphi^{(1)}|X^{(2N,1)}(r) \end{aligned}$$

for $y < 0$ (reactants) and

$$\begin{aligned} \text{NRC:}\quad & \langle\langle\lambda| = [J^{\text{NRC}}(s^{(2)}, v)]^{-1/2}\langle\langle\varphi^{(2)}|X^{(N)}(s^{(2)}) \\ \text{CC:}\quad & \langle\langle\lambda| = [J^{\text{CC}}(r, y)]^{-1/2}\langle\langle\varphi^{(2)}|X^{(2N,2)}(r) \end{aligned}$$

for $y > 0$ (products).

Now we use the fact that the asymptotic regions are treated, so even in the double representation only the functions $\varphi_i^{(1)}$ are needed in the lower half-plane ($y < 0$). The exponentially vanishing contributions from $\varphi_j^{(2)}$ can be neglected. Quite similarly, only the functions $\varphi_j^{(2)}$ can be considered in the upper half-plane ($y > 0$).

The next step is to equalize the two expressions for λ_α, indicating the two points essential in the further treatment:

(1) The mutual transformation of translational coordinates does not depend on vibrational coordinates, so the interchange $r \leftrightarrow s$ is a one-dimensional transformation (see Section II,C,4).

Hence the ratio of Jacobians is independent of the vibrational coordinates:

$$J^{\text{NRC}}/J^{\text{CC}} = \begin{cases} \xi^{(1)} = -\,(ds^{(1)}/dr)^{-1} > 0 & \text{(reactants)} \\ \xi^{(2)} = \,(ds^{(2)}/dr)^{-1} > 0 & \text{(products)} \end{cases}$$

(2) Vibrational functions φ_i are the same in both representations.

With these observations in mind the following final relation is obtained:

$$\begin{pmatrix} X^{(N)}(s^{(i)}) \\ \hline \dfrac{d}{ds^{(i)}} X^{(N)}(s^{(i)}) \end{pmatrix} = \left(\begin{array}{c|c} \xi^{(i)1/2} I & 0 \\ \hline \pm \dfrac{d}{dr}\,[\xi^{(i)-1/2}] I & \pm[-\xi^{(i)-1/2}] I \end{array}\right) \times \begin{pmatrix} X^{(2N,i)}(r) \\ \hline \dfrac{d}{dr} X^{(2N,i)}(r) \end{pmatrix}, \qquad i = 1, 2 \tag{48}$$

C. Commentary

Section III,A,1. The symmetrizing transformation (24) for NRC was introduced by Marcus (1966) and Rankin and Light (1969). It had been mentioned earlier by Wilson *et al.* (1955).

Section III,A,2. Other procedures of eliminating the singularity of the metric tensor were elaborated in earlier NRC calculations (Miller and

Light, 1971; Wu and Levine, 1971). Formulas like Eq. (33) have been thoroughly discussed by Basilevsky and Ryaboy (1978, 1979a).

Section III,A,3. The double basis treatment was originally applied to reactive scattering by Diestler (1971) and Shipsey (1972, 1973). Our presentation is based on the paper by Basilevsky and Ryaboy (1980b), but not completely. The approach here is closer to that of Diestler and Shipsey. In its present version the interaction between the reactant and product channels is gained by means of the off-diagonal blocks of the matrix $H(E)$.

The method dealing with the numerical basis functions, obtained as exact eigenfunctions of the vibrational Hamiltonian with a double-well potential (Kuppermann *et al.*, 1980; Romelt, 1980; Hauk *et al.*, 1980) can also be considered as a version of the "double representation."

The kinetic energy operator of CC has a singularity at the point $r = 0$. It may be eliminated like the NRC singularity (Section III,A,2). However, just as in the NRC case, its formal elimination does not guarantee that the basis expansion for a solution will converge. To ensure that, the point $r = 0$ should be placed in a classically inaccessible region (see Section II,C,2 for a discussion).

Section III,B,1. The double representation mostly resembles the regular formulation of many-channel scattering theory as presented in standard texts (Newton, 1966; Taylor, 1972). It is nontrivial, so that its application becomes, in fact, necessary, when reactions **H** + **LH** are considered, in which the interaction between the reactant and product channels is especially important.

IV. One-Dimensional Reactive Scattering

In standard texts (Newton, 1966; Taylor, 1972) the general scattering theory is presented in an abstract operator form. When a particular representation is considered, its conclusions are true for complete basis sets in which both matrices and the vectors operated by them are of infinite dimension.

Practical calculations deal with truncated basis sets, so that a dimension of all matrices and vectors is finite. It seems natural to consider such a formulation of the reactive scattering theory with a limited number of channels, which resembles as much as possible the standard (operator) formulation. Hence we examine the general properties of the solutions to the one-dimensional matrix Schrödinger equation $H(E)X = 0$. The main conclusion is that all the basic theorems of the scattering theory will be satisfied exactly for a basis expansion of any size if the matrix Hamiltonian $H(E)$ obeys the symmetry properties (40).

Two points are essential when the general multichannel case is dealt with.

(1) It is necessary to start with the complete formulation of the theory, as originally proposed by Diestler (1971). It is the complete $2N$ representation of one-dimensional solutions that most closely corresponds to the standard treatment of the textbooks on scattering.

(2) Even in its complete formulation the reactive scattering problem contains some peculiarities as compared to the standard theory. First, the asymptotic directions for the reactant and product waves do not coincide with the usual radial direction. Second, the boundary conditions at the scattering center differ from the usual ones for chemical coordinates. They must provide continuity of the wave function and its derivative when passing from the reactant to the product channels.

The first peculiarity is included in the theory by introducing the "mixed representation" (Basilevsky and Ryaboy, 1981). The second is taken into account by a special selection of boundary conditions for chemical coordinates. After that, a regular Wronskian analysis of the scattering S matrix is available. It is based on the concept of the generalized matrix Wronskian that can be introduced for a pair of solutions of the equation $H(E)X = 0$. The fact that this matrix is independent of a translational coordinate ensures the conservation of the probability flux in a process of a chemical rearrangement. That leads to an internally consistent closed theory underlying the practical calculations.

A. Solution of the Equation of Motion

1. *Matrix Propagator* (*the R Matrix*)

The basic equation (28) embodies a linear set of differential equations. In a regular treatment its solution is reduced to a calculation of the propagator or the matricant (Gantmakher, 1966); it is also referred to as the R matrix. The definition of the R matrix reads

$$\begin{pmatrix} X(2) \\ X'(2) \end{pmatrix} = R(2, 1)\begin{pmatrix} X(1) \\ X'(1) \end{pmatrix} \tag{49}$$

The numbers 1 and 2 denote a pair of different values of a translational coordinate; X is some general solution of the set (28) [i.e., a matrix such as (47b)]; and X' is its derivative with respect to the translational coordinate. A prescription for calculating $R(2, 1)$ follows from this definition:

$$R(2, 1) = \begin{pmatrix} X(2) \\ X'(2) \end{pmatrix}\begin{pmatrix} X(1) \\ X'(1) \end{pmatrix}^{-1} \tag{50}$$

All matrices here are implied to be square. So, if the double representation is meant, then not only $2N$ independent solutions (47b) are needed, but all $4N$ solutions.

The evaluation of R matrix is a main computational step in the reactive scattering problem.

The structure of the propagator matrix becomes evident by comparison of Eqs. (49) and (47b):

$$R(2, 1) = \begin{array}{r} N\{ \\ N\{ \end{array} \overbrace{\left(\begin{array}{c} \text{functions} \\ \hline \text{derivatives} \end{array}\right)}^{2N}$$

for a natural N representation, and

$$R(2, 1) = \begin{array}{r} N\{ \\ N\{ \\ N\{ \\ N\{ \end{array} \left(\begin{array}{c} \\ \text{functions} \\ \hline \text{derivatives} \\ \\ \end{array}\right) \begin{array}{l} \}\text{reactant channels} \\ \}\text{product channels} \\ \}\text{reactant channels} \\ \}\text{product channels} \end{array}$$

for a double $2N$ representation. The R matrix is one among possible complete sets of independent solutions of (28). So it is nonsingular. It satisfies the composition relation

$$R(3, 1) = R(3, 2)R(2, 1) \tag{51}$$

2. *Regular Solutions in the Double Representation*

In the double representation we have to select from $4N$ independent vector solutions of (28) the $2N$ physically meaningful ones. (In the natural representations all $2N$ solutions are physically meaningful.) These solutions, called "regular," are fixed by a boundary condition imposed at the point $r = 0$. It is different for physical and chemical coordinates. For physical coordinates:

$$\left(\begin{array}{c} X^{(2N)}(0) \\ \hline X'^{(2N)}(0) \end{array}\right) = \overbrace{\left(\begin{array}{c} 0 \\ \hline \Lambda \end{array}\right)}^{2N} \begin{array}{l} \}2N \\ \}2N \end{array}, \qquad \det \Lambda \neq 0 \tag{52a}$$

Here Λ is a nonsingular $2N \times 2N$ matrix. Equation (52a) states that at $r = 0$ the function $X^{(2N)}(r)$ is continuously matched when passing from the reactant to product channels, but its derivative displays a rupture. The latter conclusion follows from the condition that Λ is a nonsingular matrix, which is clearly illustrated by the particular example $\Lambda = I$. So the translational motion in the reactant and product channels is incorrelated.

For $r \neq 0$ a regular solution is defined as

$$\begin{matrix} 2N\{ \\ 2N\{ \end{matrix} \overbrace{\left(\begin{array}{c} X^{(2N)}(r) \\ \hline X'^{(2N)}(r) \end{array} \right)}^{2N} = R^{(2N)}(r, 0) \overbrace{\left(\begin{array}{c} X^{(2N)}(0) \\ \hline X'^{(2N)}(0) \end{array} \right)}^{2N} \begin{matrix} \}2N \\ \}2N \end{matrix} \tag{53}$$

Integration of the equation of motion proceeds from $r = 0$ to such a point r, corresponding to asymptotic regions for both the reactants and products.

For chemical coordinates the transition from the reactant to product channels at $r = 0$ must also provide the continuity of the solution $X^{(2N)}$. The derivative $X'^{(2N)}$ must change its sign, because the actual directions of the product translational coordinate is opposite to that of the reactant, and that leads to the boundary condition

$$\left(\begin{array}{c} X^{(2N)}(0) \\ \hline X'^{(2N)}(0) \end{array} \right) = \left(\begin{array}{c} m \\ \hline m \\ \hline n \\ \hline -n \end{array} \right) \begin{matrix} \}N \\ \}N \\ \}N \\ \}N \end{matrix} \qquad \det \left(\begin{array}{c} m \\ \hline n \end{array} \right) \neq 0 \tag{52b}$$

The rectangular $N \times 2N$ matrices are arbitrary, except for a single restriction imposed by the latter condition of nonsingularity.

There exist $2N$ linearly independent vector solutions. That is to say, the rank of the matrix in the left-hand part of Eq. (53) equals $2N$. The proof (Lankaster, 1969) uses the latter of conditions (52a) or (52b) and the fact that the propagator is a nonsingular $4N \times 4N$ matrix.

3. *Mixed Representation*

The natural N representation is visual, but it is inapplicable in the multivalued domain of NRC, where reactant and product channels interact. It is, however, always applicable in the asymptotic regions. On the other hand, the double $2N$ representation may be necessary in the interaction region, but now a description of asymptotic regions is inconvenient. The latter is a consequence of the fact that the direction of the translational coordinate r does not coincide with the asymptotic PES directions. That is why the variables are not separable in the asymptotic regions. So it is desirable to combine the $2N$ description of the interaction region with the N description of asymptotic regions.

The relations connecting the two representations in the region where both of them are valid were derived in the preceding section [Eq. (48)]. A pair of values of the NRC translational coordinate s corresponding to the reactant ($s^{(1)}$) and product ($s^{(2)}$) regions are correlated with each value of the CC translational coordinate r (see Fig. 5).

We shall consider as functions of r the quantities $s^{(1)}$ and $s^{(2)}$ as well as the derivatives $(\xi^{(1)})^{-1} = -ds^{(1)}/dr$ and $(\xi^{(2)})^{-1} = ds^{(2)}/dr$:

$$s^{(1)} = s^{(1)}(r), \quad s^{(2)} = s^{(2)}(r), \qquad \xi^{(1)} = \xi^{(1)}(r), \quad \xi^{(2)} = \xi^{(2)}(r)$$

Relations (48) allow the introduction of the mixed representation for a solution of Eq. (28)

$$\begin{aligned} X^{(\mathrm{mix})} &= \begin{array}{c} N\left\{\vphantom{X^{(N)}}\right. \\ N\left\{\vphantom{X^{(N)}}\right. \end{array} \left(\begin{array}{c} X^{(N)}(s^{(1)}) \\ \hline X^{(N)}(s^{(2)}) \end{array} \right) \begin{array}{l} \left.\vphantom{X^{(N)}}\right\}\text{reactant channels} \\ \left.\vphantom{X^{(N)}}\right\}\text{product channels} \end{array} \\ \frac{d}{ds} X^{(\mathrm{mix})} &= \begin{array}{c} N\left\{\vphantom{\frac{d}{ds^{(1)}}}\right. \\ N\left\{\vphantom{\frac{d}{ds^{(2)}}}\right. \end{array} \left(\begin{array}{c} \dfrac{d}{ds^{(1)}} X^{(N)}(s^{(1)}) \\ \hline \dfrac{d}{ds^{(2)}} X^{(N)}(s^{(2)}) \end{array} \right) \begin{array}{l} \left.\vphantom{\frac{d}{ds^{(1)}}}\right\}\text{reactant channels} \\ \left.\vphantom{\frac{d}{ds^{(2)}}}\right\}\text{product channels} \end{array} \end{aligned} \tag{54}$$

The mixed representation operates natural N solutions, but they are written in the double-$2N$ form. The d/ds operation in Eq. (54) is formally defined: the actual differentiation is performed with respect to different variables $s^{(1)}$ and $s^{(2)}$.

This representation makes sense everywhere where the natural representation of solutions, needed for the evaluation of the quantities entering the right-hand side of Eq. (54), is valid. If the regular solution has been found initially in the $2N$ representation, then those quantities are available by means of Eq. (48). If the curvature of the reaction coordinate is small and the interaction between the reactant and product channels may be neglected, then the mixed representation is applicable over the whole reaction plane, and the needed quantities are available by a straightforward integration of Eq. (28) using the N representation. In the latter case the matching conditions (52b), which are inherent to the integration procedure, follow automatically.

B. The Conservation of the Generalized Probability Flux

1. *Generalized Matrix Wronskian*

Let us consider the $2N$ representation of the one-dimensional Hamiltonian $H(E)$ having the symmetry properties (40). Two different regular solutions obey the equations

$$H(E)X_a = 0, \qquad H(E)X_b = 0$$

We multiply the first one by $\tilde{X}_b$ from the left. Then we make a transposal of the second one and multiply it by X_a from the right. The second result is then substracted from the first. After utilizing the symmetry properties of the coefficients A, B, C we obtain

$$[\tilde{X}_b A X'_a + \tilde{X}'_b A X_a + \tilde{X}_b b X_a]' = 0$$

The quantity in square brackets will be called the "generalized Wronskian":

$$W(X_b, X_a) = \tilde{X}_b A X'_a - \tilde{X}'_b A X_a + \tilde{X}_b b X_a = \text{const} \tag{55}$$

We have thus obtained the conservation law for the generalized probability flux. The law usually applied follows, if we accept $X_a = X$, $X_b = X^*$, $\tilde{X}_b = X^\dagger$ (the asterisk and dagger represent the complex and Hermitian conjugation, respectively). Then, by definition, for the diagonal elements of matrix (55),

$$\begin{pmatrix}\text{The probability flux} \\ \text{for function } |\chi_\alpha\rangle\rangle\end{pmatrix} = -\frac{i\hbar}{2\mu}[X^\dagger A X' - X'^\dagger A X + X^\dagger b X]_{\alpha\alpha} = \text{const}$$

The generalized Wronskian is invariant under the substitution $X = UY$, which converts the matrix Hamiltonian to the form of Eq. (44). Hence,

$$W(Y_b, Y_a) = \tilde{Y}_b A_1 Y'_a - \tilde{Y}'_b A_1 Y_a + \tilde{Y}_b b_1 Y_a = W(X_b, X_a) \tag{56}$$

This identity can be verified after the explicit expressions for A_1 and b_1, from Section III,A,4, are inserted into it.

2. *An Example: The Probability Flux in NRC*

The general results of the preceding section are of course valid in the natural representation as well. Then, according to Eq. (31), $A = G$ and $b = Q$:

$$-\frac{i\hbar}{2\mu}[X^\dagger G X' - X'^\dagger G X + X^\dagger Q X] = \text{const} \tag{57}$$

Let us check that the diagonal elements of this matrix represent the probability fluxes defined in a regular manner for the initial two-variable solutions λ_α [Eq. (24)].

The regular definition of the probability flux is (Landau and Lifshitz, 1963):

$$\begin{pmatrix}\text{The probability flux} \\ \text{for function } \lambda\end{pmatrix} = \frac{i\hbar}{2\mu}\int (\lambda \operatorname{grad} \lambda^* - \lambda^* \operatorname{grad} \lambda)\mathbf{n}\, dv$$

Here **n** is a unit vector normal to the line s = const. It should be treated as a contravariant vector ($\mathbf{n} \equiv n^{\nu}$). So its calculation performed with the NRC contravariant metric tensor (9) (Korn and Korn, 1961) gives

$$n^{\nu} = \begin{pmatrix} J^{-1} \\ 0 \end{pmatrix}$$

Using Eqs. (24) and (27), we obtain

$$\lambda_{\alpha} = J^{-1/2}\psi_{\alpha} = J^{-1/2}\langle\langle\varphi|\chi_{\alpha}\rangle\rangle$$

In further manipulations the gradient vector should be treated as covariant, taking into account that the Jacobian J can be treated as a constant under the operation of covariant differentiation. After calculating the internal product $(\text{grad}\,\lambda)_{\nu}n^{\nu}$, we obtain

$$\begin{aligned}
&(\text{The probability flux for function } \lambda) \\
&= \frac{i\hbar}{2\mu}\int\left(\frac{d\psi^*}{ds}\psi - \psi^*\frac{d\psi}{ds}\right) J^{-2}\,dv \\
&= (i\hbar/2\mu)[\langle\langle\chi^*|\textstyle\int|d\varphi/ds\rangle\rangle J^{-2}\langle\langle\varphi|dv|\chi\rangle\rangle \\
&\quad + \langle\langle d\chi^*/ds|\textstyle\int|\varphi\rangle\rangle J^{-2}\langle\langle\varphi|dv|\chi\rangle\rangle \\
&\quad - (\text{complex conjugate expression})] \\
&= -(i\hbar/2\mu)[\langle\langle\chi^*|G|d\chi/ds\rangle\rangle - \langle\langle d\chi/ds|G|\chi\rangle\rangle \\
&\quad + \langle\langle\chi^*|Q|\chi\rangle\rangle]
\end{aligned}$$

In this calculation we have utilized the fact that the functions φ_n are real and also the symmetry properties of the matrices G and Q. The so-obtained expressions for different $|\chi\rangle\rangle = |\chi_{\alpha}\rangle\rangle$ coincide with diagonal elements of the matrix (57).

3. *The Separation of the Reactant and Product Fluxes*

If the interaction between the reactant and product channels has vanished (the NRC are applicable), then the Hamiltonian $H(E)$ in CC becomes block diagonal [see Eq. (41)]. If we take that into account in the calculation of the generalized Wronskian (55), then

$$W(X_b, X_a) = W^{(1)}(X_b^{(1)}, X_a^{(1)}) + W^{(2)}(X_b^{(2)}, X_a^{(2)})$$

$$\begin{aligned}
W^{(i)}(X_b^{(i)}, X_a^{(i)}) &= \tilde{X}_b^{(i)}A^{(i)}X_a^{(i)\prime} - \tilde{X}_b^{(i)\prime}A^{(i)}X_a^{(i)} \\
&\quad + \tilde{X}_b^{(i)}b^{(i)}X_a^{(i)}
\end{aligned}$$

The superscript i indicates that only block matrices corresponding either to the reactant (i = 1) or to the product (i = 2) channels are calculated.

We note now that $W(X_b, X_a) = 0$ for regular solutions. This equality means nothing other than a mutual compensation of the overall generalized fluxes due to reactants and products and represents the conservation of the whole number of particles along the translational coordinate (with account taken of different signs of this variable for reactants and products). It is automatically provided by the boundary conditions (52a,b) at $r = 0$.

Now we can continue the equality $W(X_b, X_a) = 0$ to the asymptotic region (large values of r) in order to derive

$$W^{(1)}(X_b^{(1)}, X_a^{(1)}) = -W(X_b^{(2)}, X_a^{(2)})$$

This equality (with different signs of the translational variable taken into account) guarantees the conservation of $2N \times 2N$ matrix of the generalized flux, when passing from the reactant to the product asymptotic region through the interaction region.

C. Scattering Matrix

1. *Asymptotic Solutions*

In asymptotic regions the NRC (but not the CC!) variables are separable. The translation solution $X^{(N)}(s)$ [Eq. (47a)] can be expressed in terms of two square diagonal matrices, $J^{(N)}$ and $\mathcal{O}^{(N)}$:

$$X^{(N)} = N\{(\overbrace{J^{(N)}}^{N} | \overbrace{\mathcal{O}^{(N)}}^{N})$$

Their diagonal elements represent the incoming and outgoing waves, respectively. Assuming normalization to the δ function of energy, we can write

$$\begin{aligned} &\left.\begin{aligned} \mathcal{O}_\alpha &= \sigma^{1/2} k_\alpha^{-1/2} \exp(-ik_\alpha s) \\ J_\alpha &= \sigma^{1/2} k_\alpha^{-1/2} \exp(ik_\alpha s) \end{aligned}\right\} \text{reactant region} \\ &\left.\begin{aligned} \mathcal{O}_\alpha &= \sigma^{1/2} k_\alpha^{-1/2} \exp(ik_\alpha s) \\ J_\alpha &= \sigma^{1/2} k_\alpha^{-1/2} \exp(-ik_\alpha s) \end{aligned}\right\} \text{product region} \\ &\sigma = \mu/2\pi\hbar^2, \qquad k_\alpha = \hbar^{-1}[2\mu(E - V_\alpha)]^{1/2} \end{aligned} \tag{58}$$

(the positive value of the square root is taken; V_α are the asymptotic channel potentials). These definitions cover both open and closed channels. In the latter case the asymptotic wave numbers k_α are purely imaginary values. (Later, in the treatment of resonances in Section VII, k_α will become complex values). That should not be overlooked when preexponential factors are calculated. Some of the relations derived in the rest of this section are true only after careful selection [for instance, in accord with Eq. (58)] of the phase factors in the asymptotic solutions.

For closed channels the increasing depth into asymptotic regions exponents are included in $J^{(N)}$ and the decreasing exponents are included in $\mathcal{O}^{(N)}$. That agrees with the usual formulation of the scattering problem: given the amplitudes of incoming waves (J_α), one has to determine the amplitudes of the outgoing waves ($\mathcal{O}_\alpha$). We accept zero amplitudes for the increasing exponents in order to satisfy the regular boundary conditions. The amplitudes of the decreasing exponents represent the contributions to a regular solution from closed channels, which are to be determined.

We now pass to the mixed representation and write

$$\begin{aligned} J^{(\mathrm{mix})} &= \left(\begin{array}{c|c} J^{(N)}(s^{(1)}) & 0 \\ \hline 0 & J^{(N)}(s^{(2)}) \end{array}\right), \qquad \text{incoming waves} \\ \mathcal{O}^{(\mathrm{mix})} &= \left(\begin{array}{c|c} \mathcal{O}^{(N)}(s^{(1)}) & 0 \\ \hline 0 & \mathcal{O}^{(N)}(s^{(2)}) \end{array}\right), \qquad \text{outgoing waves} \end{aligned} \tag{58a}$$

These are the solutions but not the regular ones. If they are continued through the interaction region to the point $r = 0$, the boundary conditions (52) are violated.

2. *The Wronskian in Asymptotic Regions*

Next we construct the Wronskian (55) for a pair of solutions $X_a = X_a^{(2N)}$ and $X_b = X_b^{(2N)}$. In asymptotic regions $A = I$ and $b = 0$; hence, the generalized Wronskian turns into a usual Wronskian:

$$W(X_a, X_b) = \tilde{X}_a X_b' - \tilde{X}_a' X_b = \mathrm{const} \tag{59}$$

(double representation in asymptotic regions). The calculation of this quantity is performed with the use of the mixed representation, specially adapted for the treatment of asymptotic regions. The derivatives in Eq. (59) are interpreted as the operators d/dr. We transform them into $d/ds^{(1)}$ and $d/ds^{(2)}$ by Eqs. (48). The same formulas are used to transform the solutions X_a and X_b. We omit the technical details of the transformations (Basilevsky and Ryaboy, 1981) and arrive at the final result

$$\begin{gathered} W(X_a, X_b) = \tilde{X}_a^{(\mathrm{mix})} P\left(\frac{d}{ds} X_b^{(\mathrm{mix})}\right) - \left(\frac{d}{ds} \tilde{X}_a^{(\mathrm{mix})}\right) P X_b^{(\mathrm{mix})} \\ P = \begin{array}{c} N\{ \\ N\{ \end{array} \left(\begin{array}{c|c} \overbrace{-I}^{N} & \overbrace{O}^{N} \\ \hline O & I \end{array}\right) \end{gathered} \tag{60}$$

Let us demonstrate the utility of this formula by calculating the Wronskian for asymptotic solutions $\mathcal{O}^{(2N)}$ and $J^{(2N)}$. They are easily expressed in the mixed representation (and only in it!) by Eqs. (58). Substituting them into Eq. (60), we obtain

$$W(\mathcal{O}, J) = -2\sigma i I \tag{61}$$

We observe also a pair of relations

$$W(X_a, X_b) = -W(X_b, X_a) \tag{62a}$$

$$W(X, X) = 0 \tag{62b}$$

Equation (62a) represents an obvious identity; Eq. (62b) follows from the boundary condition for regular solutions (see Sections IV,A,2 and IV,B,3), but appears to be an identity for diagonal matrices J and $\mathcal{O}$ representing irregular solutions.

3. *The Jost Matrices and the Scattering Matrix*

Consider a regular solution, no matter whether physical or chemical. The two Jost matrices corresponding to it are (Newton, 1966)

$$W_{\mathcal{O}} = W(\mathcal{O}, X), \qquad W_J = W(J, X) \tag{63}$$

Being Wronskians, these quantities are independent of the translational coordinate. The following identity holds:

$$X = (-2\sigma i)^{-1}[JW_{\mathcal{O}} - \mathcal{O}W_J] \tag{64}$$

It may be verified by the calculation of the Wronskians with J and $\mathcal{O}$ in a combination with the right- and left-hand sides of Eq. (64) with account taken of relations (61) and (62b). According to the theory of linear differential equations (Gantmakher, 1966), the multiplication of Eq. (64) from the right by a constant $2N \times 2N$ matrix again gives a solution of the set of Eqs. (28), and besides, as may be easily verified, this new solution will be regular.

A particular regular solution that is searched for in the scattering problem has the following form in asymptotic regions

$$X = J - \mathcal{O}S \tag{65}$$

This relation can be regarded as the definition of the scattering matrix S. The solution (65) is obtained from the general solution (64) by multiplication by the constant matrix $-2\sigma i W_{\mathcal{O}}^{-1}$ from the right. Hence it follows that

$$S = W_J W_{\mathcal{O}}^{-1} \tag{66}$$

We obtain explicit expressions for Jost matrices calculating Wronskians (63) by means of Eq. (60). They are

$$W_J = \left(\begin{array}{c|c} -W(J_1, X_1^{(1)}) & -W(J_1, X_2^{(1)}) \\ \hline W(J_2, X_1^{(2)}) & W(J_2, X_2^{(2)}) \end{array}\right)$$
$$W_{\mathcal{O}} = \left(\begin{array}{c|c} -W(\mathcal{O}_1, X_1^{(1)}) & -W(\mathcal{O}_1, X_2^{(1)}) \\ \hline W(\mathcal{O}_2, X_1^{(2)}) & W(\mathcal{O}_2, X_2^{(2)}) \end{array}\right) \tag{67}$$

It is sufficient to comment on the definition of block Wronskians in Eq. (67) by a single example

$$W(J_1, X_1^{(1)}) \equiv J^{(N)}(s^{(1)}) \frac{d}{ds^{(1)}} X_1^{(N)}(s^{(1)}) - \frac{d}{ds^{(1)}} J^{(N)}(s^{(1)}) X_1^{(N)}(s^{(1)})$$

Here a detailed notation for blocks of the regular solution X in the mixed representation is used, the detailed treatment of Eq. (54):

$$X^{(\mathrm{mix})} = \begin{array}{r} N\{ \\ N\{ \end{array}\left(\begin{array}{c|c} \overbrace{X_1^{(N)}(s^{(1)})}^{N} & \overbrace{X_2^{(N)}(s^{(1)})}^{N} \\ \hline X_1^{(N)}(s^{(2)}) & X_2^{(N)}(s^{(2)}) \end{array}\right) \equiv \left(\begin{array}{c|c} X_1^{(1)} & X_2^{(1)} \\ \hline X_1^{(2)} & X_2^{(2)} \end{array}\right)$$

That corresponds to acually calculating the Wronskians in the natural representation for asymptotic regions.

The value of the S matrix does not change with the different choice of points r, $s^{(1)}$, and $s^{(2)}$ in the asymptotic regions because the Wronskians (67) are independent of the translational variable.

4. *Projection of the Scattering Matrix onto Open Channels*

Not all of the S matrix (66) is of practical interest: only its block, corresponding to open channels. We introduce the notation S^+ for such a physical S matrix. There exists a similar to the Eq. (66) representation of the S^+ matrix as a product:

$$S^+ = W_J^+(W_{\mathcal{O}}^+)^{-1} \tag{68}$$

In order to derive the expressions for the comultipliers in the right-hand part, we write the general solution (64) in the mixed representation

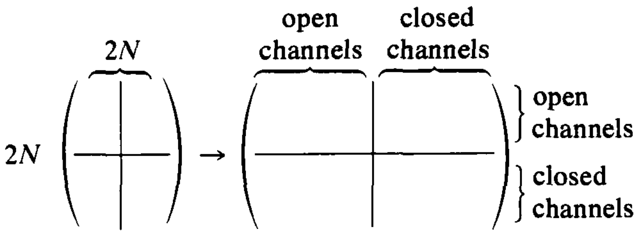
$$X^{(\mathrm{mix})} = (-2\sigma i)^{-1}[J^{(\mathrm{mix})}W_{\mathcal{O}} - \mathcal{O}^{(\mathrm{mix})}W_J] \tag{69}$$

It involves increasing exponents, the closed-channel elements of the matrix $J^{(\mathrm{mix})}$. They can be eliminated after multiplying Eq. (69) from the right by such a constant matrix c that we get

$$W_{\mathcal{O}}c = K, \qquad K = \Delta K, \qquad \Delta^2 = \Delta$$
$$\Delta(I - \Delta) = (I - \Delta)\Delta = 0$$

Here Δ is the matrix projecting onto open channels. Being diagonal in the mixed representation, it commutes with the diagonal matrices $J^{(\mathrm{mix})}$ and $\mathcal{O}^{(\mathrm{mix})}$ in asymptotic regions.

Let us redefine the indices of $2N \times 2N$ matrices in such a way as to distinguish their blocks, corresponding to open and closed channels:



In this representation

$$\Delta = \left(\begin{array}{c|c} I & 0 \\ \hline 0 & 0 \end{array}\right), \qquad K = \left(\begin{array}{c|c} K^+ & //// \\ \hline 0 & 0 \end{array}\right), \qquad S = \left(\begin{array}{c|c} S^+ & //// \\ \hline //// & //// \end{array}\right)$$
$$c = \left(\begin{array}{c|c} c_1 & c_2 \\ \hline c_3 & c_4 \end{array}\right), \qquad W_{\mathcal{O}} = \left(\begin{array}{c|c} a_{\mathcal{O}} & b_{\mathcal{O}} \\ \hline c_{\mathcal{O}} & d_{\mathcal{O}} \end{array}\right), \qquad W_J = \left(\begin{array}{c|c} a_J & b_J \\ \hline c_J & d_J \end{array}\right) \tag{70}$$

The contents of the shaded blocks are not essential. With this notation the following expressions are obtained for the projected Jost matrices (Basilevsky and Ryaboy, 1981):

$$W_J^+ = L^+ = a_J - b_J d_{\mathcal{O}}^{-1} c_{\mathcal{O}}, \qquad W_{\mathcal{O}}^+ = K^+ = a_{\mathcal{O}} - b_{\mathcal{O}} d_{\mathcal{O}}^{-1} c_{\mathcal{O}} \tag{71}$$

They follow from the formula for the general projected solution (69): $X^+ = (-2\sigma i)^{-1}[J^+K^+ - \mathcal{O}^+L^+]$. Here X^+, J^+, and $\mathcal{O}^+$ are the upper left blocks of the respective full matrices.

5. *Properties of the Scattering Matrix*

Now we have to explicitly indicate the energy dependence of the solutions $X = X(E)$ and formulate more precisely the definition of a regular solution: that is a solution obtained by Eq. (53) with the matrices of boundary conditions (52a) or (52b), which are real and energy independent. The matrix $R(2, 1)$ is real for real energies because the same is true for the Hamiltonian $H(E)$. We conclude that regular solutions are also real for real energies, whereas for complex energies,

$$X(E^*) = (X(E))^* \tag{72}$$

The definitions of J and $\mathcal{O}$ functions for open channels result in the following relations:

$$\begin{aligned} &J(E) = (\mathcal{O}(E))^*, && \mathcal{O}(E) = (J(E))^* && \text{(real energy)} \\ &(J(E))^* = \mathcal{O}(E^*), && (\mathcal{O}(E))^* = J(E^*) && \text{(complex energy)} \end{aligned} \tag{73}$$

For the closed channels

$$\left.\begin{aligned} &J(E) = i^{-1/2} && \text{(real function)} \\ &\mathcal{O}(E) = i^{-1/2} && \text{(real function)} \end{aligned}\right. \quad \text{(real energy)} \tag{74}$$

These formulas are valid only if the convention concerning the choice of phase factors in Eq. (58) is accurately obeyed.

a. Symmetry of the S matrix. It follows from Eq. (62b) $W(X, X) = 0$, in which Eq. (64) should be substituted with the utilization of Eq. (63), that

$$W(X, X) = (2\sigma i)^{-1}[\tilde{W}_J W_{\mathcal{O}} - \tilde{W}_{\mathcal{O}} W_J]$$

Then, in agreement with Eq. (66), we obtain

$$S = \tilde{S} \tag{75}$$

b. Generalized unitarity of S^+ matrix. Consider the projected Jost matrices (71). The properties of the quantities $a_{\mathcal{O},J}$ and $b_{\mathcal{O},J}$ follow from their definitions (70). Namely, they represent products of asymptotic solutions in open channels and the elements of regular matrix X or its derivative. We can write, using relations (72) and (73),

$$\begin{aligned} &(a_{\mathcal{O}}(E))^* = a_J(E^*), && (b_{\mathcal{O}}(E))^* = b_J(E^*) \\ &(a_J(E))^* = a_{\mathcal{O}}(E^*), && (b_J(E))^* = b_{\mathcal{O}}(E^*) \end{aligned}$$

The quantities $c_{\mathcal{O}}$ and $d_{\mathcal{O}}$ are the similar products with the only difference that they include asymptotic solutions $\mathcal{O}_\alpha$ from closed channels. Now we use relations (72) and (74) to obtain

$$(d_{\mathcal{O}}^{-1}(E)c_{\mathcal{O}}(E))^* = d_{\mathcal{O}}^{-1}(E^*)c_{\mathcal{O}}(E^*)$$

Next, it follows from Eq. (71) that

$$(W_J^+(E))^* = W_{\mathcal{O}}^+(E^*), \qquad (W_{\mathcal{O}}^+(E))^* = W_J^+(E^*)$$

Finally, we use the symmetry property (75) and derive from Eq. (68)

$$(S^+(E))^\dagger = (S^+(E^*))^{-1} \tag{76}$$

The usual unitarity relation is revealed for a real energy:

$$(S^+)^\dagger S^+ = S^+(S^+)^\dagger = I \qquad \text{(real energy)} \tag{77}$$

D. Commentary

Section IV,A,1. The propagator techniques have been originally applied in reactive scattering calculations in papers by Light *et al.* (Light, 1971; Rankin and Light, 1969; Miller and Light, 1971) for the natural representation.

Section IV,B,1. The matrix Wronskinan $\tilde{X}_b X'_a - \tilde{X}'_b X_a$ was introduced by Newton (1966) for the equation $X'' + CX = 0$. Equation (55) presents its generalization for the equation $AX'' + BX' + CX = 0$.

Section IV,B,3. The results obtained in this Section B,3 clarify the selection of boundary conditions (52b) for chemical CC. They should be consistent with the condition $W(X_a, X_b) = 0$ in the special case when the metric tensor, the potential, and the basis functions are the same for the reactant and product channels. It is necessary that the antisymmetric part of the Hamiltonian, namely the matrix b in Eq. (40), vanishes when $r \to 0$.

Section IV,C. In Section IV,C we adopt the arguments from the standard texts of the scattering theory (Newton, 1966; Taylor, 1972). The only modification is that we use the mixed representation in the treatment of Wronskians. The matrix P appears in Eq. (60) as a consequence of the fact that the translational variable has opposite directions for reactants and for products.

The idea of projection of the S matrix onto open channels is due to Newton (1966).

V. Quantum Calculations of Triatomic Reactions

Quantum dynamical calculations provide the most complete and exact information concerning chemical reactions. The computational methods can be classified as "one-dimensional" and "two-dimensional". The one-dimensional procedures use the matrix Hamiltonian (28) completely averaged over the vibrational variable, while the two-dimensional procedures solve numerically the original Schrödinger equation for a wave function depending on two variables. We shall consider some problems connected with ensuring the flux conservation (symmetry and unitarity of the scattering matrix) in relation to both procedures and illustrate the convergence of calculations by some examples.

Discussion of the basic peculiarities observed in quantum calculations is necessary in order to work out model concepts and to estimate their quality. The main goal is to understand on a qualitative level the laws governing the energy redistribution in the exchange reactions and their dependence on the PES properties. Qualitative understanding may be achieved by elaboration of the models permitting analytical solutions and describing the main effects registered in computer calculations. The results of exact quantum calculations are of great importance: first, they give the numerical empirical basis for the development of models; second, they serve as a criterion of their consistency.

A. Computational Methods

1. *"Two-Dimensional" Integration Procedures*

By that we mean different realizations of a straightforward numerical integration of the original Schrödinger equation [Eqs. (23)–(25)]. The reaction plane in polar coordinates is divided into elementary sectors for which local solutions can be expanded over local vibrational basis sets. The standard averaging then gives local one-dimensional translational equations, which can be integrated by the methods discussed in Section V,A,2. A problem then remains of how to switch a solution from one sector to another. That is just the stage at which one has to return to a two-variable formulation, which clears up the term "two-dimensional."

Being based on the mutual projection of a pair of neighboring local basis sets, the procedure of matching local solutions is formulated in terms of overlap integrals involving respective basis functions. The corresponding overlap matrices are unitary if the both local sets are complete. Otherwise, the unitarity is disturbed. That is why a truncation of an expansion disturbs the condition of the flux conservation. It therefore seems necessary to increase the size of the basis set in order to gain the symmetry and unitarity of the scattering matrix to a required accuracy.

However, the experience of calculations showed (Connor *et al.* 1978a) that these properties of the S matrix were attained with the accuracy up to 2% prior to achieving the full convergency of a calculation; that allows enforcing them artificially. In particular, in the state path sum method (Manz, 1974, 1975; Connor *et al.*, 1975), the exactly correct general behavior of the S matrix was provided by a special modification of some matrix elements of the Hamiltonian. Light and Walker (1976) gained the same result by applying transposes of the overlap matrices instead of their inverses when switching a solution from one sector to another. Two more methods of performing the same switching without disturbing the flux conservation were discussed by Redmon and Wyatt (1977). By this means the practically quite satisfactory solutions may usually be obtained with basis expansions of moderate size.

Different two-dimensional procedures have been suggested by Kuppermann (1970), Manz (1974, 1975), Connor *et al.* (1975), Light and Walker (1976), Askar *et al.* (1978), Johnson and Levine (1972); they are discussed in the reviews (Connor, 1979; Wyatt, 1979).

2. *"One-Dimensional" Procedures: Integration Methods for One-Dimensional Translational Equations*

In one-dimensional procedures the analytical treatment of the problem is brought to a natural termination, and it only remains to use a computer for the integration of Eq. (28). One-dimensional treatment is attractive from the physical aspect, since it holds out the possibility of introducing some approximations in the matrix Hamiltonian $H(E)$, sometimes permitting the derivation of analytical solutions (see Section VI).

Let us consider in more detail the technique of the integration of the one-dimensional equation (28). As shown in Section IV, its symmetry properties ensure the exact flux conservation. It is desirable that the computational procedure not discard this benefit. It is also understood that the calculations require a reasonable amount of computer time.

The use of conventional numerical procedures (Diestler, 1971; Wu and Levine, 1971) and the exponentional method (Light, 1971) does not obey these requirements. In conventional methods the solution within each step is approximated by a polynomial. For oscillating solutions it is necessary to reduce the integration step ($\ll$ wave length), and that usually makes the calculation enormously expensive. Accuracy of the exponential method also strongly depends on a step size.

The integration method free of these disadvantages was developed by Gordon (1969, 1971). Not the function but the potential is approximated on each integration step in such a manner that the equation within a step may be solved exactly. The potential within the step is supposed to be constant, or its linear interpolation is used. In the last case solutions may be expressed in terms of Airy functions. Gordon's method was successfully applied to inelastic scattering problems (Shafer and Gordon, 1973). There is a difficulty in its extension to the reactive scattering problem: the method requires a kinetic energy operator without a first-derivative term. However, the Hamiltonian (28) governing a chemical rearrangement always contains the first-derivative term. Because of that, the utility of Gordon's method in reactive scattering is provided only by means of a conformal transformation technique developed by Connor and Marcus (1970), which maps the wedge-shaped reactive region of Jacobi coordinates into an infinite stripe (Rosenthal and Gordon, 1976).

Gordon's idea on the simple approximation of a potential within each integration step underlies the other one-dimensional NRC method of integration along the translational coordinate (Basilevsky and Ryaboy, 1979a). In order to eliminate the first-derivative term in Eq. (28) the transformation (42) should be used with a transformation matrix satisfying Eq. (46). This equation is solved simultaneously with the main equation, in which the first-derivative term is canceled. In the spirit of Gordon's idea the whole integration region along the translational coordinate is divided into subintervals, and the matrix coefficients of Eq. (28) on each of them are assumed constant. This assumption provides an exact analytical solution over an interval and permits the calculation of the matrix propagator by pure algebraic manipulations. An exact flux conservation is provided by special matching of the local solutions on the boundaries of adjacent intervals, taking into account a stepwise change of matrix coefficients.

In such a manner the symmetry and unitarity of the scattering matrix are provided for any size of vibrational basis.

3. *The Convergence of Calculations: Some Examples*

Some data concerning the convergence of calculations are listed in Table I, and as may be seen, when calculating the H + H_2 reaction the different two-dimensional procedures require the involvement of an approximately equal number of channels. In one-dimensional procedures the needed basis expansions are slightly shorter. The calculations by the state path sum method are the most laborious, however, they are probably the most accurate (see the discussion by Connor *et al.*, 1978a). The data

TABLE I

CONVERGENCE OF CALCULATIONS IN A CLOSE-COUPLING APPROXIMATION

Reaction	N^a	p^b	Reference
H + H_2	15	280	Adams *et al.* (1974)
	11–14		Johnson (1972)
	16(11)^c	102	Light and Walker (1975)
	12		Rosenthal and Gordon (1976)
	9		Wu and Levine (1971)
	5^d	30^d	Basilevsky and Ryaboy (1979a)
F + H_2	21	210	Adams *et al.* (1974)
	20–22	333–622	Connor *et al.* (1978a)
	16^c	110	Light and Walker (1976)
	12–15		Schatz *et al.* (1975a)
H + F_2	31	415	Connor *et al.* (1978b)
	13	50	Basilevsky *et al.* (1982b)
H + Cl_2	18		Baer (1974a)
	8	50	Ryaboy and Chudinov (1981) Basilevsky *et al.* (1982b)

[a] Size of vibrational basis set.

[b] Number of subdivisions of the interaction region.

[c] Harmonic primitive basis (size of contracted basis in parentheses).

[d] A model H + H_2 PES was used.

on the convergence of calculations for $H + H_2$, $H + F_2$, and $H + Cl_2$, obtained by means of the one-dimensional procedure (Basilevsky and Ryaboy, 1979a) need some comment. It should be remembered that some terms in the matrix Hamiltonian, which seemed unessential from the physical standpoint, were neglected in this method. A satisfactory agreement of the obtained results with the other calculations (qualitative for the reaction $H + H_2$ when the model PES was used) and with the experimental data justifies the simplifications introduced, which considerably facilitated the computational labor.

One-dimensional calculations of the reactions $H + H_2$, $H + F_2$, and $H + Cl_2$ (Basilevsky and Ryaboy, 1979a; Ryaboy and Chudinov, 1981; Basilevsky *et al.*, 1982b) were executed in the original NRC formulation (Marcus, 1966) with the minimum energy path taken as the reference curve. The corresponding vibrational potentials are well adapted to reproduce the inherent properties of PES. This is its main distinction from the other NRC treatments, when the reference curve is specified independently of the PES properties (for example, as a circumference of a constant radius (Johnson, 1972; Adams *et al.*, 1974; Light and Walker, 1976). An exact compliance of the vibrational basis with the shape of a PES in the Marcus formulation of NRC is probably one of the reasons of the rapid convergence of the corresponding calculations (see Table I). However, it is necessary that the inequality $Kl\sqrt{n} < 1$ be satisfied along the whole reaction path (see Section III,A,2). (Here K is the reaction path curvature, l is the classical vibrational amplitude, and n is the number of channels involved in calculations.)

Therefore it is essential that the convergence in the one-dimensional NRC calculations should be achieved by means of a sufficiently small basis set. See Section VI,C,4 for a more detailed discussion.

B. Some Results of Quantum Calculations of Exothermic Reactions

1. *Classification of Triatomic Systems and the Main Quantum Effects*

The list of reactions for which quantum dynamical calculations were executed is presented in Table II. The full reference list may be found in the reviews of Truhlar and Wyatt, 1976; Bernstein, 1979; Connor, 1979; Wyatt, 1979. The reactions are grouped according to the mass relation in the given reactive system, which defines the angle θ_0 between the asymptotic directions of a PES. A ratio $\hbar\omega^+/\hbar\omega^-$ of the product vibrational quantum to that of reactant and a reaction exothermicity in the units of product vibrational quantum $\hbar\omega^+$ are also listed. These values represent a set of parameters which mainly determine the reaction dynamics in the scope of each group.

The ratio $\hbar\omega^+/\hbar\omega^-$ is close to unity for all thermoneutral and nearly

TABLE II

CLASSIFICATION OF TRIATOMIC EXCHANGE REACTIONS[a]

Mass relation	Reaction	θ_0	$\hbar\omega^+/\hbar\omega^-$	$Q/\hbar\omega^+$
L + LL	$H + H_2 \rightarrow H_2 + H$ and isotopic variants	60	1	0
L + HL	$H + FH \rightarrow HF + H$ and isotopic variants	87.1	1	0
	$Li + FH \rightarrow LiF + H$	83.3	0.22	−0.4
H + LL	$F + H_2 \rightarrow HF + H$ and isotopic variants	46.4	0.94	3.7
	$Cl + H_2 \rightarrow HCl + H$ and isotopic variants	45.8	0.68	−1.3
	$I + H_2 \rightarrow HI + H$	45.2	0.53	−5.4
	$O + H_2 \rightarrow OH + H$	46.7	0.85	−0.2
L + HH	$Mu + F_2 \rightarrow MuF + F$	86.9	13.6	2.9
	$H + F_2 \rightarrow HF + F$	80.9	4.7	8.3
	$D + F_2 \rightarrow DF + F$	77.4	3.4	11.4
	$T + F_2 \rightarrow TF + F$	74.9	2.9	13.7
	$H + Cl_2 \rightarrow HCl + Cl$	83.2	5.3	5.3
	$D + Cl_2 \rightarrow DCl + Cl$	80.5	3.8	7.6
H + LH	$O + HBr \rightarrow OH + Br$	15.4	1.4	2.2
	$Cl + HBr \rightarrow HCl + Br$	11.5	1.1	1.8
	$Cl + HI \rightarrow HCl + I$	10.8	1.3	4.8
	$I + HI \rightarrow HI + I$	7.2	1	0

[a] $\hbar\omega^+/\hbar\omega^-$, ratio of product and reactant vibrational quanta; $Q/\hbar\omega^+$, heat effect in units of product vibrational quanta.

thermoneutral reactions of **L + LL** and **L + HL** groups and also for **H + LL** reactions with a small (if measured in units of $\hbar\omega^+$ quanta) exothermicity. By that reason, for these groups of reactions the vibrational frequency decreases in the interaction region where both chemical bonds are loose, as compared to the asymptotic values ω^+ and ω^- (the frequency reduces by one-half for the $H + H_2$ reaction). When the potential barrier is low, the wells are expected to arise in the adiabatic channel potentials. As a result, the quasi-bound states and (as numerous quantum calculations have shown) the Feshbach-type resonances in the energy dependence of transition probabilities occur. Quantum calculation of the energy dependence for **H + LH** group (when the angle θ_0 is small) was executed only for the **I + HI** reaction (Kaye and Kuppermann, 1981; Manz and Römelt, 1981) and also have revealed a resonance. Here the small value of angle θ_0 is responsible for resonances independently of the existence of potential wells in the adiabatic channel potentials. That is confirmed by the trajectory oscillations within the corner of a PES, as observed in classical calculations (Parr *et al.*, 1973a). The resonance behavior of transition probabilities represent the most important and interesting peculiarity in the above-mentioned groups of reactions.

Three characteristic properties of **L** + **HH** reactions: large exothermicity, large $\hbar\omega^+/\hbar\omega^-$ ratio, and large value of the angle θ_0 suppress the generation of the quasi-bound states in the interaction region. These reactions are characterized by inverse vibrational populations of product states with a rather narrow bell-shaped distribution. We shall classify reactions of the **L** + **HH** type as semiclassical. The reason for that will be clear from a model investigation in Section VI.

The characteristic properties of the different types of reactive systems are most clearly manifested in energy dependencies of transition probabilities. These dependencies for reactions H + H_2 (Wu and Levine, 1971), F + H_2 (Schatz *et al.*, 1975a), and H + Cl_2 (Baer, 1974a) are shown in Fig. 6. The values of corresponding vibrational quanta (the natural energy units) are also indicated. The resonance behavior of transition probabilities for **L** + **LL** and **H** + **LL** reactions is obvious from Fig. 6a,b. A selective population of the highest open vibrational level is the characteristic property of the F + H_2 reaction. Contrary to that, a smooth energy dependence characterizes **L** + **HH** reactions (H + Cl_2, Fig. 6c). An in-

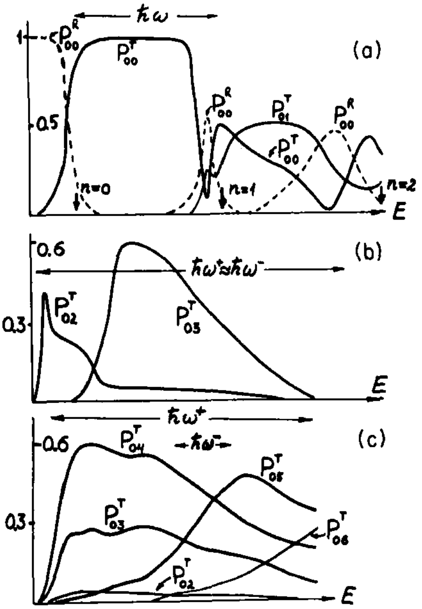


Fig. 6. Energy dependence of transition probabilities for different types of reactions: (a) H + H_2 (Wu and Levine, 1971); (b) F + H_2 (Schatz *et al.*, 1975a); (c) H + Cl_2 (Baer, 1974a).

verse population is evident, but vibrational levels are populated less selectively than in the F + H_2 reaction.

2. *Polanyi's Classification of PESs*

According to Polanyi each PES can be characterized by a certain relation between the three types of the energy release, namely, the attractive A, mixed M, and repulsive R releases. This classification was first introduced in 1966 (Kuntz *et al.*, 1966). There are three ways to define A, M, and R values for a given PES. In particular, attractive energy release $A_\perp$ is measured as an energy change along the reactant valley direction between the top of the potential barrier and the point, where attraction is changed by repulsion (see Fig. 9b). The rest of the energy change down to the asymptotic bottom of the product valley is repulsive release $R_\perp$. The A_m, M_m, and R_m values are measured along the minimum energy path and A_T, M_T, and R_T are measured along a single reactive trajectory. (For details of this classification see Polanyi, 1972; Polanyi and Schreiber, 1974b; Perry *et al.*, 1974).

A similar classification may be introduced also in terms of NRC. Here the energy release is measured along the reaction path representing the NRC reference curve (Basilevsky and Ryaboy, 1978, 1979a,b). In particular, the $A_\perp$ value corresponds to an energy change between the top of a potential barrier and the maximum curvature point. Then $R_\perp$ is the rest of the energy change down to the bottom of the product asymptotic region. When introducing A_m, M_m, and R_m values, we invoke the natural division of the reaction path into three subregions: the product and reactant asymptotic regions and the interaction zone (the nonzero curvature region). Then the A_m value corresponds to an energy change between the top of the potential barrier and the boundary of the interaction zone ($A_m = 0$ if the top of the barrier is located within the interaction zone), and the R_m value corresponds to the energy change in the asymptotic product region. The mixed-energy release M_m coincides with the energy change within the interaction zone. This value plays a primary role in reaction dynamics because transitions between vibrational levels occur only within the interaction zone. A repulsive energy release has no effect on a product vibrational distribution. Finally, the increase of the $A_\perp$ value correlates with an increase of the translational energy within an interaction zone. As this take place, a product population inversion is stimulated (see Section VI).

3. *Polanyi's Rules and Quantum Calculations*

Polanyi and his collaborators (Kuntz *et al.*, 1966; Polanyi, 1972; Ding *et al.*, 1973; Polanyi and Schreiber, 1977; Polanyi *et al.*, 1976) have performed complete experimental and theoretical (by the classical trajectory method) investigations of the exothermic exchange reactions with the aim of revealing of the main dynamical laws.

The main conclusions may be formulated as follows:

(1) The mean fraction of the product vibrational energy f_v is proportional to the fraction of the attractive energy release ($\% A_\perp$) [or to the sum of the attractive and mixed-energy releases $\%(A_m + M_m)$ if the trajectories cutting the corner of PES play an important role].

(2) The more the reactant translational energy, the more the product translational energy; as this takes place, the f_v value decreases.

(3) The more the reactant vibrational energy, the more the product vibrational energy. In this case the product vibrational distribution becomes wider and more complicated in form.

The proportionality law $f_v \sim \% A$ holds for **L** + **HH**-type reactions (the "light-atom anomaly" condition). For other mass relations a high degree of vibrational inversion may also be achieved on a repulsive PES. The F + H_2 reaction represents a good example ($\% R_\perp$ is equal to 99%). The mixed-energy release plays an important role in this case and a proportionality $f_v \sim \%(A_m + R_m)$ was observed (Polanyi and Schreiber, 1977).

It is interesting to compare these conclusions with the results of quantum dynamical calculations. For the H + F_2 reaction, Jakubetz (1978) has obtained a good linear dependence between f_v and $\% A_\perp$. The $\% A_\perp$ value was changed from 32 to 48% by the variation of PES parameters.

The same dependence for **L** + **HH** reactions was investigated on model PESs over a wide range of changing of $\% A_\perp$ parameter (Basilevsky and Ryaboy, 1978) (see Fig. 7). The $\% A_\perp$ value was varied by a displacement of the maximum curvature point along the reaction path. A linear dependence f_v on $\% A_\perp$ holds for the PESs I, II, and IV of the same type.

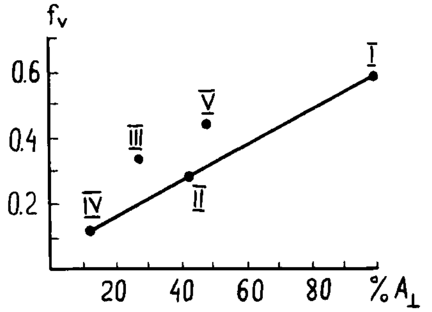


Fig. 7. The dependence of the mean fraction of the product vibrational energy f_v on the attractive energy release $\% A_\perp$ for the model **L** + **HH** reactions. The PESs I–V are characterized by the same curvature function $K(s)$. The variation of the $\% A_\perp$ values was achieved by the displacement of the maximum-curvature point along the reaction path.

(For these PESs the frequency of transversal vibrations do not change along the reaction path). The points, corresponding to PESs III and V (the $\hbar\omega^+/\hbar\omega^-$ ratio is equal to 5 for these PESs), lie above the straight line passing through the points I, II, and IV. That is, the frequency increasing along the reaction path results in increasing of the f_v value. (An exothermicity of all PESs in unity of product vibrational quanta was the same.)

These model calculations have shown that as the reactant translational energy increased up to approximately $0.5\hbar\omega^+$ above the reaction threshold, the product vibrational distribution remained practically independent of energy. That is true if the PES is repulsive ($\% R_\perp > \% A_\perp$). The P_{0n} distributions, obtained in quantum calculations of H + Cl_2 and D + Cl_2 reactions (Baer, 1974a) behave similarly. In this case, in accordance with one of Polanyi's rules, the f_v value decreases as the translational energy increases. However, a significantly greater decrease of the f_v value was observed in experiments (Ding *et al.*, 1973; Polanyi *et al.*, 1975, 1976), which registered a shift of the P_{0n} maximum to smaller product channel numbers n after an increase of the reactant translational energy. It is likely that this inconsistency indicates that a linear reaction model is insufficient.

4. *Reactions of Vibrationally Excited Reactants*

Both experimental investigations (Ding *et al.*, 1973) and trajectory calculations (Parr *et al.*, 1973b; Polanyi *et al.*, 1975) have shown that a vibrational excitation of reactants results in widening product vibrational distributions and in complicating their form. Product vibrational distributions P_{mn} (m is a reactant vibrational state number) with several extrema (two when $m = 1$ and three when $m = 2$) was first observed in quantum calculations on H + Cl_2 and D + Cl_2 (Baer, 1974a; Essen *et al.*, 1976). The LEPS-type PES was used.

Child and Whaley (1979) found a bimodal P_{1m} distribution closely resembling the quantum distribution in semiclassical calculations of the H + Cl_2 reaction. The H + Cl_2 and D + Cl_2 reactions (also on the LEPS PES with different Sato parameters) were calculated by the state path sum method with subsequent information-theoretic 1D → 3D transformation (Connor *et al.*, 1979a). The reported P_{1n} distributions were bimodal.

The P_{0n}, P_{1n}, and P_{2n} distributions obtained from NRC calculations on the LEPS PES with the same parameters as those used in trajectory calculations (Ding *et al.*, 1973) are shown in Fig. 8. They are somewhat shifted to smaller channel numbers n as compared to the previously reported calculations (Baer, 1974; Essen *et al.*, 1976; Connor *et al.*, 1979a) due to a difference of the PES parameters used. However, the P_{0n} distribution and the corresponding f_v value agree well with the trajectory results and the experimental data (Ding *et al.*, 1973).

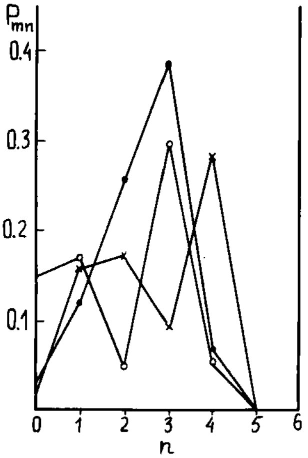


Fig. 8. Quantum P_{mn} distributions for the H + Cl_2 reaction. Total reactant energy $E = 3.8\hbar\omega_{Cl_2}$: (●) $m = 0$; (×) $m = 1$; (O) $m = 2$.

In accordance with the NRC quantum calculations on model PESs (Basilevsky and Ryaboy, 1978, 1979b), the reactant vibrational excitation results in two maxima appearing in the P_{1n} distribution, three maxima appearing in the P_{2n} distribution, and so on. The further increase of the reactant vibrational state number m results in obtaining wide and smooth distributions. If the overall number of product open channels is not large, the effect of "polymodality" of distributions is suppressed.

5. *Quantum Calculations in the Threshold Energy Region*

Only quantum calculations are reliable in a threshold energy region (see, for example, Truhlar *et al.*, 1976), because tunneling contributes considerably to transition probabilities. In particular, adiabatic tunneling explains the difference between the quantum and classical calculations of rate constants for F + H_2 and F + D_2 reactions at low temperatures (Schatz *et al.*, 1975a,b).

It should be remembered, that the value of threshold energy depends on the "dimension" of a quantum calculation (1D, 2D, or 3D). As the dimension increases, the threshold energy increases by the bending zero-point energy of the transition state. The threshold energy shift per one degree of freedom is significant for H + H_2 and F + H_2 reactions (0.06 and 0.08 eV, respectively; Schatz and Kuppermann, 1975; Elkowitz and Wyatt, 1975; Redmon and Wyatt, 1977). The zero-point energy of bending modes is small for L + HH reactions, since in this case the transition state occurs early in the reactant valley (Connor *et al.*, 1979b). Thereby at least the low-energy 1D calculations must be in good agreement with 3D results, and the corresponding rate constants may be directly compared with experimental data.

The energy dependence of the total reaction probability P_0^T in a threshold region was investigated in detail for X + F_2 (X = Mu, H, D, T) reactions (Connor *et al.*, 1976a, 1977, 1978b). The value of P_0^T is equal to 0.5 at the reactant energy, coinciding with a classical reaction threshold, which equals (without anharmonicity corrections) $u_0 + \hbar\omega^{\neq}/2$ (where u_0 is a barrier height and $\hbar\omega^{\neq}$ is a transversal vibrational energy at the top of the barrier). Classical threshold values are almost the same for X = H, D, T, since the vibrational quantum $\hbar\omega^{\neq}$ for all these systems is approximately $\sim 0.9\hbar\omega_{F_2}$ (Jakubetz, 1979; Basilevsky *et al.*, 1982b). The value $\hbar\omega^{\neq}$ is appreciably greater for X = Mu. Probably, it may be explained by a greater enlargement of the vibrational frequency when moving from the reactant to the product valley for this system (see Table II) and results in raising its threshold. The threshold energy dependences of P_0^T (Connor *et al.*, 1978b) may be generally interpreted as a combination of tunneling and the overbarrier reflection processes on 1D adiabatic potentials.

This conclusion was confirmed by the calculation of 1D tunneling along the reaction coordinate for X + F_2 and X + Cl_2 reactions (Jakubetz, 1979). Energy dependences of transition probabilities through the 1D barrier coincided well with the results of complete quantum dynamical calculations.

By this means for **L** + **HH** reactions at low energy the reflection occurs on the potential barrier located in the reactant valley, and this process is adiabatic since the curvature of the reaction path is negligibly small in that region (Basilevsky *et al.*, 1982b). In the quasi-classical trajectory calculations (Connor and Laganá, 1979) the same statement was visualized as a reflection in the "bottle-neck" region (corresponding to narrowing of the reactant valley) near the saddle point.

The conclusion that reflection in **L** + **HH** reactions occurs essentially in the reactant valley is important both from both technical and principle standpoints. It enables the concept of "line of no return" (Connor *et al.*, 1978b) to be introduced. By the definition, reflection processes fail to occur after this line and that facilitates calculations of reaction probability P_0^T. The fact that the reflection and the energy transformation processes occur in the different regions along the reaction path means that the corresponding transition amplitudes do not interfere. This conclusion is important as a background to several models (Section VI).

C. Commentary

Section V,A,2. Gordon's method (1969) is often used in 2D integration procedures to solve the local translational equation of motion in the individual sectors. Within the sector the vibrational basis set does not vary and the first-derivative term in Eq. (28) vanishes. The problems concerning a choice of the step size over the interaction region are discussed in the papers by Connor *et al.* (1978a), Stechel *et al.* (1978), and Light *et al.* (1979).

Section V,B. The validity of the linear model for L + **HH** reactions is confirmed by the results of information-theoretic 1D → 3D transformation. Connor *et al.* (1976b, 1978b, 1979c) have made two assumptions:

(1) dynamical effects which determine the 1D product vibrational distribution are also dominant for the 3D internal energy distribution;

(2) the average fraction of product rotational energy is equal to a predetermined value (for example, to an experimental value). Assumption (2) replaces another one introduced by Bernstein and Levine (1974), which postulated that for each product vibrational state the rotational states are populated according to their statistical weights. Product distributions $P(J, n)$ obtained by means of 1D → 3D transformation agree well with the results of classical 3D trajectory calculations. A satisfactory agreement between the 1D → 3D distribution $P(J, n)$ and that of the classical trajectory was obtained also for the reaction of **H** + **LL** type ($F + H_2$) (Connor *et al.*, 1979c), but only in a limited energy range because for larger energy, nonlinear configurations play an increasingly important role. (Here J is the rotational quantum number.)

VI. Approximations and Models

In this section we consider two main approximations encountered in the multichannel theory of reactive scattering: the matrix semiclassical method and the distorted-wave approximation (DWA). To illustrate their application some model theories of the high-energy inversion of the product vibrational state distributions are discussed. That is one of the two important effects discovered in dynamical calculations of exothermic reactions. The resonances, which are another important effect, generate the population inversion at lower product energies in reactions with less exothermicity; they are treated in Section VII.

The problem of qualitative interpretation of the vibrational inversion, as originally raised by Hofacker and Levine (1971), has been repeatedly investigated both in terms of DWA theory and by using different semiclassical NRC-type models. It should be noted, that the DWA treatment of chemical reactions is based on the ideology of physical coordinates. That is why the two alternative approaches seem at first glance to be mutually incompatible. Nonetheless, they both lead to similar qualitative conclusions agreeing with accurate quantum calculations and with experiment.

That is a consequence of the semiclassical nature of the effect, which presents itself regardless of what formal method has been chosen for its description.

A. Semiclassical Approximation

1. *The Definition and Semiclassical Conditions for the Multichannel Case*

Consider the simplest equation of the type (28):

$$X'' + P^2 X = 0 \tag{78}$$

Matrix P^2 is real and symmetrical, which follows from the symmetry properties (40):

$$P^2 = \tilde{P}^2, \qquad P^2 = P^{2*}, \qquad P^2 = P^{2+} \tag{79}$$

One more condition that we take is the positive definiteness of P^2:

$$\tilde{U}P^2U = p^2, \qquad \tilde{U}U = U\tilde{U} = I, \qquad p^2_{ij} = \delta_{ij}p^2_{ii}, \qquad p^2_{ii} > 0 \tag{80}$$

Then Eq. (78) is reduced to a first-order equation:

$$X' = \pm iPX \tag{81}$$

The test is to differentiate its right- and left-hand parts. On the right we assume

$$\mp iP'X \ll \mp iPX' = P^2X \tag{82}$$

This symbolic inequality is a formal motivation of semiclassical treatment. It suggests that the first term may be omitted in the sum $P'X + PX'$. That immediately regenerates the initial equation (78).

The meaning of this procedure is clarified in terms of the adiabatic representation (80). Let us designate ${}^aP' = \tilde{U}P'U$. The basic assumption is a small difference between the eigenvalues and eigenvectors of matrices P^2 and $P^2 + iP'$ (iP' is treated as a perturbation):

$$(p^2_{ii} \pm i\,{}^aP'_{ii})/p^2_{ii} = 1 \pm i({}^aP'_{ii}/p^2_{ii}) \approx 1, \qquad |{}^aP'_{ii}/p^2_{ii}| \ll 1 \tag{83a}$$

$$|{}^aP'_{ij}/(p^2_{ii} - p^2_{jj})| \ll 1, \qquad i \neq j \tag{83b}$$

These conditions imply the absence of classical turning points ($p^2_{ii} \neq 0$) and of the intersection points of adiabatic terms ($p^2_{ii} \neq p^2_{jj}$). Both constraints must hold not only for real values of a translational coordinate but also for its complex values near the real axis.

The simplest version is

$$P^2 = (2\mu/\hbar^2)(EI - W_{\text{pot}}) \tag{84}$$

Here W_{pot} represents a matrix potential and μ is the mass of a system. Conditions (80) and (83a) represent a high-energy situation described in some chemical coordinates (for instance, in NRC). If physical coordinates are applied, then classical turning points are inevitably present close to the coordinate origin.

2. *Solutions of the Semiclassical Equation*

Let us denote as $X^{(1)}$ and $X^{(2)}$ the solutions to Eq. (81): $X^{(1)\prime} = iPX^{(1)}$; $X^{(2)\prime} = -iPX^{(2)}$. We define the square root of matrix P^2 as

$$P = Up\tilde{U}, \qquad p_{ii} = +(p_{ii}^2)^{1/2} > 0 \qquad \text{(real value)}$$

$$P = \tilde{P} = P^{\dagger}$$

These solutions correspond to semiclassical waves propagating in opposite directions along a translational coordinate that will be called x.

Now we take special boundary conditions at some point $x = -x_0$:

$$X^{(1)}(-x_0) = X^{(2)}(-x_0) = I \tag{85}$$

The following equalities are valid:

$$\tilde{X}^{(1)}X^{(2)} = \tilde{X}^{(2)}X^{(1)} = I \tag{86a}$$

which is the relation between semiclassical solutions, and

$$X^{(1)\dagger}X^{(1)} = X^{(2)\dagger}X^{(2)} = I \tag{86b}$$

is the property of unitarity of semiclassical solutions. The combination of Eqs. (86a) and (86b) gives

$$X^{(2)} = (\tilde{X}^{(1)})^{-1} = X^{(1)*} \tag{87}$$

Equations (85)–(87) make a multichannel generalization of usual properties of one-channel semiclassical exponents. They follow from the symmetry and hermiticity of matrix P. The proof of Eq. (86) is given in Section VI,D.

The normalized semiclassical solutions are

$$NX^{(1)} = P^{-1/2}X^{(1)}, \qquad NX^{(2)} = P^{-1/2}X^{(2)}$$

Proceeding semiclassically, we take $N' = 0$, then the normalized expressions satisfy Eq. (81). The correctness of such a normalization is verified by calculating the Wronskian:

$$\begin{aligned}\text{(constant matrix)} \quad &= \tilde{X}^{(1)}\tilde{N}NX^{(2)\prime} - \tilde{X}^{(1)\prime}\tilde{N}NX^{(2)} \\ &= -i(\tilde{X}^{(1)}\tilde{N}NPX^{(2)} + \tilde{X}^{(1)}P\tilde{N}NX^{(2)}) \\ &= -2i\tilde{X}^{(1)}X^{(2)} = -2iI\end{aligned}$$

Finally, we construct a complete semiclassical solution of Eq. (78):

$$X = \left(\begin{array}{c|c} NX^{(1)} & NX^{(2)} \\ \hline iNPX^{(1)} & -iNPX^{(2)} \end{array}\right) = \left(\begin{array}{c|c} P^{-1/2} & 0 \\ \hline 0 & iP^{-1/2} \end{array}\right)\left(\begin{array}{c|c} X^{(1)} & X^{(2)} \\ \hline X^{(1)} & -X^{(2)} \end{array}\right)$$

We may operate in a standard fashion to find the Jost matrices and the S matrix (Section IV,C); all the needed calculations consist of multiplications and inversions of block matrices with an appeal to Eqs. (85)–(87). Locating the points $\pm x_0$ in the asymptotic product and reactant regions and making a special selection of physically inessential phase factors, the following result can be obtained

$$S = \left(\begin{array}{c|c} 0 & [X^{(2)}(x_0)]^{-1} \\ \hline X^{(1)}(x_0) & 0 \end{array}\right) \tag{88}$$

This formula is physically clear. It acknowledges the lack of interference between semiclassical waves moving in opposite directions. The reflection is missing, since there are no turning points. The unitarity and symmetry of this S matrix are guaranteed by the properties (86b) and (87). We also draw attention to the fact that the normalization factor has dropped out from the resulting expression.

3. *Approximate Estimation of the Matrix Momentum. The Trajectory Approximation*

Consider the square root of a special matrix

$$P^2 = t + gu$$

Here matrix t is diagonal and matrix u is arbitrary; g is a small numerical parameter. The expansion in powers of g is trivial if the matrices t and u commute. For instance, as in Eq. (84), if we take $t = (2\mu/\hbar^2)EI$, then

$$P \approx (2\mu E/\hbar^2)^{1/2}[I - \tfrac{1}{2}(W_{\text{pot}}/E)]$$

The first term generates an inessential phase factor in the solution of Eq. (81) and can be omitted. After introducing the classical velocity $v = (2E/\mu)^{1/2}$, the equations of the trajectory approximation are obtained (Mott, 1931; Child, 1974):

$$dX/dq^1 = \pm(i/\hbar v)W_{\text{pot}}X, \qquad dX/dt = \pm(i/\hbar)W_{\text{pot}}X, \qquad dq^1 = v\,dt$$

If the matrices t and u do not commute, then the following expansion arises (Basilevsky and Ryaboy, 1979c):

$$\begin{gathered} P = (t + gu)^{1/2} = P_0 + gP_1 + \cdots \\ P_0 = t^{1/2}, \qquad (P_1)_{ij} = u_{ij}/(t_{ii}^{1/2} + t_{jj}^{1/2}) \end{gathered} \tag{89}$$

The explicit expressions for matrix momentum P enable constructing approximate and, sometimes, exact analytical solutions to Eq. (81). A lot of known methods have utility: the adiabatic perturbation theory (Landau and Lifshitz, 1963; Messiah, 1961; Child, 1974), the Magnus expansion and its first (sudden) approximation (Magnus, 1954; Pechukas and Light, 1966; Child, 1974).

We can somewhat generalize the trajectory approximation by changing in Eq. (89) the matrix $t^{1/2}$ by a number $\bar{t}^{1/2}$, which may depend on the translational variable. A reasonable estimate of this number can be extracted from a minimization of the relative error arising due to such a change. When the sequential elements of matrix t differ in a constant value ($t_{kk} - t_{k-1\,k-1} = -\hbar\omega$: the harmonic approximation for the vibrational variable), then this definition yields (Basilevsky and Ryaboy, 1979b):

$$t_{kk} = (2\mu/\hbar^2)(E - k\hbar\omega), \qquad \bar{t} = (4\mu/3\hbar^2)(E + \hbar\omega) \tag{90}$$

B. Distorted Wave Approximation (DWA)

1. *Expression for the Transition Amplitude*

This is a quite different theory deriving approximate-transition probabilities for a system obeying the Schrödinger equation:

$$(\mathcal{H} - E)\lambda^{\pm}(E, n) = 0$$

The background for that is the exact relation for the elements of the S matrix (Newton, 1966; Taylor, 1972):

$$S_{fi}(E) = S^{0}_{fi}(E) - 2\pi i T_{fi}(E)$$

$$T_{fi}(E) = \langle \lambda_0^-(E,f)|V^-|\lambda^+(E,i)\rangle \tag{91a}$$

$$= \langle \lambda^-(E,f)|V^+|\lambda_0^+(E,i)\rangle \tag{91b}$$

The total Hamiltonian is cast into one of two forms: $\mathcal{H} = \mathcal{H}_0^+ + V^+ = \mathcal{H}_0^- + V^-$. It is understood that the solutions, corresponding to $\mathcal{H}_0^{\pm}$, are already known: $(\mathcal{H}_0^{\pm} - E)\lambda_0^{\pm}(E, n) = 0$. The superscripts indicate what boundary conditions are taken. In the complete 3D theory the functions λ^+, λ_0^+ are asymptotically represented as states with an outgoing spherical wave, and the functions λ^-, λ_0^- convert into states with an incoming spherical wave. For "+" states that plane wave corresponds to a single initial channel i; for "−" states it corresponds to a single final channel f. Both plane waves are normalized to a unit flux (to the δ function of energy).

These definitions need some modification in the 1D theory. The functions λ^+, λ_0^+ have a single normalized incoming exponent in the entrance channel i; all other exponents are outgoing. Opposite to that, the functions λ^-, λ_0^- have a single normalized outgoing exponent in the exit channel f, all other exponents being incoming. For instance, if we take the Cartesian coordinates $(x^{(1)}, z^{(1)})$ for reactants (the channel indices i, i') and $(x^{(2)}, z^{(2)})$ for products (the channel indices f, f', see Section II,B,1), then the following asymptotic representations arise:

$$\lambda^+(E, i) \to \begin{cases} k_i^{-1/2} \exp(-ik_i x^{(1)}) \varphi_i^{(1)} \\ \qquad + \sum\limits_{i'} [k_{i'}^{-1/2} \exp(ik_{i'} x^{(1)}) \varphi_{i'}^{(1)}] c_{i'i} \\ \qquad \text{(reactant valley)} \\ \sum\limits_{f'} [k_{f'}^{-1/2} \exp(ik_{f'} x^{(2)}) \varphi_{f'}^{(2)}] c_{f'i} \\ \qquad \text{(product valley)} \end{cases}$$

$$\lambda^-(E, f) \to \begin{cases} k_f^{-1/2} \exp(ik_f x^{(2)}) \varphi_f^{(2)} \\ \qquad + \sum\limits_{f'} [k_{f'}^{-1/2} \exp(-ik_{f'} x^{(2)}) \varphi_{f'}^{(2)}] c_{f'f} \\ \qquad \text{(product valley)} \\ \sum\limits_{i'} [k_{i'}^{-1/2} \exp(-ik_{i'} x^{(1)}) \varphi_{i'}^{(1)}] c_{i'f} \\ \qquad \text{(reactant valley)} \end{cases} \tag{92}$$

Here the k terms designate wave numbers and the $\varphi^{(1,2)}$ terms stand for vibrational basis functions. The functions $\lambda_0^\pm$ differ from the exact solutions in their amplitudes $c_{i'i}$, $c_{f'i}$, $c_{f'f}$, $c_{i'f}$ that are supposed to be known for them.

Now an approximate estimate for the transition matrix $T(E)$ is obtained by means of the substitution of approximate functions λ_0^+ instead of the exact ones λ^+ into Eqs. (91):

$$T_{fi}(E) \approx \langle \lambda_0^-(E, f) | V^- | \lambda_0^+(E, i) \rangle \tag{93a}$$

$$\approx \langle \lambda_0^-(E, f) | V^+ | \lambda_0^+(E, i) \rangle \tag{93b}$$

As may be shown, the right-hand parts of these two relations are the same (Messiah, 1961; Taylor, 1972).

2. *Selection Rule*

Chemical systems are usually semiclassical, so that their wave functions rapidly decrease in depth to classically inaccessible regions. With that in mind, the following conclusion can be deduced from Eqs. (91):

The amplitude $T_{fi}(E)$ is negligibly small if the interaction zone, where the potential promoting a transition is located, is separated from an asymptotic region corresponding to either an i or an f state by a region, which is classically inaccessible for a given energy E (the potential barrier).

This rule is intuitively evident. For the proof it suffices to point out, that the wave functions specified by asymptotic conditions (92) (both λ^+ and λ_0^+ have this asymptotic form) are regular. This results in their exponential decreasing depth into classically inaccessible regions. (That is not so for the functions J and $\mathcal{O}$ described in Section IV,B,4.)

The rule may be violated if the interaction zone is classically inaccessible from the both sides; that is, both for i and f states. Then the resonance behavior may appear at certain energies, disturbing the whole reasoning.

3. *Discussion on the DWA Method*

In practical calculations the distorting potentials are selected in such a manner so as to eliminate the proceeding of a reaction in a zero approximation. The potentials V^- and V^+ have to lock the reactant valley or the product valley, respectively. Then the term $\Sigma_{f'}$ vanishes in the function λ_0^+ and $\Sigma_{i'}$ vanishes in λ_0^-. An extra vibrationally adiabatic approximation (VADW) is often used which retains a single term in the remaining sum, namely, the reflected wave in channel i for $\lambda_0^+(E, i)$ or the transmitted wave in channel f for $\lambda_0^-(E, f)$. Such a choice for a zero approximation annihilates zero-order transitions $S_{fi}^0(E)$, hence Eqs. (93) provide a direct estimation of a transition amplitude.

In 3D calculations the 6D integrals (93) reduce to three dimensions after explicitly taking into account the conservation of angular momentum; in 1D calculations we deal with 2D integrals. If the functions of the type (92) are used in the integrand, then it is necessary to express the coordinates $(z^{(1)}, x^{(1)})$ in terms of $(z^{(2)}, x^{(2)})$ or vice versa.

It is very important for an understanding of the character of approximation (93) that the functions λ_0^+ and λ_0^- be eigenfunctions of quite different Hamiltonians. If it were $\mathcal{H}_0^+ = \mathcal{H}_0^-$, $V^+ = V^-$, then one would deal with a first Born approximation, which is only suitable for treating weak transitions. We consider specific peculiarities of nonperturbative formulas (93), using the first of them [Eq. (93a)] as an example. The localization region of its integrand is determined by a particular choice of the potentials V^+ and V^-. If an approximate relation $\lambda_0^+(E, i) \approx \lambda^+(E, i)$ holds sufficiently accurately in the region of localization of the product $[\lambda_0(E, f)]^* V^- \lambda_0^+(E, i)$, then good results are expected even when the perturbations V^+ and V^- are not at all small and the transition probabilities are close to unity.

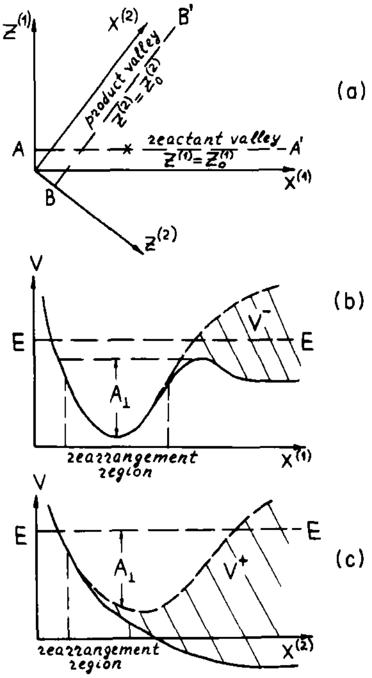


Fig. 9. Choosing the V^+ and V^- potentials in the DWA method (Fischer and Venzl, 1977). (a) Cartesian coordinate systems; the dotted lines *AA'* and *BB'* coincide with the bottom of the respective asymptotic valleys; × is the saddle point. (b) The PES cut along the *AA'* line; *E* is an energy of the system; $A_\perp$ is an attractive energy release (see Section V,B,2); potential V^- is shown by the dotted line; the lower solid line represents the exact PES cut. (c) The PES cut along the *BB'* line; notation is the same as in Fig. 8b.

In order to arrive at such a situation, the overlap of the potentials V^+ and V^- should be made as small as possible. This can be illustrated by an exothermic reaction L + HH (Fig. 9).

The function λ_0^+ always involves a pair of waves: that directed to the product valley (falling on the potential V^+) and that with the opposite direction (reflected from the potential V^+). However, the reflected wave is missing in the accurate solution. This discrepancy cannot be eliminated regardless of how accurately the function λ_0^+ is determined in the region unperturbed by the locking potential V^+. We conclude that it is most important to annihilate the contribution to the integral from the region close to the border of the potential V^+ (the broken curved line, Fig. 9c). The potential V^+ must be shifted deep enough into the product valley, which it locks. Then two factors operate near its border, supplying us with the desired effect:

(1) The potential V^- nearly vanishes, since it is only needed to lock the reactant valley (see Fig. 9b).

(2) The function $\lambda_0^-(E, f)$ oscillates rapidly along the direction of the $x^{(2)}$ axis, so that only a small coordinate region in the vicinity of its turning point makes a significant contribution to the integral.

Moreover, the above accepted assumption that the difference between the functions λ^+ and λ_0^+ does not matter when moving away from the border of V^+ is actually equivalent to the assumption about the semiclassical character of these functions. That indicates the importance of the condition of exothermicity, which assures semiclassical properties of all wave functions in the "dangerous" region.

4. *Calculations Using the DWA Method. The Frank–Condon Model of a Chemical Reaction*

The technique of DWA calculations has been elaborated by Tang and Karplus (1968, 1971) and refined by Choi and Tang (1974). It was successfully applied to the 3D investigation of vibrational–rotational transitions in such systems as H + H_2 (Choi and Tang, 1974, 1976; Clary and Connor, 1980), F + H_2 (Suck, 1977, 1981; Chan et al., 1978), and H + F_2 (Clary and Connor, 1979).

Table III illustrates the discussion of the preceding section on the validity of the DWA method. It is seen that the vibrationally adiabatic approximation (VADW) works quite satisfactorily. Moreover, it is evident

TABLE III

RELATIVE POPULATIONS OF THE PRODUCT VIBRATIONAL STATES P_{0n}/P_{06} FOR THE $H + F_2 \rightarrow HF + F$ REACTION[a]

	Method				Method		
	VADW	DWA (static reactant model)	Exact quantum 1D calculation		VADW	DWA (static reactant model)	Exact quantum 1D calculation
0	0	0.45	0	6	1.00	1.00	1.00
1	0	0.58	0	7	0.26	0.13	0.30
2	0	5.19	0.01	8	0.01	0.09	0.03
3	0.02	3.82	0.02	9	0	0	0
4	0.12	10.00	0.13	10	0	0	0
5	0.77	4.57	0.50	11	0	0	0

[a] Clary and Connor (1979).

that it is necessary to calculate accurately function λ_0^+ in the region, which makes an essential contribution to the integral (93), that is, where the reactant valley flows into the interaction zone. This is confirmed by the failure of the static DWA model, neglecting the change in shape of the reactant valley cross sections in the interaction zone (it worked with the asymptotical cross section, namely, the potential curve of the reactant molecule F_2, throughout the entire calculation).

Several authors considered approximate estimates for the integral (93a) in order to obtain analytical expressions for the reactive transition probabilities (Halavee and Shapiro, 1976; Shatz and Ross, 1977; Fischer and Venzl, 1977; Venzl and Fischer, 1978, 1979). The transition probabilities were expressed in terms of Frank–Condon factors, that is, the overlap integrals of vibrational wave functions of reactants and products, extrapolated to the interaction zone by means of potentials V^+ and V^-. The relative arrangement and frequencies of the respective oscillators are different in different models, being determined by a particular choice of the perturbing potentials. These tentative calculations gave a reasonable account of the inversion of vibrational populations in exothermic reactions **L** + **HH** → **LH** + **H**. We write out one of the analytical distributions (Fischer and Venzl, 1977):

$$P_{0n} \sim (2^{-n}/n!)|\alpha|^n|H_n(g)|^2 \exp\{-(X_n - \tilde{X})/\tilde{\sigma}^2\}E_n^{-1} \tag{94}$$

In this formula E_n is the asymptotic translational energy for the state n of the products; H_n is the Hermitian polynomial. The terms $\alpha, g, X_n, \tilde{X}, \tilde{\sigma}$ are expressed in a complicated manner through the parameters of a chemical system. In particular, some of them explicitly involve the Polanyi's parameter $A_\perp$ (see Section V,B,2); it is seen from Fig. 9 that $A_\perp$ can significantly influence the dynamics. The reactions with other mass combinations were also discussed in the above-mentioned papers.

The simplest approximation for the distributions $P_{if} = |T_{fi}|^2$ with fixed initial state i is obtained when the integrals of Eq. (93) are substituted by a 2D Frank–Condon integral $\langle\lambda_0^-(E,f)|\lambda_0^+(E,i)\rangle$ (Levich *et al.*, 1970; Berry, 1974; Shatz and Ross, 1977). After appealing to the semiclassical character of a translational motion it reduces to a calculation of 1D Frank–Condon integrals.

Such a description of a chemical reaction as a nonadiabatic transition between a pair of shifted oscillators (the reactant and the product) (Levich *et al.*, 1970), seems quite reliable when the intensity of reactive transitions is small. Then the basic relation of the DWA [Eq. (93)] becomes a standard prescription of Born perturbation theory for any choice of the quantities $V^\pm$. For instance, an appropriate situation occurs at low temperatures in the radical exchange reactions $R_1H + R_2 \rightarrow R_1 + HR_2$ ($R_{1,2}$ are the hydrocarbon radicals) with sufficiently high potential barriers (Ovchinnikova, 1977). Such processes proceed as tunneling transitions between the reactant and product valleys in the vicinity of a single trajectory, cutting the PES corner far apart from the saddle point. Their model treatment may be found in Klochikhin *et al.*, 1978; Trakhtenberg *et al.*, 1981; Babamov and Marcus, 1981.

C. The NRC Approximation

1. *The Model NRC Hamiltonian for a Treatment of the High-Energy Vibrational Inversion*

As noted in Section II,B,2, the NRC approximation is suitable for the investigation of reactions **L** + **HH** → **LH** + **H**. We shall apply it to a qualitative study of the high-energy population inversion in exothermic reactions of this type.

It should be recalled that the NRC description characterizes a PES by three functions of the translational coordinate s. These are the frequency $\omega(s)$, the curvature $K(s)$, and the potential $V_1(s)$. Treating the translational motion as semiclassical, we neglect the s derivatives of these physical characteristics and the respective matrices. We therefore use the substitution (42) $X \rightarrow G^{-1/2}X$ and neglect the derivatives of $G^{-1/2}$. Thus the transformed NRC Hamiltonian (31) takes the form $H(E) = (d^2/ds^2) + (2\mu/\hbar^2)G^{-1/2}(EI - \epsilon)G^{-1/2}$.

By analogy with Eq. (33) the matrix $G^{-1/2}$ may be calculated as $G^{-1/2} = I + KW$. It is convenient to derive $H(E)$ in a dimensionless form. We therefore introduce the quantities $\hbar\omega_0$ (as an energy unit) and $l_0 = [\hbar/(2\mu\omega_0)]$ (as a length unit). The point s_0, where the frequency ω_0 is taken, is located in the asymptotic reactant valley. Next we define the dimensionless frequency $\rho(s) = \omega(s)/\omega_0$ and the scaled length

$$l(s) = l_0\rho^{-1/2}(s) = l_0[\omega_0/\omega(s)]^{1/2} = [\hbar/2\mu\omega(s)]^{1/2}$$

The three physical characteristics of a PES become

$$\begin{gathered} \rho(s) = \omega(s)/\omega_0, \qquad g(s) = K(s)l(s) = K(s)l_0\rho^{-1/2}(s) \\ \epsilon(s) = \{[E - V_1(s)]/\hbar\omega_0\rho(s)\} - \tfrac{1}{2} \end{gathered} \tag{95}$$

The main NRC condition is

$$g \ll 1 \tag{96}$$

Our hypothesis is that it is always satisfied, and we apply it several times in the subsequent treatment.

On introducing the dimensionless length $x = s/l_0$, we obtain the model Hamiltonian in form

$$H_{\mathrm{mod}}(E) = (d^2/dx^2) + P^2, \qquad P^2 = \rho[t + g(tw + wt)] \tag{97}$$

which involves two matrices. Matrix t represents an operator of dimensionless translational kinetic energy. It is diagonal:

$$t_{kk} = \epsilon(s) - k \tag{98}$$

Matrix w represents the operator of the dimensionless vibrational coordinate:

$$w = l(s)^{-1}w \tag{99}$$

The terms of order of g^2 are omitted in the Hamiltonian (97) according to Eq. (96). Some of these terms have already been omitted in the initial Hamiltonian $H(E)$.

The vibrational inversion cannot be treated by perturbation theory, considering the second term of P^2 as a perturbation. Matrix w is the only off-diagonal matrix present in this term, but it generates transitions only between neighboring levels if the first Born approximation is used. (The first Born approximation is, in principle, not suitable for treating intensive nonadiabatic transitions.) Nonetheless, the effect of the inversion is contained in the Hamiltonian (97). This is because it has no small parameter in the case of large kinetic energy: when $t_{kk} \gg 1$ the product gt_{kk} is not small. Therefore, the usual series expansions are inefficient for obtaining the physically interesting solutions of the equation $H_{\mathrm{mod}}(E)X = (d^2X/dx^2) + P^2X = 0$.

2. *Semiclassical Models*

The semiclassical equation corresponding to the quantum Hamiltonian (97) reads

$$dX/dx = iPX \tag{100}$$

Our purpose is to find approximate analytical solutions to it. First of all an analytical expression for matric P is needed, so we derive an expansion of the square root of P^2 over the small parameter g. In doing so it is expedient to operate with the creation and annihilation operators a^+ and a (Messiah, 1961). They satisfy the commutation relation $[a, a^+] = 1$. Matrix w equals $w = a + a^+$. Applying Eq. (89) yields

$$P \approx \rho^{1/2}[t^{1/2} + g(\tau a + a^+\tau)] + O(g^2) \tag{101}$$

Matrix τ is diagonal. For the high-energy situation ($\epsilon \gg 1$), it may be regarded as $\tau \approx t^{1/2}$ where $\tau_{kk} \approx (\epsilon - k)^{1/2}$. If we want to obtain analytical solutions to Eq. (100), then some additional simplifications are needed.

Model I (*the trajectory approximation*). We change matrices $t^{1/2}$ and τ by the number $\bar{t}^{1/2}$ in Eq. (101):

$$P \approx \rho^{1/2}\bar{t}^{1/2}(I + gw) \tag{102a}$$

Model II (Hofacker and Levine, 1975). In Eq. (101) we change matrix τ by the number $\bar{t}^{1/2}$ and matrix $t^{1/2}$ by a different matrix $\bar{t}^{-1/2}t$:

$$P \approx \rho^{1/2}\bar{t}^{-1/2}(t + g\bar{t}w) \tag{102b}$$

Model III (Basilevsky and Ryaboy, 1979b,c). In Eq. (101) we change matrix $t^{1/2}$ by the number $\bar{t}^{1/2}$:

$$P \approx \rho^{1/2}[\bar{t}^{1/2} + g(\tau a + a^{+}\tau)] \approx \rho^{1/2}[\bar{t}^{1/2} + g(t^{1/2}a + a^{+}t^{1/2})] \tag{102c}$$

where $\bar{\rho}^{1/2}\bar{t}^{1/2} = \text{const}$, and $\rho^{1/2}t^{1/2} = \text{const}$ (independent of x). For all models the value of number $\bar{t}$ is calculated by Eq. (90). All three models lead to a solution

$$X = \exp(iA) \tag{103}$$

It follows from Eq. (88) that the elements of this matrix represent amplitudes of nonadiabatic transitions.

Now we write out the three expressions for matrix A discarding insufficient phase factors (that facilitates the calculation):

Model I:

$$A = \beta(a + a^{+}), \qquad \beta = \int \rho^{1/2}\bar{t}^{1/2}g\,dx$$

Model II:

$$A = \beta a^{+} + \beta^{*}a, \qquad \beta = -\int \rho^{1/2}\bar{t}^{1/2}g\exp[i(\rho/\bar{t})^{1/2}x]\,dx$$

Model III:

$$A = \beta(t^{1/2}a + a^{+}t^{1/2}), \qquad \beta = \arcsin \lambda^{1/2}$$

The expression for λ in Model III is generally obtained by the numerical integration of a normal second-order differential equation. However, there exists an analytical result for a particular choice of the function $g(x)$:

$$g(x) = g_0 \operatorname{sech}(x/\sigma), \qquad \lambda^{1/2} = \sin(\pi g_0\sigma)\operatorname{sech}(\pi\sigma/4\bar{t}^{1/2}) \tag{104}$$

Models I and II result in similar explicit expressions for transition amplitudes, differing only in the definition of the basic parameter β:

$$\begin{aligned} X_{nm} &= \exp(-|\beta|^2/2)(m!n!)^{1/2}(i\beta^*)^{n-m} \\ &\quad \times \sum_{k=0}^{m} \frac{(-1)^k|\beta|^{2k}}{k!(n-m-k)!(m-k)!} \qquad (m \le n) \qquad (105a) \\ X_{nm}^* &= X_{mn} \qquad (m \ge n) \end{aligned}$$

Model III results in[1]

$$\begin{aligned} X_{nm} &= \sum_{k=0}^{m} (i)^{n-m+2k}\lambda^{(n-m+2k)/2}(1-\lambda)^{(\epsilon-m-n)/2} \\ &\quad \times \left[\binom{\epsilon-m+k}{k}\binom{\epsilon-m+k}{n-m+k}\binom{m}{k}\binom{n}{m-k}\right]^{1/2} \qquad (105b) \end{aligned}$$

Hence transition probabilities as obtained from Models I and II depend on a single parameter $|\beta|^2$; in Model III they depend on a pair of parameters, namely, λ and ϵ. That is why the latter model is more flexible and efficient. However, it involves the extra restriction (absent in Models I and II) that the quantity $(\rho\bar{l})^{1/2}$ must be close to constant.

3. *Semiclassical Product Population Distribution for the Ground-State Reactants. Comparison with Quantum Calculations and Experiment*

Models I and II result in Poisson distributions if the transitions from the zero level are considered

$$P_{0n} = \exp(-|\beta|^2)|\beta|^{2n}/n! \qquad (106)$$

The average value of n, the index number $n_{\max}$ of the maximally populated level and the dispersion are all equal to $|\beta|^2$. When $|\beta|^2 > 1$, Eq. (106) exhibits a population inversion with a broad distribution of states.

Model III leads to a binomial distribution

$$P_{0n} = \binom{\epsilon}{n}\lambda^n(1-\lambda)^{\epsilon-n} \qquad (107)$$

Now $n_{\max}$ is the integer of the product $(\epsilon + 1)\lambda$, the average value of n is $\epsilon\lambda$, and the dispersion is $\Delta = [\epsilon\lambda(1-\lambda)]^{1/2}$. The inverse population arises when $\lambda > (\epsilon + 1)^{-1}$. Parameter λ is equal to the mean fraction of the product vibrational energy f_v. It increases with the fraction of attractive energy release $A_\perp$ (Basilevsky and Ryaboy, 1979b), which agrees with

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[1] Two binomial coefficients were misprinted in the original paper (Basilevsky and Ryaboy, 1979b,c).

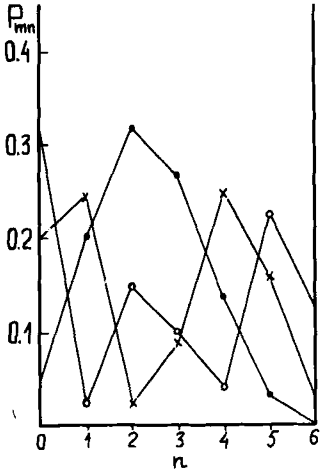

Fig. 10. Semiclassical (Model III) P_{mn} distributions for H + Cl_2 reactions. Notation is the same as in Fig. 8.

experimental observations and with the results of classical and quantum calculations (see Section V,B,3).

We calculated the values of parameter β for Models I and II with the LEPS-type PES of reaction H + Cl_2 (Ding *et al.*, 1973) for the total reactant energy taken as $E = 3.8\hbar\omega_{Cl_2}$. The primary test is a comparison with the actual index number of the maximally populated level, which is $n_{max} = 2-3$ for this reaction.

We obtained $|\beta|^2 = 10.6$ for Model I and $|\beta|^2 = 0.88$ for Model II. According to Eq. (106) these values determine n_{max} where n_{max} is the integer part of $|\beta|^2$. We thus conclude that Model I is absolutely inefficient, while Model II significantly underestimates the degree of the vibrational inversion. Besides that, the Poisson distribution (if empirically calibrated to give the correct value of n_{max}) is too broad as compared to experimental P_{0n} distributions. The deficiencies of the Poisson-like distributions and the related models have been already discussed (Fisher *et al.*, 1978).

Similar calculations for Model III gave $\beta = 0.65$ and $f_v = \lambda = 0.37$. The corresponding P_{mn} distributions ($m = 0, 1, 2$) are shown in Fig. 10. They satisfactorily reproduce the results of quantum calculations (Fig. 8, Section V,B,4), although they have a somewhat larger width.

4. *Semiclassical Product Population Distributions for the Vibrationally Excited Reactants*

All semiclassical NRC models lead to the appearance of dips in P_{mn} distributions for $m \neq 0$. The number of dips coincides with the index number m of the initial reactant state. This observation agrees with the results of quantum calculations (Section V,B,4). The peculiarity of vibrational distributions may be generally deduced from a semiclassical model (Basilevsky and Ryaboy, 1979b), being a consequence of the orthogonality condition for the columns of the semiclassical S matrix (88). Each of these columns represents a product wave function in the channel space for a certain reactant state $m = 0, 1, 2, \ldots$. If many channels are open in the product region, then the absolute values $|S_{nm}|^2 = P_{mn}$ can be considered as quasi-continuous functions of n. The orthogonality condition implies that the nodes, i.e., the zeros of P_{mn}, should exist for $m > 0$ (they do not necessarily correspond to integer values of n). An important comment necessary to prove this is that the phases of S_{nm} vary in a discrete manner with the variation of n. [Hence, the alternate symmetry (Coulson and Longuet-Higgins, 1947) of matrix A in Eq. (103) results in elements which are by turns purely real or purely imaginary numbers.) By this argument the existence of dips in P_{mn} distributions may be regarded as a manifestation of the semiclassical nature of a chemical process.

5. *Discussion on the Validity Range of the NRC Approximation*

We start with the definition of NRC due to Marcus (1966), associating their reference curve with the minimum energy path. Its construction presents the first step in representing a PES in NRC. The two algorithms, specially designed to calculate a minimum energy path along the valley of a PES given a saddle point, were elaborated by Ishida *et al.* (1977) and Müller and Braun (1979). The reference curves calculated by these two methods for several exothermic reactions **L** + **HH** (listed in Table IV) appeared to be clearly distinct in the interaction region (Ryaboy and Chudinov, 1981; Basilevsky *et al.*, 1982b), although they coincided when passing to asymptotic regions. The difference arose inside a steep descent region of a PES directed to the product valley. The maximum separation of the two curves reached half of the classical amplitude of the transversal vibration. The main result was quite a different form of curvature function, which was very sensitive to slight variation in the shape of the reference curve. Thus, $K(s)$ displayed two maxima when the algorithm of Ishida *et al.* (1977) was used and only one maximum, significantly larger in value, when that of Müller and Braun (1979) (see Table IV) was used.

Reaction paths with complicated (several extrema) curvature functions have been observed earlier (Duff and Truhlar, 1975) on the PESs of the "rotated Morse function" type as well as on the LEPS-type PESs. It seems that the forms of curvature functions reported in these calculations were also strongly influenced by the search method applied to construct the reaction path.

TABLE IV

MAXIMUM CURVATURE OF THE REACTION PATH (NRC REFERENCE CURVE) AS FOUND BY THE ALGORITHMS OF ISHIDA *et al.* (1977) AND MÜLLER AND BRAUN (1979), AND ITS EMPIRICAL ESTIMATION BY THE SEMICLASSICAL MODEL III

	Maximum value of g [Eq. (95)]		
Reaction	Ishida *et al.* (1977)[a]	Müller and Braun (1979)	Model III
$H + F_2$	0.270 0.254	1.431	0.239
$D + F_2$	0.341 0.588	2.037	0.244
$H + Cl_2$	0.291 0.308	0.767	0.211
$D + Cl_2$	0.200 0.229	0.600	0.182
$H + Br_2$	0.300 0.581	1.431	0.265
$D + Br_2$	0.215 0.523	1.107	0.338
H + ICl	0.342 1.039	2.169	0.237
H + ClI	0.251 0.324	0.694	0.201

[a] The curvature of the reference curve has two maxima.

Having calculated the reference curve, a PES is approximated by the potential cross section $V(s)$ along that curve and by the harmonic frequency $\omega(s)$. It appeared that the distinction between the reference curves led to a moderate variation of these functions and, which was most important, that the total errors in approximating the PESs by both methods did not exceed 0.01 eV.

For four reactions ($H + F_2$, $H + Cl_2$, $D + Cl_2$, H + ClI), the curvature calculated with the algorithm by Ishida *et al.* was no larger than the value $g = Kl \approx 0.3$. The quantum dynamic 1D (see Section V,A,2) calculations for these reactions demonstrated a convergence of basis expansions (Basilevsky *et al.*, 1982b). The semiclassical calculations using Model III of Section VI,C,3 were in reasonable agreement with the quantum calculations, although the respective vibrational distributions were slightly broadened (cf. Figs. 8 and 10).

It should be mentioned that semiclassical distributions P_{0n} reproduced the quantum distributions well in even the near-threshold energy range, when substantial reflection was observed and the semiclassical reasoning seemed inconsistent. A simple explanation is that the interaction zone, where the population inversion was generated, was disposed after the potential barrier on the reaction coordinate. Hence the different space regions responsible for the reflection and for the vibrational transitions did not overlap, and the respective amplitudes failed to interfere (see the discussion in Section V,B,5).

The final step of this investigation was an attempt to extend the NRC treatment to all the reactions presented in Table IV, including those for which the straightforward calculation gave large g values. The respective experimental vibrational distributions P_{0n} were approximated by the binomial law [Eq. (107)], calibrated to correctly reproduce the fractions of the product vibrational energy. That is to say, $\lambda = f_{\mathrm{V}}^{(\mathrm{experimental})}$. The second parameter ϵ of the binomial distribution was estimated as a number of open channels in the product valley. From these two values an empirical estimate of the maximum curvature was possible, and it proved to lie in the bounds of $0.2 < g < 0.4$ (Table IV). The condition $g \ll 1$ thereby holds for all the reactions considered, demonstrating the internal consistency of this semiempirical NRC description.

The interpretation of this result may be presented as follows. A smooth trajectory is supposed to exist on each PES such that from one side it has a curvature small enough to permit NRC treatment, and from the other side, it only slightly deviates from the two reference curves with large curvature actually calculated. One way of drawing such a curve has been reported by Ryaboy and Chudinov (1981).

We conclude with the statement that all exothermic **L** + **HH** reactions seem to be satisfactorily described by a combination of two approximations: the NRC approximation (the neglect of a multivalued region) and the semiclassical treatment of the translational motion.

D. Commentary

Section VI, A,1. In the case of the complete quantum equation $AX'' + BX' + C = 0$, the matrix equation for P reads as $AP^2 + BP + C = 0$. Usually there is no need in such a complication. Matrix B always depends on translational derivatives of physical characteristics that are negligible in a semiclassical treatment. Then one may accept $B = 0$, and the complete equation reduces to Eq. (78) (see the example in Section VI,C,1).

The situation eliminating turning points is trivial and uninteresting in a one-channel case. However, in a many-channel problem it permits pure investigation of semiclassical nonadiabatic transitions.

Section VI,A,2. Proof of Relations (86). We begin with equations $X^{(1)\prime} = iPX^{(1)}$ and $X^{(2)\prime} = \bar{i}PX^{(2)}$. The symmetry $P = \tilde{P}$ is used throughout. Transpose the second equation and calculate the quantity

$$(\tilde{X}^{(2)}X^{(1)})' = \tilde{X}^{(2)\prime}X^{(1)} + \tilde{X}^{(2)}X^{(1)\prime} = -i\tilde{X}^{(2)}PX^{(1)} + i\tilde{X}^{(2)}PX^{(1)} = 0$$

The integration gives Eq. (86a).

For the Hermitian conjugate solution, $(X^{\dagger})' = \sqrt{\mp}iX^{\dagger}P$, so we can obtain

$$(X^{(1)\dagger}X^{(1)})' = (X^{(1)\dagger})'X^{(1)} + X^{(1)\dagger}X^{(1)\prime} = -iX^{(1)\dagger}PX^{(1)} + iX^{(1)\dagger}PX^{(1)} = 0$$

and the similar relation for $X^{(2)}$. The integration of these relations leads to the conclusion that $X^{(1)\dagger}X^{(1)}$ and $X^{(2)\dagger}X^{(2)}$ are constant matrices. Then using Eq. (85) immediately gives Eq. (86b).

Section VI,B,1. The derivation of Eqs. (93) for reactive scattering was thoroughly discussed by Tang and Karplus (1968, 1971).

Section VI,B,4. The papers cited in this section contain a complete bibliography on the application of the DWA theory to chemical reactions (see also the review by Connor, 1979).

Section VI,C,1. The account here follows the papers by Basilevsky and Ryaboy (1979b,c). Note that the usually accepted dimensionless vibrational variable is $w/\sqrt{2}$. Here we take a non-standard-length unit that simplifies the final expressions for the transition probabilities.

Section VI,C,2. Hofacker and Levine (1975) have deduced model II in a different manner. The same model Hamiltonian occurs in the problem of an externally forced oscillator; the respective solution is well known. The form presented here is due to Pechukas and Light (1966). The solution of Model III was described by Basilevsky and Ryaboy (1979b,c). An exponential Magnus approximation is a natural development of semiclassical schemes (Magnus, 1954; Pechukas and Light, 1966; Child, 1974); it is actually utilized in Models I and II.

Section VI,C,3. The proportionality law $f_v \sim A_{\perp}$ follows also from the model of the sudden energy release (Körsch, 1977, 1978).

Section VI,C,4. The interpretation of dips in distributions P_{mn} for $m > 0$ may also be drawn from the Frank–Condon model, Section VI,B,4. The shape of a vibrational distribution, as presented by this model, is closely related to the nodal properties of an initial reactant state m on which the final product states are projected (Baer, 1974a; Halavee and Shapiro, 1976; Child, 1978). That is to say, the reason for a bimodal form of P_{1n} distribution lies in the fact that the square of the absolute value $|\varphi_{m=1}|^2$ of the reactant vibrational wave function has two maxima.

VII. Multichannel Resonances in Reactive Scattering

Resonances in reactive scattering were revealed in early quantum calculations, but were investigated in detail later. The resonances in quantum calculations appear as sharp singularities of the energy dependence of transition probabilities. The position and width of a resonance can be estimated by investigating such a dependence, but other characteristics of a resonance remain undetected.

The complete description of a multichannel resonance is an important problem. Namely, the above-discussed methods for the calculation of triatomic exchange reaction dynamics may be useful in a treatment of the decay dynamics of triatomic molecules. In this case the complete description of a resonance (partial width amplitudes) would provide all the dynamical information.

Only the procedures based on the solution of the scattering problem are considered here. These procedures are best suited to an interpretation of dynamical calculations of chemical reactions. The corresponding theory is a natural development of the 1D scattering theory of Section IV.

We discuss neither the known methods of resonance calculations, which based on discrete basis variational procedures, nor the perturbational methods for the resonance width calculations.

A. Multichannel Resonance Analysis

1. *Laurent Expansion of the Scattering Matrix*

The direct method of the resonance analysis consists of an investigation of the scattering-matrix singularities at complex energy values (Newton, 1966). The energy and width of the resonance represent the real and imaginary parts of the energy value at the pole point, respectively. The partial widths are defined by the matrix residue at the pole point.

In this section we always consider the scattering matrix projected onto open channels denoting it as S rather than S^+ as in Section IV,C,4. Since the S matrix is symmetric, it can be diagonalized by means of a complex orthogonal transformation

$$\tilde{U}SU = \rho, \qquad S = U\rho\tilde{U}, \qquad U\tilde{U} = \tilde{U}U = I \tag{108}$$

where ρ is a diagonal matrix.

We use the Laurent expansions at the pole point $E = E_\lambda = \mathscr{E}_\lambda - i\Gamma_\lambda/2$

$$\begin{aligned} S &= S_{-1}/(E - E_\lambda) + S_0 + S_1(E - E_\lambda) + \cdots \\ \rho &= \rho_{-1}/(E - E_\lambda) + \rho_0 + \rho_1(E - E_\lambda) + \cdots \\ U &= U_0 + U_1(E - E_\lambda) + \cdots, \qquad \tilde{U}_0U = U_0\tilde{U} = I \end{aligned} \tag{109}$$

The matrix U is expanded in a Taylor series due to its orthogonality.

Let the residue of the matrix ρ be

$$\rho_{-1} = r_\lambda \begin{pmatrix} 1 & & & \\ & 0 & & 0 \\ & & \ddots & \\ 0 & & & 0 \end{pmatrix}$$

Then in accordance with Eqs. (108) and (109), the residue of the S matrix equals

$$S_{-1} = r_\lambda |u_\lambda\rangle\rangle\langle\langle u_\lambda|, \qquad \langle\langle u_\lambda|u_\lambda\rangle\rangle = 1 \tag{110}$$

Here $|u_\lambda\rangle\rangle$ is the first column of the matrix U_0.

Generally, resonances can overlap; that is to say, the spacing between the different poles may not considerably exceed their widths. For that case we use the resonance expansion by Siegert–Humblet–Rosenfeld (Humblet and Rosenfeld, 1961):

$$S = S_0(E) + \sum_\lambda [\,|\gamma_\lambda\rangle\rangle\langle\langle\gamma_\lambda|/(E - E_\lambda)] \tag{111}$$

Partial-width vectors may be derived by the comparison of Eqs. (110) and (111):

$$|\gamma_\lambda\rangle\rangle = -r_\lambda^{1/2}|u_\lambda\rangle\rangle \tag{112}$$

The background matrix S_0 in the multipole expansion (111) does not coincide with the constant term in the Laurent expansion (109).

The unitary condition of the S matrix at real energy for a case of isolated Breight–Wigner resonance gives the normalization condition

$$|r_\lambda| = \Gamma_\lambda/\langle\langle u_\lambda^*|u_\lambda\rangle\rangle, \qquad \langle\langle\gamma_\lambda^*|\gamma_\lambda\rangle\rangle = \Gamma_\lambda \tag{113}$$

If the vector $|u_\lambda\rangle\rangle$ may be thought to be real and, besides, $S_0^\dagger|u_\lambda\rangle\rangle = |u_\lambda\rangle\rangle$ (for example, if $S_0 = I$), then it follows from the unitary condition that $r_\lambda = -i\Gamma_\lambda$ and the conventional Breight–Wigner formula may be derived:

$$S \approx S_0 - i\Gamma \frac{|u\rangle\rangle\langle\langle u|}{E - \mathscr{E} + i\Gamma/2}, \qquad \langle\langle u|u\rangle\rangle = 1 \tag{114}$$

In the general case, a normalization factor r_λ may be calculated by a limit transition $E \to E_\lambda$ (Basilevsky and Ryaboy, 1981).

The relations presented are sufficient to calculate all the resonant properties. The matrix U_0 (and the vector $|u_\lambda\rangle\rangle$)) may be derived by the diagonalization of the nonsingular matrix $[S(E_\lambda^*)]^\dagger$ at $E_\lambda^* = \mathscr{E}_\lambda + i\Gamma_\lambda/2$. (The matrices $S(E_\lambda)$ and $[S(E_\lambda^*)]$ may be diagonalized by the same transformation due to the unitary condition (76)). The condition of the resonance existence takes the form

$$\det[S(E_\lambda^*)]^\dagger = 0 \tag{115}$$

Due to relation (66) the Jost matrix W_c may as well be used in a search of a pole and in the calculation of the vector $|u_\lambda\rangle\rangle$:

$$\det W_c = 0, \qquad W_c|u_\lambda\rangle\rangle = 0 \tag{116}$$

2. *One-Dimensional Formulation of the R-Matrix Theory. The Definition of the Resonant States*

Contrary to the Laurent expansion method, the R-matrix theory[2] (Wigner and Eisenbud, 1947; Lane and Thomas, 1958) does not require dealing with complex energy values when considering resonant states, which is an important benefit. However, the R-matrix theory cannot provide a simple resonant expansion if resonances overlap.

The whole configuration space, where a reaction occurs, may be divided into outer and inner regions, the value $r = \bar{r}$ of the translational coordinate being the boundary between them. Since the boundary is located in the asymptotic region, it is possible to pass over to mixed representation (54) by considering a pair of the reaction coordinate values $s^{(1)} = -a$, $s^{(2)} = a$ instead of $\bar{r}$.

The solutions of Schrödinger equation in the inner region represent the columns of the $2N \times 2N$ matrix X:

$$X = \begin{array}{r} N\left\{\vphantom{\begin{array}{c}a\\a\end{array}}\right. \\ N\left\{\vphantom{\begin{array}{c}a\\a\end{array}}\right. \end{array} \overset{2N}{\left(\begin{array}{c} \vphantom{\begin{array}{c}a\\a\end{array}} \\ \hline \vphantom{\begin{array}{c}a\\a\end{array}} \end{array}\right)} \begin{array}{l} \left.\vphantom{\begin{array}{c}a\\a\end{array}}\right\}\begin{array}{l}\text{reactant}\\ \text{channels}\end{array} \\ \left.\vphantom{\begin{array}{c}a\\a\end{array}}\right\}\begin{array}{l}\text{product}\\ \text{channels}\end{array} \end{array}$$

We consider them as basis functions and represent the resonant state in the form

$$|\chi_\lambda\rangle\rangle = X|b_\lambda\rangle\rangle$$

The vectors $|b_\lambda\rangle\rangle$ (that is, the expansion coeffieients of the resonant states over the columns of the matrix X) may be calculated as eigenvectors of the matrix $A(E)$, the explicit form of which is not presented here (see Basilevsky, 1976):

$$A(E)|b_\lambda\rangle\rangle = 0, \qquad \det A(E) = 0 \tag{117}$$

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[2] Do not mix this term with the propagator R from Section IV!

The second formula (a consistency condition) is similar to the first formula [Eq. (116)] and represents an equation for the resonant energies $E = E_\lambda$.

An expression for the matrix $A(E)$ is defined by specifying boundary conditions for the resonant states at the point $r = \bar{r}$, $s^{(1)} = -a$, $s^{(2)} = a$:

$$|\chi'_\lambda(\bar{r})\rangle\rangle = \beta|\chi_\lambda(\bar{r})\rangle\rangle, \qquad \beta = \left(\begin{array}{c|c} \beta_l(-a) & 0 \\ \hline 0 & \beta_l(a) \end{array}\right) \tag{118}$$

Here β is an arbitrary real diagonal matrix. (Its reality is provided by the reality of the energy E_λ.) In accordance with Eq. (118), the value of the logarithmic derivative at the boundary point in each channel i is equal to β_i, that is to the diagonal element of the matrix β. This value is the same for all resonant states.

A different choice of the β_i values in Eq. (118) corresponds to different ways of defining the resonant state. In particular, it is possible to show that expressions (116) and (117) become equivalent if we accept $\beta = M(E_\lambda)$ and $M = \mathcal{O}'(\bar{r})/\mathcal{O}(\bar{r})$. The scattered waves $\mathcal{O}(r)$ are defined by Eqs. (58a). The logarithmic derivatives M_i are complex values (imaginary values when an energy is real).

3. *Resonance Expansion in the R-Matrix Theory*

Operating in a conventional way (Lane and Thomas, 1958) it is possible to express the Green's function, connecting an arbitrary solution in the inner region with its value at the boundary, in terms of resonant states $|\chi_\lambda\rangle\rangle$ and to derive the following expression for the R matrix:

$$R = -\frac{\hbar^2}{2\mu F}\sum_\lambda \frac{|\gamma_\lambda\rangle\rangle\langle\langle\gamma_\lambda|}{E - E_\lambda}, \qquad |\gamma_\lambda\rangle\rangle = |\chi_\lambda(\bar{r})\rangle\rangle$$

where μ and F are mass and normalization factors, respectively (see Basilevsky, 1976).

A solution in the outer region may be expressed as a linear combination of the incoming and outgoing waves J and $\mathcal{O}$, defined by Eqs. (58) and (58a). Let us introduce diagonal $2N \times 2N$ matrices L and M of the boundary values of their logarithmic derivatives: $J'(\bar{r}) = LJ(\bar{r})$ and $\mathcal{O}'(\bar{r}) = M\mathcal{O}(\bar{r})$. The continuity conditions of the solutions and their logarithmic derivatives at the boundary result in the following expression for the scattering matrix:

$$S = \mathcal{O}^{-1}[I - RP(M - \beta)]^{-1}[I - RP(L - \beta)]J$$

$$P = \left(\begin{array}{c|c} -I & 0 \\ \hline 0 & I \end{array}\right)$$

The way to extract the information on the resonant properties (the width and the partial widths) from this formula is considered in detail by Lane and Thomas (1958); for a general case it is a difficult problem.

For the case of isolated resonances only one level λ gives the main contribution to the R matrix in a particular energy range. Then

$$S_{\alpha\alpha'} \approx \delta_{\alpha\alpha'} - \frac{i\Gamma^{1/2}_{\lambda\alpha}\Gamma^{1/2}_{\lambda\alpha'}}{E - E_\lambda - \Delta_\lambda + i\Gamma_\lambda/2}$$

We shall not write out general expressions for the partial widths $\Gamma_{\lambda\alpha}$, the level width $\Gamma_\lambda = \Sigma_\alpha \Gamma_{\lambda\alpha}$, and the shift Δ_λ (see, for example, Lane and Thomas, 1958). Note only that these values are defined in terms of the boundary values of resonant states and their logarithmic derivatives. For a narrow resonance the level shift is small and the observed resonant energy is close to the E_λ value.

B. Some Results of Quantum Calculations of Resonant States in Reactive Scattering

1. *One-Dimensional Calculations*

The great majority of papers on the subject of resonant states in reactive scattering are devoted to H + H_2 and F + H_2 reactions. Complete reference lists may be found in several reviews (Truhlar and Wyatt, 1976; Connor, 1979; Wyatt, 1979, 1980). The resonance behavior of the energy dependence of transition probabilities has been revealed also in the reactions Cl + H_2 (Baer, 1974b; Persky and Baer, 1974), O + H_2 (Clary *et al.*, 1979), I + H_2 (Chapman and Hayes, 1977; Gray *et al.*, 1978), He + H_2^+ (Kouri and Baer, 1974; Adams, 1975; Chapman and Hayes, 1975, 1976), Li + FH (Walker *et al.*, 1981), I + HI (Kaye and Kuppermann, 1981), and some isotopic variants of these reactions.

Most of the calculations have used the linear reaction model. The phase variation of S-matrix elements in the vicinity of resonance, the Argand diagrams of S-matrix elements (Schatz and Kuppermann, 1973), the probability density, and the flux distribution in the interaction region (Wyatt, 1980) were studied to detect the origin of resonances. As a rule, the resonances in reactive scattering occur as quasi-bound states in the closed channels (Feshbach resonances). A shape resonance was observed in the I + HI reaction (Kaye and Kuppermann, 1981; Babamov and Marcus, 1981). Both shape and Feshbach resonances occur also in the inelastic scattering process in He + H_2^+ system below the reaction threshold (Chapman and Hayes, 1976).

Potential wells generating quasi-bound states in the adiabatic channel potentials usually have their origin in the decreasing transversal vibrational frequency in the interaction region. As this takes place, the number of quasi-bound states in the energy range between the thresholds of the neighboring channels is usually small. There is only one quasi-bound state between the thresholds of $n = 0$ and $n = 1$ channels for the thermoneutral and nearly thermoneutral reactions ($H + H_2$, $O + H_2$, $H + FH$, $Cl + H_2$), and the energy dependences of transition probabilities for these reactions are very similar.

The systems considered up to now displayed no wells in the PES cross sections along the reaction coordinate. That is not the case for endothermic reactions $I + H_2$, $He + H_2^+$, and $Li + FH$. There are two potential wells in the PES section of the $I + H_2$ system arranged in the product and reactant valleys close to the rearrangement region, as there is only one well on the PES of $He + H_2^+$ system arranged in the reactant valley. The potential along the reaction path of $Li + FH$ system displays two barriers of different heights, separated by a potential well. Due to the existence of potential wells in PES sections, the number of quasi-bound states per a definite energy range may be large. Quasi-bound states attributed to different channel adiabatic potentials may also overlap. As calculations show, in this case the oscillations of transition probabilities are observed instead of isolated resonant peaks. Calculations of resonant parameters characterizing the decay of long-living complexes formed in such systems are of particular interest from the point of view of future studies of decay processes in highly vibrationally excited molecules (for example, as a result of multiphoton IR absorption).

Resonant properties are very sensitive to a variation of the type of PES representation, even though the PESs used are almost the same numerically (Connor *et al.*, 1978a, 1980). Even a local variation of the PES properties is decisive (Chapman and Hayes, 1976). For this reason, the prediction of the resonant properties requires very accurate PES calculations.

2. *Resonant Phenomena as a Result of the Interference of Resonant and Background Amplitudes*

The Feshbach resonance in the $H + H_2$ reaction (Diestler, 1971; Wu and Levine, 1971; Levine and Wu, 1971; Wu *et al.*, 1973; Schatz and Kuppermann, 1973, 1975) is conditioned by the potential well in the adiabatic channel potential $n = 1$ (see Fig. 11a). A way of its manifestation in reactive scattering may be understood in terms of the simple Breit–Wigner formula (114):

$$S_{\alpha\beta} = S_{0_{\alpha\beta}} - \frac{i\Gamma u_\alpha u_\beta}{E - \mathscr{E} + i\Gamma/2}$$

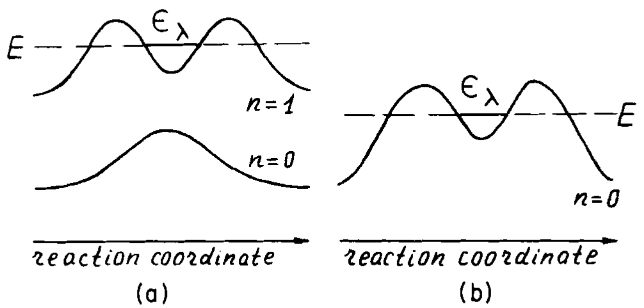

Fig. 11. Adiabatic channel potentials: quasi-bound states in (a) the $n = 1$ channel and (b) the $n = 0$ channel.

We are interested in the scattering on the $n = 0$ level in the NRC approximation. Then, $\alpha = 1, 2$, where the indices 1 and 2 label the reactant and product channels, respectively. It seems reasonable that for the resonant energy $E = \mathscr{E}$, the background scattering on the bottom level corresponds to the complete transmission:

$$S_0 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Suppose that resonant state decays only onto the bottom level due to nonadiabatic coupling. Then, as a result of symmetry ($u_\alpha = u_\beta$), the normalization condition gives $u = 2^{-1/2}$. For the resonant condition $E = \mathscr{E}$, we derive the S matrix for the bottom level:

$$S = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} = - \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

which corresponds to the complete reflection. A sharp peak of the resonant reflection was observed in quantum calculations; however, the corresponding probability falls short of unity. The presence of the rest transmission may be easily comprehended by recalling that there is a probability of the resonant decay into the $n = 1$ level, so that $u < 2^{-1/2}$.

Let us consider a model example with a potential well in the $n = 0$ adiabatic potential (Fig. 11b).

In this case

$$S_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

(the complete reflection in the background term). By the Breit–Wigner formula, we derive a well-known result (the Ramsauer effect):

$$S = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

The resonance corresponds to the complete transmission through the barrier.

3. *Three-Dimensional Calculations*

Three-dimensional calculations of resonances have been only reported for H + H_2 and F + H_2 reactions. The main subject under discussion is whether the resonant behavior of transition probabilities remains unchanged when averaging over the rotational quantum number J.

Calculations have shown (Schatz and Kuppermann, 1975) that the first resonance in the total reaction probability of the H + H_2 reaction does not disappear when averaging over J and its width is nearly the same as that obtained in 1D calculations. However, the resonance in the partial transition probability P^T_{00} disappears, since the corresponding resonance amplitude vanishes beginning at $J = 7$, whereas the nonresonance amplitude remains considerable up to $J \approx 17$.

Three-dimensional calculations of the F + H_2 reaction have shown (Redmon and Wyatt, 1975, 1977, 1979; Wyatt, 1980), that the resonant peak in the P^T_{02} transition probability previously obtained in the 1D calculations was retained only when $J = 0$. However, this peak may be smoothed out by averaging over J. The origin of that is the sudden shift in the P_{02} peak probability to higher J values as the translational energy increases by only 3 kcal/mol in the resonant range (Redmon and Wyatt, 1979; Redmon, 1979; Wyatt, 1980). This effect results in a variation of the angular distribution of the scattered product and was confirmed in the molecular beam experiment by Sparks *et al.*, 1980.

4. *Direct Search of Resonances in the* H + H_2 *Reactive System*

A direct method for searching for the poles of the S matrix, based on the construction of its Laurent expansion in the complex plane (see Section VI,A,1) was used to study the H + H_2 reaction on the model PES in NRC (Basilevsky and Ryaboy, 1981). The method developed for real energy values (Basilevsky and Ryaboy, 1979a) turned out to be acceptable for solving the dynamical problem in complex energy plane. The only complication arising when solving Eq. (28) is the necessity of diagonalizing the complex non-Hermitian matrix $A^{-1/2}CA^{-1/2}$ (Wilkinson and Reinsch, 1973). We search for the poles of the scattering matrix $S(\mathcal{E}$

$- i\Gamma/2$), considering it as a function of two arguments $\mathscr{E}$ and $\Gamma/2$. Either of the two conditions of the pole existence, det $W_{\mathscr{E}}(E) = 0$ or det $S^{+}(E^{*}) = 0$, is available. Any standard procedure (Himmelblau, 1972) may be used to minimize absolute values of the determinants. We have used Jost matrices projected onto open channels (see Section IV,C,3) to avoid the computational difficulties that originate from large values of the matrix elements of the propagator in closed channels.

The calculated energy dependence of the transition probabilities is shown in Fig. 12. The positions of the S matrix poles (the resonant energies) and partial widths, found by the direct search, are listed in the Table V. The positions of the resonances E_1 and E_3 may be compared with the two singularities in the transition probabilities (Fig. 12). The two extra poles (E_2 and E_4) are not distinctly manifested in the energy dependence curves of transition probabilities. The reason for that is easily comprehended. The maximum values (at the points E_2 and E_4) of the absolute values of the resonant terms in Eq. (111), coming from the resonances E_2 and E_4, are considerably smaller than those corresponding to the resonances E_1 and E_3. This fact is mainly associated with the large widths of

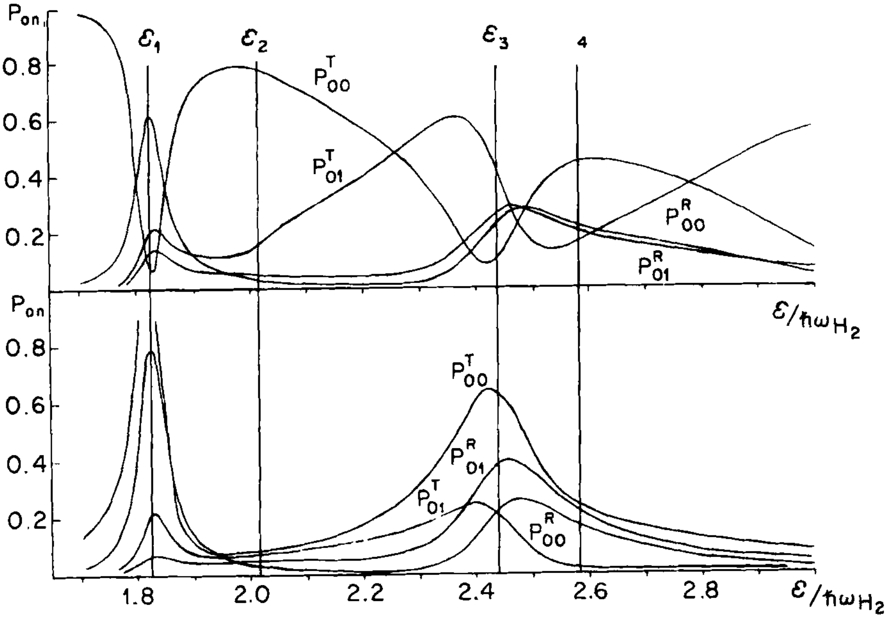

Fig. 12. Energy dependence of transition probabilities with reaction (P^T_{0n}) and reflection (P^R_{0n}) (the upper panel) and squares of the absolute values of the corresponding matrix elements for the resonant contribution to the S-matrix expansion [Eq. (111)] (the lower panel; notation is the same as in the upper panel).

TABLE V

RESONANCE ENERGIES E_λ AND PARTIAL WIDTHS $|\gamma_{\lambda n}|^2$ (IN $\hbar\omega_{H_2}$ UNITS)

Energy $E_\lambda = \mathscr{E}_\lambda - i\Gamma_\lambda/2$	n	$\lvert\gamma_{\lambda n}\rvert^2$
$E_1 = 1.8225 - 10.0277$	0	0.0252
	1	0.0047
$E_2 = 2.0140 - 10.1883$	0	0.0049
	1	0.0606
$E_3 = 2.4380 - 10.0934$	0	0.0460
	1	0.0439
$E_4 = 2.5812 - 10.3607$	0	0.1106
	1	0.0480

the resonances E_2 and E_4. The data listed in Table V show that the normalization condition (113) is approximately valid for the resonances with small widths.

Since the spacing between resonances is comparable in magnitude to their widths, the interference of resonant terms in Eq. (111) takes place. It is essential in this respect that the elements of the partial-width amplitude vectors γ_2 and γ_4, representing the decay of the broad resonances E_2 and E_4 to the reactant and the product valleys, differ by π in their phases, while the corresponding elements of the vectors γ_1 and γ_3 coincide. As a result of interference, squaring the absolute values of the resonance contributions to S-matrix elements results in different values for the reactive and nonreactive scattering in spite of the symmetry of the $H + H_2$ system (Fig. 12). Besides that, for different S-matrix elements the maxima of squares of their absolute values occur at different energies. That is especially noticeable in the region close to the energy $\mathscr{E}_3$. These displacements may be compared with extrema displacements of the reactive P^T and nonreactive P^R transition probabilities relative to the resonance position $\mathscr{E}_3$, observable in the upper panel of Fig. 12.

C. Commentary

Section VII,A,1. There is no direct way to calculate the background term in expansion (111). It may be defined only by the subtraction of the resonant term from the complete S matrix (if the S matrix is known). The treatment in this section implies that the resonant states are the main subject of the investigation.

Section VII,A,2. A comparative description of the different theories of resonant nuclear reactions and an analysis of their advantages and disadvantages was presented by Lane and Robson (1966, 1969). We mention only the theory by Kapur and Peierls (1938), in which the boundary conditions differ from Eq. (118). They accept $\beta = M(E)$, that is, the boundary condition becomes energy dependent and complex. In this case an expression for the S matrix takes the simple form:

$$S = S_0 - \frac{i}{2\pi F}\sum_{\lambda}\frac{\mathcal{O}^{-1}|\gamma_\lambda)(\gamma_\lambda|\mathcal{O}^{-1}}{E - E_\lambda}$$

Note that this boundary condition differs from the complex condition $\beta = M(E_\lambda)$ corresponding to the Laurent expansion of the scattering matrix.

Section VII,B,1. The origin of the resonances in reactive scattering was first investigated for the case of $H + H_2$ (Levine and Wu, 1971, Schatz and Kuppermann, 1973). A variation of the phases of the S-matrix elements and their Argand diagrams at resonant energies were examined. A perturbation method was used to confirm the Feshbach origin of the resonances in the $I + H_2$ reaction (Chapman and Hayes, 1975, 1977). The Feshbach projection operator was used to calculate the parameters of resonances in $He + H_2^+$ and $I + H_2$ reactions (Liedtke *et al.*, 1977). The model problem with a rectangular well in channel potentials was studied by Wyatt (1980). The resonances were also studied in terms of the semiclassical S-matrix theory. In particular, the first resonance in the $H + H_2$ reaction was investigated (Marcus, 1973; Stine and Marcus, 1974).

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Vibronic Interactions and the Jahn-Teller Effect

I. B. BERSUKER and V. Z. POLINGER
Institute of Chemistry, Academy of Sciences, MoSSR
Kishinev, USSR

I. Introduction

As is well known, the main laws governing the structure and properties of isolated polyatomic systems (molecules and crystals) are determined by the Schrödinger equation. In most cases of not very small molecules, exact analytical solutions of this equation are impossible, while numerical solutions are practically inaccessible. Therefore approximate models, methods, and solutions are of special importance in quantum chemistry.

The first and most essential approximation introduced in solutions to molecular problems is the adiabatic approximation (Born and Oppenheimer, 1927; Born and Huang, 1954). It is based on the difference in the masses (and hence velocities) of the electrons and nuclei; due to this difference for every position of the nuclei at any instant, a stationary distribution of the electrons is attained, and this can be described by means of a wave function (instead of by a density matrix). Note that without the adiabatic approximation the notion of spatial structure (nuclear configuration) of a polyatomic system loses its physical sense.

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Almost immediately after the introduction of the adiabatic approximation the most striking deviations from this approximation were also understood. In 1934, L. D. Landau in a discussion with E. Teller (Teller, 1972) pointed out that if the electronic state of a certain symmetric nuclear configuration is degenerate, then this configuration is unstable with respect to nuclear displacements which remove the degeneracy. This statement was afterward verified by Teller and Jahn and formulated as the so-called Jahn–Teller (JT) theorem (Jahn and Teller, 1937; Jahn, 1938). Actually, not only degenerate but also near-lying (quasi-degenerate or pseudodegenerate) energy terms cannot be treated by the adiabatic approximation, the general criterion of validity of the latter being $(\Delta E_n/\Delta E_{el}) \ll 1$, where ΔE_n and ΔE_{el} are the energy-level intervals in the slow (nuclear) and fast (electronic) subsystems, respectively (Born and Huang, 1954).

In a more useful formulation, the most important deviations from the adiabatic approximation are due to the mixing of different electronic states by nuclear displacements (by vibronic interaction terms in the Hamiltonian), and this vibronic mixing is the stronger the closer in energy are the mixed states and the greater is the appropriate vibronic constant. In this formulation there are no *a priori* limitations of molecular systems to be treated by the vibronic theory. In fact, the vibronic approach may be regarded as a new concept which enlarges essentially the structure-property bridge in physics and chemistry. The above-mentioned Jahn–Teller instability is a particular case when the vibronically mixed electronic states have the same energy. Although the concept of vibronic interaction is much more general (and more adequate to the phenomena and effects under consideration), a great many works on this subject are published under the title of the Jahn–Teller effects.

Although the JT theorem was formulated more than four decades ago, the rapid development of this area began only two decades ago. Until that time there was a very poor understanding of what kind of observable effects could be expected as a result of the JT instability. The reason is that the JT instability was taken quite literally to be the origin of spontaneous distortion of the nuclear configuration. In fact, the real meaning of the JT theorem is concerned with the behavior of different adiabatic potential (AP) surfaces near the point of their intersection, where these surfaces have no physical sense (due to the breakdown of the adiabatic approximation). Therefore the JT theorem itself does not contain information about observable magnitudes (Bersuker, 1966a). The complicated behavior of the AP near the point of degeneracy, predicted by the JT theorem, results in a system of coupled (vibronic) equations for the nuclear dynamics; their solution reveals a number of new effects and regularities which cannot in general be reduced to nuclear configuration instability and degeneracy removal—the vibronic effects are much more rich.

At the present time the vibronic approach forms a well-defined area of research activity in physics and chemistry of molecules and crystals with applications to the full range of spectroscopy (including ESR, visible, UV, IR, Raman, and radiospectroscopy, as well as NMR, NGR, and ultrasonics); crystal physics and chemistry, including crystal isomer formation, structural phase transitions and ferroelectricity; and chemical reaction mechanisms, chemical activation, and catalysis—the overall number of publications on this subject is about 3000 (Bersuker, 1982a,b). Some of these works, mainly the early ones, are considered in several reviews (Sturge, 1967; Ham, 1972; Gehring and Gehring, 1975; Bersuker *et al.*, 1975; Bersuker, 1975; Bates, 1978; Bersuker and Vekhter, 1978), and in the book of Englman (1972).

The aim of this article is to give a review of the latest achievements of the theory of vibronic interactions and JT effects (some of the earlier works are only mentioned briefly). In Section II of this article the theoretical background and AP calculations, as well as symmetry properties of JT systems are discussed. Section III is devoted to solutions of the vibronic equations obtained mostly in more recent years. Section IV is concerned with one of the newest developments of the theory of vibronic interactions, the multimode JT effect. In spite of the review nature of this article, many questions are treated here for the first time. These include the rigorous deduction of the vibronic Hamiltonian and the separation of force constants from the vibronic ones, and the reduction of the multimode AP problem to the appropriate ideal one, etc. Note, however, that not all important vibronic problems are considered here. In particular, the very exciting results on the so-called cooperative JT effects are excluded from this review. Also omitted are the above-mentioned applications of the theory. The interested reader can find them in some of the above-cited review papers, in the book of Bersuker and Polinger (1982), and in the bibliography review (Bersuker, 1982a,b).

II. The Vibronic Hamiltonian. The Jahn–Teller Theorem

As mentioned before, because of the essential difference in the masses (and velocities) of the nuclei and electrons, the latter follow the former adiabatically, and for every position of the nuclei at any instant a stationary distribution of electrons is adjusted. Therefore when considering the electronic states, the nuclei in the first approximation may be taken as fixed, and in the next approximations their motions can be taken into account by the perturbation theory (Born and Oppenheimer, 1927; Born and Huang, 1954).

As long as the space is considered isotropic and uniform, the translational and rotational degrees of freedom of an isolated polyatomic system are described by cyclic coordinates and can be separated from the other ones. Note that the rigorous separation of the rotational coordinates is not trivial (Kiselev, 1978). Considering this problem solved, the Hamiltonian of the remaining degrees of freedom may be taken in the form:

$$H(r, Q) = H(r) + V(r, Q) + T(Q) \tag{1}$$

Here $H(r)$ is the operator of the kinetic energy of the electrons and of their mutual Coloumb interaction, $V(r, Q)$ is the operator of the electron–nucleus plus nucleus–nucleus interactions, r and Q being the configurational coordinates of the electrons and nuclei, respectively, and $T(Q)$ is the operator of the kinetic energy of the nuclei (the relativistic interactions are neglected).

As mentioned above, when considering the electronic motions, the nuclear kinetic energy $T(Q)$ may be taken as a small perturbation. The perturbation approach is qualitatively different for nondegenerate and degenerate electronic states. In the former case it results in the traditional adiabatic approximation. In the case of degeneracy (or pseudodegeneracy), the nonzero nuclear displacements lead to the so-called vibronic Hamiltonian which takes into account the nonadiabatic mixing of different electronic states.

A. Nonadiabacity and the Vibronic Hamiltonian

In the zeroth-order perturbation theory with respect to $T(Q)$, the Schrödinger equation is

$$[H(r) + V(r, Q)]\varphi_n(r, Q) = \epsilon_n(Q)\varphi_n(r, Q) \tag{2}$$

where n is the electronic quantum number. Its eigenvalues $\epsilon_n(Q)$ and wave functions $\varphi_n(r, Q)$ depend on the nuclear coordinates as on parameters, the set of $\varphi_n(r, Q)$ functions being complete and orthonormal for every Q value. We look for the eigenfunctions of the total Hamiltonian in the form of the following expansion:

$$\Psi(r, Q) = \sum_n \chi_n(Q)\varphi_n(r, Q) \tag{3}$$

where the coefficients $\chi_n(Q)$ are also functions of Q. For them, taking into account that $T(Q) = -\hbar^2/2)\Sigma_i M_i^{-1} \partial^2/\partial Q_i^2$ (where i labels the nuclear degrees of freedom and M the appropriate reduced masses), after some simple transformations we obtain

$$\sum_n [T_{mn} + U_{mn}(Q)]\chi_n(Q) = E\chi_m(Q) \tag{4}$$

where $U_{mn}(Q) = \epsilon_n(Q)\,\delta_{mn}$, $T_{mn} = T(Q)\,\delta_{mn} + \Lambda_{mn}$,

$$\Lambda_{mn} = -\hbar^2 \sum_i M_i^{-1}[A_{mn}^{(i)}(Q)(\partial/\partial Q_i) + \tfrac{1}{2}B_{mn}^{(i)}(Q)] \tag{5}$$

$$A_{mn}^{(i)} = \int \varphi_m^*(\partial\varphi_n/\partial Q_i)\,dr, \qquad B_{mn}^{(i)} = \int \varphi_m^*(\partial^2\varphi_n/\partial Q_i^2)\,dr \tag{6}$$

The infinite system of coupled equations (4) can be presented in matrix form $\mathbf{H}\chi = E\chi$, provided that the matrix Hamiltonian with the elements $H_{mn} = T_{mn} + U_{mn}$ and the column form of the eigenfunction $\chi(Q)$ are used.

The nondiagonal matrix elements Λ_{mn}, $m \neq n$, which couple Eq. (4), are differential operators called the nonadiabacity operators. Note that T_{mn} is the matrix presentation of the operator $T(Q)$ with the basis electronic functions $\varphi_n(r, Q)$, and all the T_{mn} terms including Λ_{mn} are of the order of M_i^{-1}, i.e., for infinite heavy nuclei ($M_i \to \infty$), all the T_{mn} values vanish. Therefore, if the energy intervals $|\epsilon_n(Q) - \epsilon_m(Q)|$ for the zeroth-order problem are much larger than the nonadiabacity contribution, the previously mentioned perturbation theory with respect to the small M_i^{-1} values can be used.

Let us consider first a nondegenerate state $\varphi_n(r, Q)$ (which is supposed to remain nondegenerate for any Q values). In the first approximation, taking into account only the diagonal elements of the matrix Hamiltonian $\|H_{mn}\| = \|T_{mn} + U_{mn}\|$, we obtain the following Hamiltonian for the $\chi_n(Q)$ functions:

$$H_n = T(Q) + \Lambda_{nn} + \epsilon_n(Q) \tag{7}$$

which is equivalent to the neglect of all the terms in Eq. (3), except the nth: $\Psi(r, Q) = \chi_n(Q)\varphi_n(r, Q)$. This result is not trivial. Due to electron–nuclear interactions the behavior of the nuclei should be described by means of the density matrix satisfying the quantum Liouville equation, and only the neglect of the nonadiabacity mixings Λ_{mn}, $m \neq n$ allows to pass from mixed states to pure ones of the nuclear subsystem. The multiplicative form of the total wave function means that the change of the nuclear configuration leads to appropriate deformations of the electron distribution not causing electron transitions between different electronic states. In other words, the electrons follow adiabatically the nuclear displacements, whereas the nuclear distribution is determined by the wave function $\chi_n(Q)$ satisfying the Schrödinger equations with the Hamiltonian

Eq. (7), which includes in its potential energy $\epsilon_n(Q)$ the average field produced by the electrons; this is the adiabatic approximation.

In the harmonic approximation the solution of the equation for $\chi_n(Q)$ is simple. Suppose that the potential energy $\epsilon_n(Q) + \Lambda_{nn}(Q)$ has an absolute minimum at the point $Q = Q_0$ and consider that there are small vibrations near this point. Expanding the potential energy with respect to the small nuclear displacements from the point Q_0 and neglecting the cubic and higher order terms in Q, we have

$$\epsilon_n + \Lambda_{nn} = E_n^{(0)} + \frac{1}{2} \sum_{ij} K_{ij}(Q_i - Q_{0i})(Q_j - Q_{0j}) \tag{8}$$

where $E_n^{(0)} = \epsilon_n(Q_0) + \Lambda_{nn}(Q_0)$, $K_{ij} = \partial^2(\epsilon_n + \Lambda_{nn})/\partial Q_i \, \partial Q_j$.

Equation (4) with the potential equations (7) and (8) can be easily solved in normal coordinates, resulting in oscillator solutions. The adiabatic approximation is valid when the nonadiabacity perturbation first-order correction to the wave function $\Psi(r, Q) = \chi_n(Q)\varphi_n(r, Q)$ is small enough. Using the $\chi_n(Q)$ oscillator wave functions and approximate values of Λ_{mn}, $m \neq n$, in which the $A_{mn}^{(i)}(Q)$ and $B_{mn}^{(i)}(Q)$ functions are substituted by their values at the point Q_0, one can easily deduce the following criterion of validity of the adiabatic approximation

$$\hbar\omega \ll |E_n^{(0)} - E_m^{(0)}| \tag{9}$$

where ω is the largest frequency of vibrations near the minimum point Q_0. This criterion is hence applicable to stable configurations having a descrete vibrational spectrum. In the case of a continuous spectrum (unstable configuration), the criterion of adiabatic approximation has another form; it can be reduced to the requirement that the so-called Massey parameter $|E - \epsilon_n(Q)|/|\epsilon_m(Q) - \epsilon_n(Q)|$ is small (Nikitin, 1970).

If the adiabatic approximation criterion [Eq. (9)] is fulfilled, then using the uncertainty relations and the virial theorem, one can obtain the following useful estimation

$$\overline{V} \sim v(m/M)^{3/4}, \qquad \overline{Q} \sim d(m/M)^{1/4}, \qquad \hbar\omega/\Delta E_{\mathrm{el}} \sim (m/M)^{1/2} \tag{10}$$

where $\overline{V}$ and $\overline{Q}$ are the mean square values of the nuclear velocity and coordinate, respectively, v is the mean electron velocity, d is the linear dimension of the electron distribution, and $\Delta E_{\mathrm{el}} = |E_n^{(0)} - E_m^{(0)}|$. If the latter is zero or small enough and the criterion equation (9) does not hold, the adiabatic approximation [and hence the estimations of Eq. (10)] is invalid. In particular, in symmetric molecular systems containing rotation axes C_n with $n \geq 3$, there are two (or several) different electron distributions with the same energy (electronic degeneracy), for which $\Delta E_{\mathrm{el}} = 0$. This and other important cases of invalidity of the adiabatic approximation resulting in new effects and regularities are considered below in the next sections.

From the estimation of Eq. (10) it follows that $\overline{Q}/d \sim (m/M)^{1/4}$ and hence the harmonic approximation employing Eq. (8) is valid up to the order of $(m/M)^{1/4}$. It means that as far as the harmonic approximation is also used, the small parameter of the theory is in fact $\kappa = (m/M)^{1/4}$, but not $(m/M)^{1/2}$ [or even $(m/M)^{3/4}$]. A substitution $\kappa q = Q - Q_0$ leads to new coordinates $q = \{q_i\}$ which do not contain small parameters. It allows us the explicit introduction of the small parameter κ in the Hamiltonian and to use it as the expansion parameter of the perturbation theory (Born and Oppenheimer, 1927). The zeroth-order Hamiltonian can be obtained from the exact one Eq. (1) by excluding the kinetic energy operator $T(Q)$ and assuming $Q = Q_0$ (since for $Q = Q_0$, $\kappa q = Q - Q_0 = 0$). Hence the starting basis functions in this case are $\psi_n(r) = \varphi_n(r, Q_0)$, which are eigenfunctions of the Hamiltonian

$$H(r, Q_0) = H(r) + V(r, Q_0) \tag{11}$$

and instead of the expansion equation (3), we have

$$\Psi(r, Q) = \sum_n \chi_n(Q)\psi_n(r) \tag{12}$$

The physical meaning of this approach can be understood if one takes into account the fact that in the ground vibrational state the nuclear distribution has the form $|\chi(q)|^2 = (\kappa\pi)^{1/2} \exp[-(Q - Q_0)^2/\kappa^2]$, which at small κ values ($\kappa \rightarrow 0$) is a δ function. This allows the adiabatic total wave function to be presented approximately[1] as $\Psi(r, Q) = \chi(Q)\varphi_n(r, Q) \approx \chi(Q)\varphi_n(r, Q_0) = \chi(Q)\psi_n(r)$. In other words, in the limit of very heavy nuclei, the latter are localized at the minimum point Q_0, and there is a reason to consider only electronic states corresponding to this fixed nuclear configuration. This approach, as distinguished from the above adiabatic approximation is often called the "crude," or the simple (or the Born–Oppenheimer) approximation.[2] Although not less rigorous from the theoretical point of view, the simple adiabatic approximation may be essentially less accurate in calculations with a limited basis of functions.

The Q_0 point nuclear configuration can in principle be obtained from empirical data. In a more consistent theory it has to be determined as a

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[1] Note that $f(Q)\,\delta(Q - Q_0) = f(Q_0)\,\delta(Q - Q_0)$ if the function $f(Q)$ is not singular at the point Q_0.

[2] There is a discrepancy in the names of different variants of the adiabatic approximation used by different authors (Azumi and Matsuzaki, 1977).

quantum mechanical averaged value $Q_i^{(0)} = \langle 0|Q_i|0\rangle$, which implies that not only the electronic ground state, but that the nuclear and the total $|0\rangle$ states are calculated as well. This is a very difficult problem. Some information about the Q_0 point can be obtained by symmetry considerations. Indeed, the exact Hamiltonian of a polyatomic system is invariant with respect to permutations of identical nuclei and inversion of the coordinate system. All these symmetry elements form a group often called the Longuet-Higgins group (Longuet-Higgins, 1963). It contains some operations R which, being applied to the Q_0 configuration, may be reduced to rotations or inversion of its nuclear framework. The remaining "nonrotational" operations permute the system between equivalent configurations, which in most cases are divided by very high barriers, except the so-called nonrigid molecules. For rigid molecules only the R elements should be taken into account. Then the Q_0 configuration must be chosen such that it has a maximum number of R elements. The appropriate group is denoted by G_0.

For instance, for the triatomic molecule X_3 the G group is isomorphic with the symmetry group of a equilateral triangle D_{3h}, and therefore the Q_0 configuration has to be taken in the form of an equilateral triangle. For a ML_4 system the Longuet-Higgins group is $\pi(4) \times C_i$, where $\pi(4)$ is the group of permutations (exchanges) of four identical ligands and C_i is a group containing two elements, the identity and inversion. Since the point of the M nucleus is privileged and takes no part in the symmetry transformations, and the $\pi(4)$ group is isomorphic with the group of a tetrahedron T_d, it is clear that the Q_0 configuration in this case should be a tetrahedron with the M atom in the center and L in the apexes. (The existence of square-planar complexes, thus, may be due to either JT, or pseudo JT instability of the tetrahedral structure (see Pearson, 1976; Bersuker, 1982b). The permutation groups $\pi(6)$ and $\pi(8)$ which correspond to ligand exchanges in the ML_6 and ML_8 systems, have no isomorphic analogies among the point groups, while the O_h group is the richest in rotational symmetry elements and therefore has to be chosen as the symmetry group G_0 of the Q_0 configuration. The latter is thus an octahedron for ML_6 and a cube for ML_8.

In this procedure of determining the Q_0 point, the totally symmetric coordinates remain uncertain. As shown below, they can be separated from the others and excluded from the vibronic problem.

If the displacements $Q_i - Q_i^{(0)}$ from the point Q_0 are small enough [see the estimations of Eq. (10)], the operator $V(r, Q)$ in the total Hamiltonian equation (1) can be taken in the form of the expansion in which only several first terms are retained:

$$V(r, Q) = V(r, Q_0) + \sum_i \left(\frac{\partial V}{\partial Q_i}\right)_0 (Q_i - Q_i^{(0)}) + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial Q_i\, \partial Q_j}\right)_0 (Q_i - Q_i^{(0)})(Q_j - Q_j^{(0)}) \tag{13}$$

Note that the Hamiltonian $H(r, Q)$ is invariant with respect to the transformations of the Longuet-Higgins group G, and hence it is a scalar of the subgroup G_0 not only at the point Q_0, but also in any of its neighborhood. The approximate Hamiltonian with $V(r, Q)$ after Eq. (13) is also an invariant of the group G_0, but it is devoid of the other symmetry properties which complete the group G_0 until G.

The $Q_i - Q_i^{(0)}$ displacements may be transformed to symmetrized combinations $Q_{\Gamma\gamma}$ belonging to the γ line of the Γ representation. This transformation, performed by means of projection operators, is straightforward. Some details concerned the separation of independent bases, in particular, the separation of translational and rotational degrees of freedom may be found in the book of Wilson *et al.* (1956). In $Q_{\Gamma\gamma}$ coordinates the approximate Hamiltonian [with $V(r, Q)$ after Eq. (13)] is

$$H(r, Q) = T(Q) + U(r, Q) \tag{14}$$

$$U(r, Q) = H(r, Q_0) + \sum_{\Gamma\gamma} V_{\Gamma\gamma}(r) Q_{\Gamma\gamma} + \frac{1}{2} \sum_{\Gamma_1\gamma_1} \sum_{\Gamma_2\gamma_2} W_{\Gamma_1\gamma_1\Gamma_2\gamma_2}(r) Q_{\Gamma_1\gamma_1} Q_{\Gamma_2\gamma_2} \tag{15}$$

where $H(r, Q_0)$ is given by Eq. (11) and

$$V_{\Gamma\gamma}(r) = \partial V(r, Q_0)/\partial Q_{\Gamma\gamma}, \qquad W_{\Gamma_1\gamma_1\Gamma_2\gamma_2}(r) = \partial^2 V(r, Q_0)/\partial Q_{\Gamma_1\gamma_1} Q_{\Gamma_2\gamma_2} \tag{16}$$

As mentioned above the Hamiltonian equation (14) is a scalar of the point group G_0. It means that the last sum in Eq. (15) is a scalar convolution of two tensors of the second rank, $W_{\Gamma_1\gamma_1\Gamma_2\gamma_2}$ and $Q_{\Gamma_1\gamma_1} Q_{\Gamma_2\gamma_2}$, their components realizing the basis of the direct production of Γ_1 and Γ_2. Since $\Gamma_1 \times \Gamma_2$ is reducible, one can continue on to such convolutions of these tensors which transform as the irreducible representations of the G_0 group:

$$\{W(\Gamma_1 \times \Gamma_2)\}_{\Gamma\gamma} = \sum_{\gamma_1\gamma_2} W_{\Gamma_1\gamma_1\Gamma_2\gamma_2}(r) \langle \Gamma_1\gamma_1\Gamma_2\gamma_2 | \Gamma\gamma \rangle \tag{17}$$

$$\{Q_{\Gamma_1} \times Q_{\Gamma_2}\}_{\Gamma\gamma} = \sum_{\gamma_1\gamma_2} Q_{\Gamma_1\gamma_1} Q_{\Gamma_2\gamma_2} \langle \Gamma_1\gamma_1\Gamma_2\gamma_2 | \Gamma\gamma \rangle \tag{18}$$

Here $\langle \Gamma_1\gamma_1\Gamma_2\gamma_2|\Gamma\gamma\rangle$ is the Clebsh–Gordan coefficient of the G_0 group (Koster *et al.*, 1963). Using these presentations and taking into account the orthogonality relations between Clebsh–Gordan coefficients, we have

$$U(r, Q) = H(r, Q_0) + \sum_{\Gamma\gamma} V_{\Gamma\gamma}(r)Q_{\Gamma\gamma} + \frac{1}{2}\sum_{\Gamma_1\Gamma_2}\sum_{\Gamma\gamma} \{W(\Gamma_1 \times \Gamma_2)\}_{\Gamma\gamma}\{Q_{\Gamma_1} \times Q_{\Gamma_2}\}_{\Gamma\gamma} \tag{19}$$

and for the vibronic problem, we get formally the same system of coupled equations (4), in which, however, $T_{mn} = T(Q)\,\delta_{mn}$ and

$$U_{mn}(Q) = \int \psi_m^*(r)U(r, Q)\psi_n(r)\,dr \tag{20}$$

Except for the harmonic approximation [Eq. (13)], the two systems of vibronic equations are exact and differ only by a unitary transformation of the basis functions. In Eq. (4) the potential energy matrix is diagonal, whereas the kinetic energy matrix is nondiagonal; however, with the $\psi_n(r)$ basis the kinetic energy is diagonal and the potential energy is nondiagonal. The equivalency of the two approaches breaks down when approximate methods are employed in concrete calculations.

Consider now the case of f-fold degeneracy or pseudodegeneracy with states, $\psi_1(r), \psi_2(r), \ldots, \psi_f(r)$, having the same or close energies. In accordance with the perturbation theory for degenerate terms, the matrix Hamiltonian with these basis functions consists of $f \times f$ matrixes, their elements being differential operators of nuclear coordinates, and the vibronic system of equations contains f coupled differential equations with respect to the unknown functions $\chi_k(Q)$. The latter determine the zeroth-order correct functions

$$\Psi(r, Q) = \sum_{k=1}^{f} \chi_k(Q)\psi_k(r) \tag{21}$$

Note that in contrast to the adiabatic or simple adiabatic approximations, the total wave function [Eq. (21)] is essentially nonmultiplicative [all the $\chi_k(Q)$ functions are of the same order of magnitude]. Close energy values for different electronic states mean low electron velocities comparable with the nuclear ones. Therefore the latter cannot be separated from the electronic motion and considered as small vibrations in the mean field of electrons. The wave function Eq. (21) describes vibronic states to be distinguished from electron–vibrational states $\Psi(r, Q) = \chi_n(Q)\psi_n(r)$ with appropriate independent electronic and vibrational energy spectra. If all the functions $\psi_k(r)$, $k = 1, 2, \ldots, f$ belong to the same irreducible representation $\overline{\Gamma}$ of the G_0 group, the potential energy matrix using the

Wigner–Eckart theorem and assuming $\langle \Psi_{\bar{\Gamma}\gamma} | H(r, Q_0) | \psi_{\bar{\Gamma}\gamma} \rangle = 0$ takes the form:

$$\mathbf{U} = \sum_{\Gamma\gamma} V_\Gamma Q_{\Gamma\gamma} \mathbf{C}_{\Gamma\gamma} + \frac{1}{2} \sum_{\Gamma_1\Gamma_2} \sum_{\Gamma\gamma} W_\Gamma(\Gamma_1 \times \Gamma_2)\{Q_{\Gamma_1} \times Q_{\Gamma_2}\}_{\Gamma\gamma} \mathbf{C}_{\Gamma\gamma} \quad (22)$$

Here V_Γ and $W_\Gamma(\Gamma_1 \times \Gamma_2)$ are the reduced matrix elements of the operators $V_{\Gamma\gamma}(r)$ and $\{W(\Gamma_1 \times \Gamma_2)\}_{\Gamma\gamma}$ from Eq. (19), and $\mathbf{C}_{\Gamma\gamma}$ are matrixes of appropriate Clebsh–Gordan coefficients of the G_0 group determined in the space of the degenerate electronic states. In the second sum in Eq. (22) the totally symmetric terms with $\Gamma = A_1$ (proportional to $\mathbf{C}_{A_1}$) can be separated and united with the kinetic energy $T(Q)C_{A_1}$, resulting in a bilinear form of coordinates and momenta, which can be reduced to oscillator form by means of an orthogonal transformation to normal coordinates. Finally, we arrive at the vibronic Hamiltonian in the matrix form:

$$\mathbf{H} = \frac{1}{2} \sum_{\Gamma\gamma} (P^2_{\Gamma\gamma} + \omega^2_\Gamma Q^2_{\Gamma\gamma}) \mathbf{C}_{A_1} + \sum_{\Gamma \neq A_1} \sum_{\gamma} V_\Gamma Q_{\Gamma\gamma} \mathbf{C}_{\Gamma\gamma}$$

$$+ \frac{1}{2} \sum_{\Gamma_1\Gamma_2} \sum_{\Gamma \neq A_1} \sum_{\gamma} W_\Gamma(\Gamma_1 \times \Gamma_2)\{Q_{\Gamma_1} \times Q_{\Gamma_2}\}_{\Gamma\gamma} \mathbf{C}_{\Gamma\gamma} \quad (23)$$

Here the totally symmetric linear terms $V_\Gamma Q_{\Gamma\gamma} \mathbf{C}_{\Gamma\gamma}$ with $\Gamma = A_1$ are excluded by means of reading off the Q_{A_1} coordinate from its equilibrium position $Q^{(0)}_{A_1} = -V_{A_1}/\omega^2_{A_1}$. The last two terms in the vibronic Hamiltonian Eq. (23), containing coordinates $Q_{\Gamma\gamma}$ for which $V_\Gamma \neq 0$ and/or $W_\Gamma(\Gamma_1 \times \Gamma_2) \neq 0$, are the so-called linear and quadratic vibronic interaction terms, respectively, while the parameters V_Γ and $W_\Gamma(\Gamma_1 \times \Gamma_2)$ are the linear and quadratic vibronic coupling constants. Note that since mixing of only f degenerate states is taken into account in the above consideration, the vibronic Hamiltonian Eq. (23) is valid only when there are no other near-lying states with which under nuclear displacements, mixing may be essential.

B. The Jahn–Teller Theorem

Let us consider the shapes of the adiabatic potentials (AP), $\epsilon_n(Q)$, $n = 1, 2, \ldots, f$, near the point of intersection Q_0 ($Q_{\Gamma\gamma} = 0$, $\Gamma \neq A_1$). Assuming the $Q_{\Gamma\gamma}$ values to be sufficiently small, only the linear terms should be retained in the potential energy matrix Eq. (22), $\mathbf{U} = \Sigma_{\Gamma\gamma} V_\Gamma Q_{\Gamma\gamma} \mathbf{C}_{\Gamma\gamma}$. Its f eigenvalues, as can be easily shown, have conical-shaped surfaces (which are not necessarily rotation surfaces) with the apex at the point at Q_0. Indeed, consider the cross section of the $\epsilon_n(Q)$ surface along an arbitrary direction specified by the unit vector $\mathbf{e} = \{e_{\Gamma\gamma}\}$ in the space of nuclear displacements $\{Q_{\Gamma\gamma}\}$. Along this section $Q_{\Gamma\gamma} = qe_{\Gamma\gamma}$, $\mathbf{U} = q\Sigma_{\Gamma\gamma} V_\Gamma e_{\Gamma\gamma} \mathbf{C}_{\Gamma\gamma}$, and the eigenvalues of the U matrix are linear in q: $\epsilon_n(Q) = \lambda_n q$, where λ_n are the eigenvalues of the numerical matrix $\Sigma_{\Gamma\gamma} V_\Gamma e_{\Gamma\gamma} C_{\Gamma\gamma}$.

Since the spur of the $C_{\Gamma\gamma}$ matrixes, $\Gamma \neq A_1$, is zero and hence the "center of gravity" of the split term near the point Q_0 is preserved (the sum of all eigenvalues is zero), some of these cone surfaces should be oriented with the apex up and the bell shape down. It means that at least one of the AP sheets near the point of degeneracy Q_0 is a conical-like surface oriented with the bell shape down, and hence the surface as a whole has no extremum at this point, provided the linear terms of the vibronic interactions (the linear vibronic constants V_Γ) are nonzero. As mentioned above this statement was first formulated in terms of instability by Landau and then verified by Jahn and Teller (1937) and Jahn (1938) by means of group-theoretical considerations. Looking over all the point groups and all the possible types of molecular systems belonging to a certain point group, Jahn and Teller have shown that in all possible cases, except linear molecules, and for all degenerate terms, except twofold spin degeneracy (Kramers degeneracy), there are such nuclear displacements $Q_{\Gamma\gamma}$ for which the reduced matrix element $V_\Gamma = \langle\bar{\Gamma}\|V_\Gamma(r)\|\bar{\Gamma}\rangle$, calculated with the electronic functions $\psi_{\Gamma\gamma}(r)$, is nonzero ($\Gamma \in [\bar{\Gamma}^2]$).

Thus the following theorem is valid: *In the case of f-fold electronic degeneracy ($f > 1$) of a polyatomic system among the f adiabatic potential sheets intersecting at the point Q_0, there is at least one which has no extremum at this point. Exceptions are the cases of (1) linear configuration of the atoms at the point Q_0 and (2) spin twofold (Kramers) degeneracy of the electronic term.* More constructive analytic proofs of this theorem were suggested by Ruch and Schonhofer (1965) and independently by Blount (1971).

These proofs are not exhaustive, since they deal with only 32 crystal point groups and two icosahedral ones. The symmetry considerations used in most cases are sufficient but not necessary conditions of lack of extremum of the AP at the point of degeneracy Q_0; the latter can be of "accidental" origin. Also accidentally all the linear vibronic constants V_Γ may be zero.

The proof for both space and point groups based on the Frobenius theorem was suggested by Raghavacharyulu (1973a,b). A direct verification of the Jahn–Teller (JT) theorem for several space groups was performed by Birman (1962a,b). Algebraic proof of this theorem which also includes cases of accidental degeneracy is given by Aronovitz (1976).

The lack of minimum of the AP at the point Q_0 is usually interpreted as an instability of the molecular system with an orbital degenerate electronic state resulting in its spontaneous distortion and degeneracy removal. This interpretation, literally understood, is incorrect (Bersuker, 1966a). Indeed, in the neighborhood of the point of degeneracy Q_0 (small $Q_{\Gamma\gamma}$, $\epsilon_m \approx \epsilon_n$), the nonadiabacity corrections $\sim\Lambda_{mn}/(\epsilon_m - \epsilon_n) \sim (V_\Gamma Q_{\Gamma\gamma})^{-1}$ are not sufficiently small, and hence the adiabatic potential loses its physical meaning as the potential energy of the nuclei in the field of electrons. The real behavior of the nuclei in this case follows the Schrödinger equation with the vibronic matrix Hamiltonian [Eq. (23)], whereas the adiabatic Hamiltonian [Eq. (7)] is invalid. Nevertheless, for sufficiently strong vibronic couplings ($V_\Gamma \rightarrow \infty$), the area of applicability of the approximation $\mathbf{U} \approx \sum_{\Gamma\gamma} V_\Gamma \mathbf{Q}_{\Gamma\gamma} \mathbf{C}_{\Gamma\gamma}$ may be larger than the region of small $\mathbf{Q}_{\Gamma\gamma}$ values where the adiabatic approximation is invalid, and the conclusion about the instability of the nuclear configurations may be valid. But even in these cases the nuclear configuration, if correctly calculated as quantum mechanical averaged nuclear coordinates, is not distorted, and the degeneracy of the ground state is not removed (see Section III).

Note that the two exceptions to the JT theorem are quite different in nature. The Kramers degeneracy is determined by the symmetry of the system with respect to time inversion. This symmetry cannot be destroyed by any means of nuclear configuration distortion; the Kramers degeneracy cannot be removed by nuclear displacements and it remains in the range of all $Q_{\Gamma\gamma}$ values. On the contrary, the exception of linear molecules is due to the fact that the orbital momentum determines also the parity of the irreducible representation: as a result of inversion the basis functions ψ_{LM} are multiplied by $(-1)^L$. Therefore all the irreducible representations with even values of L are even, and those with odd values of L are odd. Since the double degenerate vibrations of a linear molecule are E_L, $L = 1$, i.e., they are odd, the selection rules of parity result in $V_{E_1} = 0$, and there is no splitting of the AP in the first-order perturbation theory with respect to the nuclear displacements $Q_{E\gamma}$.

However, there is such a splitting in the second-order approximation. Indeed, $Q_{E\gamma}\, Q_{E\gamma'}$, transforms as $[E_1^2] = A_1 + E_2$, and the mentioned forbiddenness on parity is removed. Visually this is due to the fact that for the distorted (bent) configuration, the L value ceases to be a good quantum number. It follows that although for linear molecules distinguished from the nonlinear case the AP in the point of degeneracy has an extremum, it may be split due to different curvatures of different sheets. This is the so-called Renner effect (Renner, 1934).

From the JT theorem it follows that the lack of extremum of the AP in the point of degeneracy is due to the linear vibronic coupling. This allows us to assume that there may be cases when the nonadiabatic mixing of electronic states by nuclear displacements (vibronic mixing) can be considered in the linear approximation, i.e., when the quadratic vibronic constants are neglected, $W_\Gamma(\Gamma_1 \times \Gamma_2) = 0$. In these cases the vibronic

Hamiltonian [Eq. (23)] is essentially simplified. All the terms can be divided into two parts, one of which contains the $Q_{\Gamma\gamma}$ coordinates with $\Gamma \in [\overline{\Gamma}^2]$ (JT active coordinates), the other includes the remaining (non-JT) coordinates for which $V_\Gamma = 0$. Accordingly, the Hamiltonian can be presented as the sum of two commuting components, and the appropriate variables can be separated. For the non-JT modes the motion remains trivial (say, harmonic), and the total JT effect is described by the JT active part of the Hamiltonian

$$\mathbf{H} = \frac{1}{2} \sum_{\Gamma\gamma} (\mathbf{P}^2_{\Gamma\gamma} + \omega^2_\Gamma Q^2_{\Gamma\gamma}) \mathbf{C}_A + \sum_{\Gamma\gamma} V_\Gamma Q_{\Gamma\gamma} \mathbf{C}_{\Gamma\gamma} \tag{24}$$

where the sum over Γ includes only the JT active irreducible representations. Their number is usually much less than the number of vibrational degrees of freedom of the molecule, but the problem still remains complicated.

C. Adiabatic Potentials

Calculation of the AP $\epsilon_n(Q)$ is an important step in the solution of vibronic equation (23). Knowledge of the AP has a special meaning in the case of strong vibronic coupling when the energy gap between different sheets of the AP in the regions far from the point of degeneracy Q_0 is sufficiently large and solutions with the Hamiltonian [Eq. (7)] are approximately valid. In these cases many qualitative features of the JT effect may be predicted by the AP shape without the solution of the vibronic equations.

The simplest JT system is a molecule in a double orbital (non-Kramers) degenerate state belonging to the simple E representation of the molecular point group. These representations are inherent in polyatomic systems, for which the point group G_0 possesses at least one rotational (C_n) or rotoflexion (S_n) axis of the order $n \geq 3$. There are two types of E terms. For odd values of n, and for even n not multiple with 4, the symmetric square of the E_k representations [$k = 1, 2, \ldots, (n-2)/2$, for even values of n, and $k = 1, 2, \ldots, (n-1)/2$, for odd values] is $[E_k^2] = A_1 + E_{2k}$. It means that for such an electronic term E the JT active modes are of type E, and the vibronic problem is of the type $E - e$. For even n multiple with 4 there are also E_k representations for which $[E_k^2] = A_1 + B_1 + B_2$, and the vibronic problem is $E - (b_1 + b_2)$. The first case is typical for molecules with C_{3v}, T_d, O_h, etc., symmetries, whereas the $E - (b_1 + b_2)$, problem is inherent in systems with C_{4h}, D_{4h}, etc., symmetries.

Consider first the linear $E - e$ problem. If the complex coordinates $Q_+ \sim \exp(2ik\varphi)$ and $Q_- \sim \exp(-2ik\varphi)$ are chosen as normal (φ is the angle of rotation around the symmetry axis and $k = 0, 1, 2, \ldots, n$), the operator of linear vibronic interactions can be written in the form of a scalar convolution $V_+(r)Q_- + V_-(r)Q_+$. Using the basis functions $\psi_\pm \sim \exp(\pm ik\varphi)$ and the transformation properties $V_\pm(r) \sim \exp(\pm 2ik\varphi)$, it can be transformed to the matrix form $V_E\sqrt{2}(Q_+\sigma_- + Q_-\sigma_+)$, where V_E is the reduced-matrix element, the vibronic constant, and $\sigma_\pm = (\sigma_x \pm i\sigma_y)/2$, and σ_i, $i = 0, x, y, z$ are the four well-known Pauli matrixes (the coefficient $\sqrt{2}$ being introduced for convenience). For real coordinates Q_θ, Q_ϵ and wave functions $\psi_\theta(r)$, $\psi_\epsilon(r)$,

$$\begin{aligned} Q_\theta &= (1/\sqrt{2})(Q_+ + Q_-), & \psi_\theta &= (1/\sqrt{2})(\psi_+ + \psi_-) \\ Q_\epsilon &= -(i/\sqrt{2})(Q_+ - Q_-), & \psi_\epsilon &= -(i/\sqrt{2})(\psi_+ - \psi_-) \end{aligned} \tag{25}$$

the operator of linear vibronic interaction in the $E - e$ problem takes the following form:

$$\mathbf{V} = V_E(Q_\theta\sigma_z + Q_\epsilon\sigma_x) \tag{26}$$

The same result can be obtained by the method described earlier in Section II,A using appropriate values of the Clebsh–Gordan coefficients. The difference in the sign of Q_θ for cubic symmetry groups arises due to the difference in the "right" and "left" coordinate systems assumed for trigonal and cubic systems, respectively.

For the potential energy matrix, using Eq. (26) we have

$$\mathbf{U} = \tfrac{1}{2}\omega_E^2(Q_\theta^2 + Q_\epsilon^2)\sigma_0 + V_E(Q_\theta\sigma_z + Q_\epsilon\sigma_x) \tag{27}$$

Its diagonalization leads directly to the AP (in polar coordinates $Q_\theta = \rho \cos \varphi$, $Q_\epsilon = \rho \sin \varphi$):

$$\epsilon_\pm = \tfrac{1}{2}\omega_E^2\rho^2 \pm |V_E|\rho \tag{28}$$

which is a rotation body (Fig. 1). Note the conical form of AP surface near the point of degeneracy Q_0 and the equipotential trough of minima points in its ϵ_- sheet, resembling a Mexican hat (sombrero). The radius of the trough and its depth—the JT stabilization energy E_{JT}—are

$$\rho_0 = |V_E|/\omega_E^2, \qquad E_{\mathrm{JT}} = -\epsilon_-(\rho_0) = \tfrac{1}{2}(V_E^2/\omega_E^2) \tag{29}$$

At the point of minimum, the difference $\epsilon_+(\rho_0) - \epsilon_-(\rho_0) = 4E_{\mathrm{JT}}$ may be sufficiently large, provided the vibronic constant is large. If this is the case the nuclear motion in the ground state is localized near the bottom of the trough and has the nature of free rotations along the latter (Section III). Figure 2 illustrates the change in shape of an equilateral triangle molecule during this motion. The wave of deformations transforming the equilateral triangle into an isosceles is running around the geometry center of the

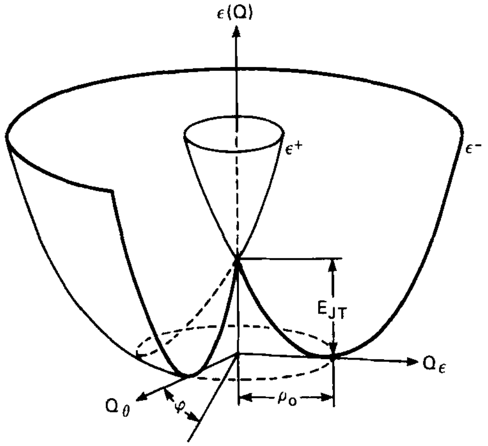


Fig. 1. The adiabatic potential of the electronic E term linearly coupled to E vibrations (the "Mexican hat").

triangle. But the molecule as a whole is not rotating: the atoms are describing circles around their own equilibrium position and not around a common axis of the molecule as a whole.

Quite similarly, the quadratic terms of the operator of vibronic interactions in the $E - e$ problem take the following form

$$\mathbf{W} = W_E[(Q_\theta^2 - Q_\epsilon^2)\sigma_z - 2Q_\theta Q_\epsilon \sigma_x], \tag{30}$$

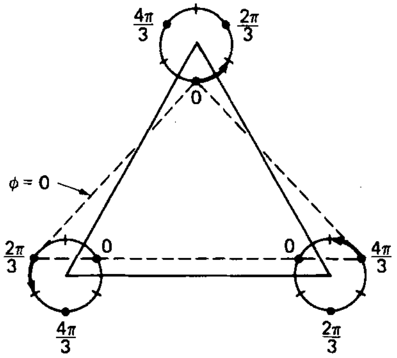


Fig. 2. The change of the shape of a triangle molecule when moving along the bottom of the trough of the lower sheet of the AP in the linear $E - e$ problem. The circles represent the trajectories of the atoms of the molecular framework. The extrema points along the bottom of the trough arising due to the quadratic terms of the vibronic interaction are marked by points on the circles (after Liehr, 1963).

where W_E is the corresponding reduced matrix element, the quadratic vibronic constant. With the quadratic terms [Eq. (30)] included, the AP becomes more complicated. As seen from Fig. 3 and compared to the linear case (Fig. 1), when the quadratic terms are taken into account, the AP surface becomes warped: three wells alternating with three humps occur along the bottom of the trough transforming the Mexican hat into a cocked hat ("tricorn"). The extrema points of the $\epsilon_-(\rho, \varphi)$ sheet of the surface are

$$\rho_0^{(n)} = \frac{V_E^2}{|V_E|\omega_E^2 - (-1)^n 2W_E V_E}, \qquad \varphi_0^{(n)} = \frac{\pi n}{6}, \quad n = 0, 1, 2, \ldots \tag{31}$$

the points $n = 1, 3, 5$ being absolute minima (and $n = 0, 2, 4$ saddlepoints) when $W_E V_E > 0$, and vice versa for $W_E V_E < 0$. The minima depths—the JT stabilization energy E_{JT} and the minimal barrier height between them are

$$E_{\mathrm{JT}} = \frac{1}{2}\,\frac{V_E^2}{\omega_E^2 - 2|W_E|}, \qquad \Delta = \frac{4|W_E|E_{\mathrm{JT}}}{\omega_E^2 + 2|W_E|} \tag{32}$$

The steep slope connecting all the extrema points of the $\epsilon_-(\rho, \varphi)$ sheet of the AP (Fig. 3b) is given parametrically by the following functions:

$$\begin{aligned} Q_\theta &= \frac{V_E}{\omega_E^4 - 4W_E^2}(\omega_E^2 \cos\alpha + 2W_E \cos 2\alpha) \\ Q_\epsilon &= \frac{V_E}{\omega_E^4 - 4W_E^2}(\omega_E^2 \sin\alpha - 2W_E \sin 2\alpha) \end{aligned} \tag{33}$$

Here again the energy gap between the two sheets of the AP surface near the minima points is $\epsilon_+ - \epsilon_- \sim V_E^2/\omega_E^2$. Therefore, if V_E is sufficiently large, the nonadiabatic contributions Λ_{+-} and Λ_{-+} are negligible, and the AP surface $\epsilon_-(\rho, \varphi)$ acquires the properties of the potential energy of the nuclei, qualitatively illustrating their possible motions. If Δ is not negligible the above-mentioned free rotations along the bottom of the trough become hindered by the potential barriers between the minima. For sufficiently large Δ values the nuclear motion is localized in the minima in which the nuclear configuration of the molecular system is distorted (the C_{3v} symmetry is reduced to C_{2v}, $T_d \rightarrow D_{2d}$, $O_h \rightarrow D_{4h}$, etc.). The degenerate E vibrations in such a minimum configuration are split into A and B vibrations with frequencies determined by the appropriate AP curvatures:

$$\tilde{\omega}_A^2 = \omega_E^2 - 2|W_E|, \qquad \tilde{\omega}_B^2 = 9|W_E|\,\frac{\omega_E^2 - 2|W_E|}{\omega_E^2 - |W_E|} \tag{34}$$

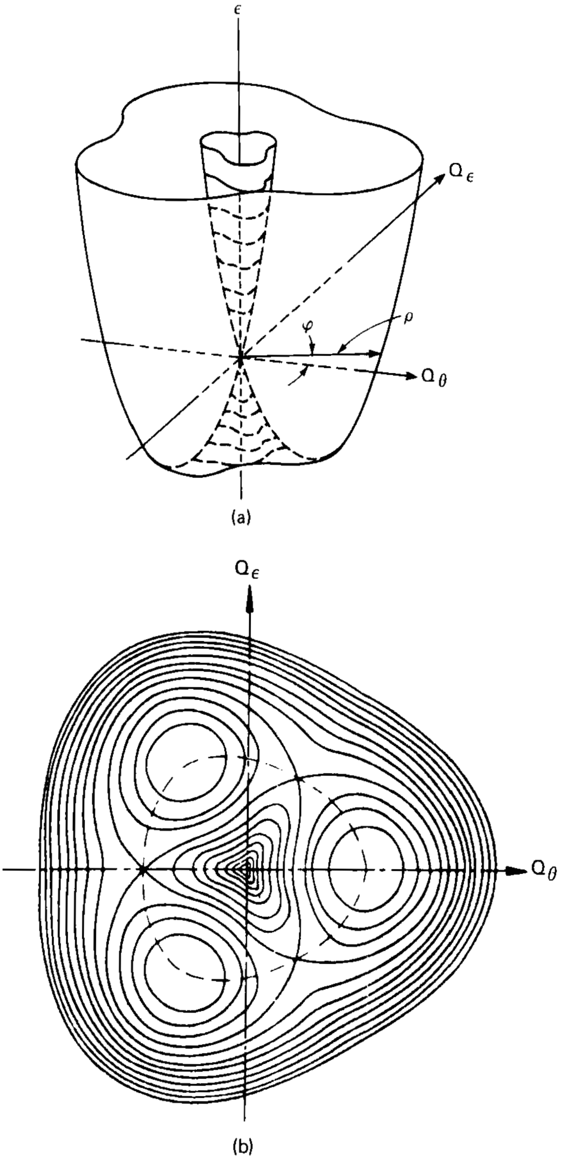


Fig. 3. The adiabatic potential in the $E - e$ problem with both linear and quadratic terms of vibronic interactions taken into account ("the tricorn"): (a) general view; (b) equipotential sections of the lower sheet ϵ_-. The steep slope line from the saddle points to the minima is shown by a dashed line.

In particular, if $|W_E| > \omega_E^2/2$, the system becomes unstable with regard the E-type nuclear displacements, provided the higher order terms in Q do not contribute to the stabilization of the nuclear configuration under consideration. This explains the origin of instability of a series of molecular systems with ground E terms, in particular H_3 (Liehr, 1963; Porter *et al.*, 1968). For stable systems the nuclear motion is rather complicated and it is not reduced purely to vibrations with the $\tilde{\omega}_A$ and $\tilde{\omega}_B$ frequencies, one of its important features being the tunneling between the minima (Section III,A,2).

For linear molecules, as mentioned above, $V_E = 0$, and the vibronic interaction operator contains only quadratic terms [Eq. (30)]. The appropriate AP have axial symmetry (Fig. 4):

$$\epsilon_{\pm} = \tfrac{1}{2}\omega_E^2\rho^2 \pm |W_E|\rho^2 = \tfrac{1}{2}(\omega_E^2 \pm 2|W_E|)\rho^2 \qquad (35)$$

If $|W_E| > \omega_E^2/2$, the lower sheet of the surface ϵ_- has a maximum at $\rho = 0$ and the system is unstable at this point (Renner instability). It may be stable for $\rho > 0$, owing to the contribution of the higher order terms in ρ.

Consider now the other E-term problem, $E - (b_1 + b_2)$. In real B_1 and B_2 normal coordinates Q_1 and Q_2 and real basis wave functions ψ_θ and ψ_ϵ, the linear vibronic interaction operator has the form $\mathbf{V} = V_1Q_1\sigma_x +$

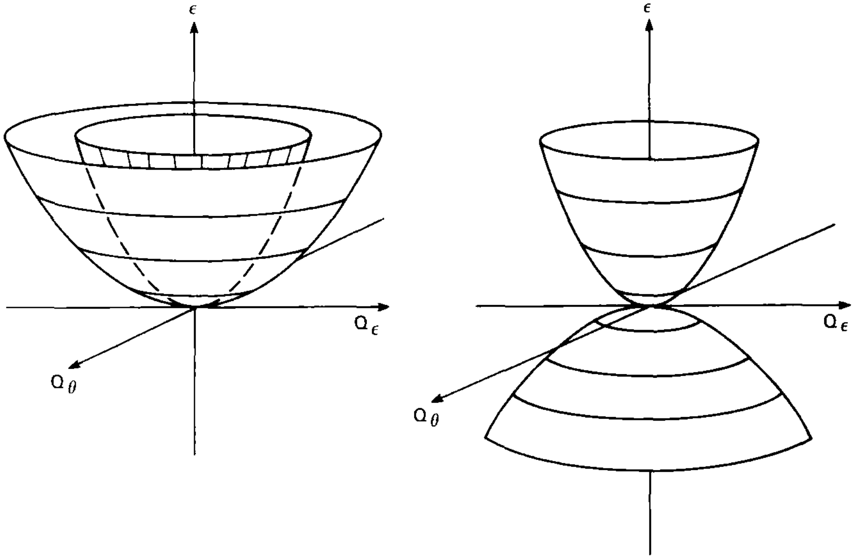


Fig. 4. The adiabatic potential of a Renner-type molecule near the point of degeneracy Q_0: (a) the case of weak Renner effects with stable configurations at $Q = Q_0$; (b) the case of strong Renner effect leading to dynamic instability at $Q = Q_0$ in the lower sheet state.

$V_2Q_2\sigma_z$, where V_1 and V_2 are the reduced-matrix elements, the linear vibronic constants of the coupling to B_1 and B_2 displacements, respectively. The AP as eigenvalues of the potential energy matrix $\mathbf{U} = \frac{1}{2}(\omega_1^2Q_1^2 + \omega_2^2Q_2^2) + \mathbf{V}$ can be found immediately. The appropriate surface is shown in Fig. 5. For the lower sheet $\epsilon_-(Q_1, Q_2)$, there are two types of extrema points: $Q_1^{(0)} = \pm V_1/\omega_1^2$, $Q_2^{(0)} = 0$, $E_{\mathrm{JT}}^{(1)} = \frac{1}{2}V_1^2/\omega_1^2$, and $Q_1^{(0)} = 0$, $Q_2^{(0)} = \pm V_2/\omega_2^2$, $E_{\mathrm{JT}}^{(2)} = \frac{1}{2}V_2^2/\omega_2^2$. If $E_{\mathrm{JT}}^{(1)} > E_{\mathrm{JT}}^{(2)}$ the first type of extrema points are absolute minima in which, say, a quadratic square-planar molecule is distorted to a rhomb, while the second type of extrema points (in which the quadrat is distorted to a rectangle) are saddlepoints. And if $E_{\mathrm{JT}}^{(1)} < E_{\mathrm{JT}}^{(2)}$, the opposite case is valid, in which the rectangle configuration has the

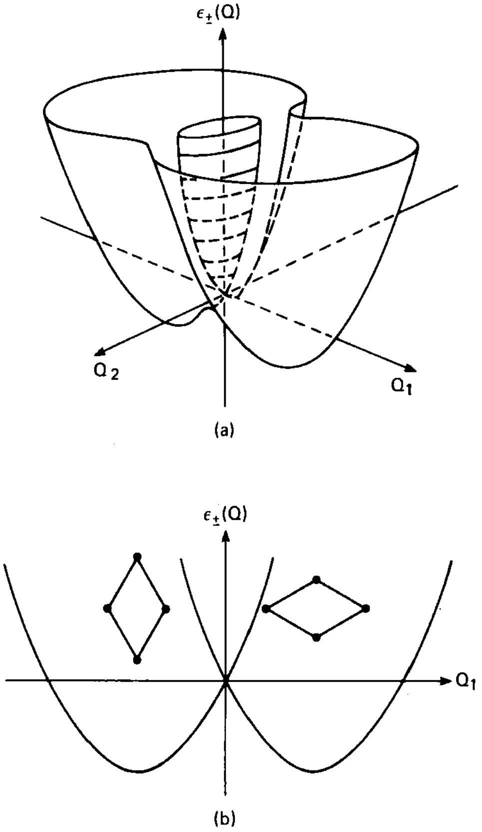


Fig. 5. The adiabatic potential of a tetragonal molecular system with an electronic E term linearly coupled to B_1 and B_2 vibrations: (1) general view; (b) the section along the Q_1 coordinate (by the plane $Q_2 = 0$) and the appropriate distortions at the minima points.

minimal energy and the rhombic configuration is at the saddlepoints. In the quadratic $E - (b_1 + b_2)$ problem there are some vibronic constant values for which the coexistence of the two types of minima is possible (Bacci, 1978).

Threefold degenerate irreducible representations are inherent in cubic symmetry groups T, T_d, O, T_h, and O_h and in icosahedral groups I and I_h. For cubic systems without inversion symmetry $[T_1^2] = [T_2^2] = A_1 + E + T_2$. For JT centers possessing inversion symmetry $[T_{1g}^2] = [T_{1u}^2] = [T_{2g}^2] = [T_{2g}^2] = A_{1g} + E_g + T_{2g}$. It follows that for triplet electronic states the double degenerate E and triple degenerate T_2 vibrations are JT active. This results in the so-called $T - (e + t_2)$ problem. As shown below (Section II,D) the $T - (e + t_2)$ problem has a similar mathematical form for all cubic systems, and therefore we consider here the T_{1u} term of an octahedral ML_6 system with O_h symmetry as a typical example.

It is convenient to discuss the transformation properties of the irreducible representations of molecular groups starting from the spherical symmetry $R(3)$. By reducing the latter to O_h symmetry the quintet representation $D^{(2)}$, to which the hydrogen atomic d functions belong, is split into a doublet and triplet: $D^{(2)} = E_g + T_{2g}$. The three p functions belong to the $D^{(1)}$ representation which transforms to T_{1u} by the same symmetry reduction $R(3) \rightarrow O_h$. It follows that the P–d problem of an atomic P term interacting with quintet d displacements of the isotropic environment is a high-symmetry particular case of the cubic symmetry $T - (e + t_2)$ problem, in which the cubic splitting of the d mode is very small. This is just the case expected for the 2p states of the hydrogen-like F^+ center in the CaO crystal; owing to their diffuseness the p orbitals do not sense the lower symmetry cubic structure of the lattice environment (Escribe, Hughes, 1971; see, however, Kushkulei *et al.*, 1976).

Therefore we consider first the particular case of the $T - (e + t_2)$ problem, the T – d problem. The potential energy matrix determined by real basis functions of the T_{1u} term, $\psi_x(r) \sim x$, $\psi_y(r) \sim y$, $\psi_z(r) \sim z$, has the form

$$\mathbf{U} = \tfrac{1}{2}\omega^2 \sum_{\gamma} Q_{\gamma}^2 \mathbf{C}_A + V \sum_{\gamma} Q_{\gamma} \mathbf{C}_{\gamma} \tag{36}$$

where $\mathbf{C}_A$ is a unit matrix, V is the reduced-matrix element (the linear vibronic constant), Q_γ are real normal coordinates transforming as the γ line of the $D^{(2)}$ representation of the $R(3)$ group, i.e., having the transformation properties of hydrogen atomic d functions: $Q_\theta \sim (2z^2 - x^2 - y^2)/\sqrt{3}$, $Q_\epsilon \sim x^2 - y^2$, $Q_\xi \sim 2yz$, $Q_\eta \sim 2xz$, $Q_\zeta \sim 2xy$, and C_γ are the matrices of Clebsh–Gordon coefficients of the $R(3)$ group. Using the known 3 × 3 matrixes of a spin $S = 1$ system,

$$\mathbf{S}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad \mathbf{S}_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \quad \mathbf{S}_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (37)$$

one can obtain easily: $\mathbf{C}_\theta = (2\mathbf{S}_z^2 - \mathbf{S}_x^2 - \mathbf{S}_y^2)/\sqrt{3}$, $\mathbf{C}_\epsilon = \mathbf{S}_x^2 - \mathbf{S}_y^2$, $\mathbf{C}_\xi = \mathbf{S}_y\mathbf{S}_z + \mathbf{S}_z\mathbf{S}_y$, $\mathbf{C}_\eta = \mathbf{S}_x\mathbf{S}_z + \mathbf{S}_z\mathbf{S}_x$, $\mathbf{C}_\zeta$,$= \mathbf{S}_x\mathbf{S}_y + \mathbf{S}_y\mathbf{S}_x$. The AP of the $T - \mathrm{d}$ problem—the eigenvalues of the matrix (36) have been obtained by O'Brien (1969). The minima of the lower sheet of the AP surface form a two-dimensional continuum (a trough) of equipotential points with the following coordinates:

$$\begin{aligned} &Q_\theta^{(0)} = (V/\omega^2\sqrt{3})(3\cos^2\theta - 1), \quad Q_\epsilon^{(0)} = (V/\omega^2)\sin^2\theta\cos 2\varphi \\ &Q_\xi^{(0)} = (V/\omega^2)\sin 2\theta\sin\varphi, \qquad Q_\eta^{(0)} = (V/\omega^2)\sin 2\theta\cos\varphi \qquad (38) \\ &Q_\zeta^{(0)} = (V/\omega^2)\sin 2\theta\sin 2\varphi \end{aligned}$$

$(0 \leq \theta \leq \pi, 0 \leq \varphi \leq 2\pi)$, the JT stabilization energy being $E_{\mathrm{JT}} = 2V^2/3\omega^2$. The change of the molecular shape of an octahedral system due to the rotation of the wave of distortion along this two-dimensional trough has been considered by Judd (1978).

For the linear $T - (e + t_2)$ problem the potential energy differs from Eq. (36) by the splitting of the frequency and the vibronic constant,

$$\begin{aligned} \mathbf{U} = {} & \tfrac{1}{2}\omega_E^2(Q_\theta^2 + Q_\epsilon^2)\mathbf{C}_A + \tfrac{1}{2}\omega_T^2(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2)\mathbf{C}_A \\ & + V_E(Q_\theta\mathbf{C}_\theta + Q_\epsilon\mathbf{C}_\epsilon) + V_T(Q_\xi\mathbf{C}_\xi + Q_\eta\mathbf{C}_\eta + Q_\zeta\mathbf{C}_\zeta) \qquad (39) \end{aligned}$$

The appropriate AP were studied by Opik and Pryce (1957). The lower sheet of the AP surface has three types of extrema points: four equivalent trigonal extrema points (in which only trigonal coordinates are displaced), $Q_\theta^{(0)} = Q_\epsilon = 0$, $|Q_\xi^{(0)}| = |Q_\eta^{(0)}| = |Q_\zeta^{(0)}| = 2|V_T|/3\omega_T^2$, $E_{\mathrm{JT}}(T) = 2V_T^2/3\omega_T^2$; three equivalent tetragonal extrema points in which only tetragonal coordinates are displaced, $\rho_n^{(0)} = 2|V_E|/(\omega_E^2\sqrt{3})$, $\varphi_n = \pi n/6$, $(Q_\theta = \rho\cos\varphi, Q_\epsilon = \rho\sin\varphi)$, $n = 1, 3, 5$ for $V_E < 0$ and $n = 2, 4, 6$ for $V_E > 0$, $Q_\epsilon^{(0)} = Q_\eta^{(0)} = Q_\zeta^{(0)} = 0$, $E_{\mathrm{JT}}(E) = 2V_E^2/3\omega_E^2$; six equivalent orthorhombic extrema points with both tetragonal and trigonal coordinates displaced and $E_{\mathrm{JT}}(OR) = [E_{\mathrm{JT}}(E) + 3E_{\mathrm{JT}}(T)]/4$. At the trigonal extrema points the O_{h} symmetry of the octahedral system is lowered to $D_{3\mathrm{d}}$, while at the tetragonal ones it becomes $D_{4\mathrm{h}}$. In the linear approximation under consideration if $E_{\mathrm{JT}}(E) > E_{\mathrm{JT}}(T)$, the tetragonal extrema points are minima and the trigonal ones are saddle points, and the opposite is true when $E_{\mathrm{JT}}(E) < E_{\mathrm{JT}}(T)$, the orthorhombic extrema being always saddle points.

There are some particular simplifying cases when the coupling to either E or T_2 vibrations is negligible. If $V_T = 0$, $V_E \neq 0$ ($T - e$ problem),

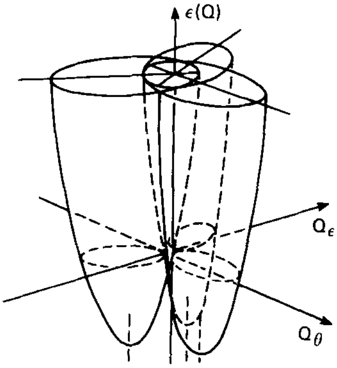


Fig. 6. The adiabatic potentials of the $T - e$ problem: three displaced parabolloids.

the matrix (39) is diagonal and its eigenvalues in the space of the tetragonal Q_θ and Q_ϵ displacements have the form of three rotation paraboloids, their axes crossing the tetragonal extrema points (Fig. 6). Note that the nonadiabacity terms in the $T - e$ problem vanish and the AP in Fig. 6 have the physical sense of nuclear potential energies for arbitrary V_E values and nuclear displacements. If $V_E = 0$, $V_T \neq 0$ ($T - t_2$ problem), the AP are surfaces in the four-dimensional space of ϵ, Q_ξ, Q_η, and Q_ζ. The lower sheet has four equivalent trigonal minima divided by six orthorhombic saddle points.

Taking account of the quadratic terms, the AP of the $T - (e + t_2)$ problem becomes rather complicated. The reduced-matrix elements $W_\Gamma(\Gamma_1 \times \Gamma_2)$ (quadratic vibronic constants) in the Hamiltonian (23) are nonzero only for $\Gamma \in \Gamma_1 \times \Gamma_2$, and therefore in the space of the E and T_2 displacements the following quadratic forms are possible: $[E^2] = A_1 + E$, $E \times T_2 = T_1 + T_2$, and $[T_2^2] = A_1 + E + T_2$. Since the total symmetric combination $\{Q_\Gamma \times Q_\Gamma\}_{A_1}$ is excluded and $W_{T_1}(E \times T_2) = 0$ (the operator **W** is real and Hermitian), the quadratic vibronic coupling in the $T - (e + t_2)$ problem is described in general by four independent vibronic constants $W_E(E \times E)$, $W_{T_2}(E \times T_2)$, $W_E(T_2 \times T_2)$, and $W_{T_2}(T_2 \times T_2)$. The influence of the $T_2 \times T_2$ terms (neglecting the others) was considered by Muramatsu and Iida (1970). The more complicated $E \times T_2$ were taken into account by Bersuker and Polinger (1973b, 1974). The general case including all four quadratic vibronic constants was discussed by Bacci *et al.* (1975a,b) and Ranfagni *et al.* (1979).

Three important conclusions can be drawn from these works:

(1) The quadratic terms of the vibronic coupling essentially change the energy and curvature of the trigonal, tetragonal, and orthorhombic

extrema points of the linear approximation AP; as a result the orthorhombic extrema points may become absolute minima

(2) For some relations between the vibronic constant values there may coexist different types of minima on the AP lower sheet: tetragonal with trigonal, tetragonal with orthorhombic, trigonal with orthorhombic, or all three types of minima simultaneously

(3) Besides the three types of extrema points discussed above some new types of extrema points, 12-fold (12 equivalent) and 24-fold, are possible. They may become minima only for very exotic combinations of vibronic parameters, and absolute minima only with taking account of the higher order terms in the low symmetry displacements in the expansion equation (13).

The most favorable condition for the orthorhombic, as well as other new types of extrema points, to become minima is the approximate equality of the tetragonal and trigonal extrema stabilization energies, $E_{\mathrm{JT}}(E) \approx E_{\mathrm{JT}}(T)$, for which without quadratic terms the AP has the form similar to the two-dimensional trough of the $T - \mathrm{d}$ problem discussed above. The contribution of the quadratic terms warps the trough, alternating wells and humps occuring along its bottom similar to the case of the $E - e$ problem (Fig. 7).

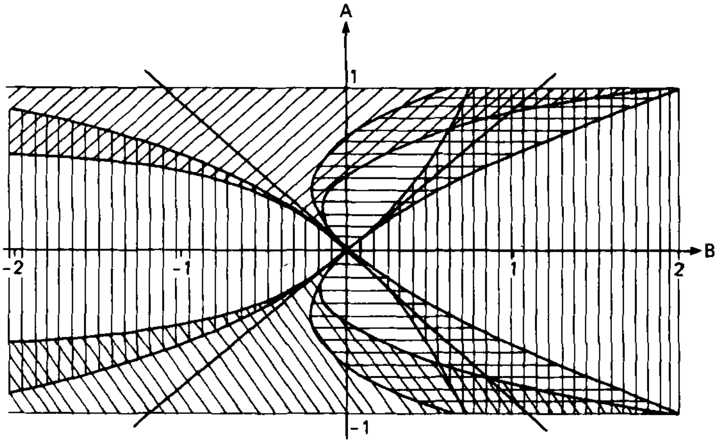


Fig. 7. The domains of existence (occurrence zones) of different types of minima points in the quadratic $T - (e + t_2)$ problem with $E \times T_2$-type quadratic terms of vibronic interactions, $W_{T_2}(E \times T_2) = W \neq 0$, in dimensionless parameters $A = W/\omega_E\omega_T$, $B = WV_E/\omega_E^{3/2}V_T$. The area of stability is limited by the inequality $|A| < 1$. Along the lines $A = \pm B\sqrt{3}/2$, the depths of tetragonal and trigonal minima are the same. The vertical, horizontal, and inclined shadings indicate the domains of tetragonal, trigonal, and orthorhombic minima points, respectively.

In the papers of Bacci *et al.* (1975b) and Ranfagni *et al.* (1979), besides the quadratic terms of vibronic interaction the cubic terms $E \times E \times E$ and $T_2 \times T_2 \times T_2$ types were also considered, and simultaneously the totally symmetric coordinates Q_{A_1} have been included explicitly in the calculation of the AP. The latter acquires different equilibrium values for different types of minima.

The simplest case of an electronic quadruplet term is realized in cubic polyatomic systems having an odd number of electrons. This term belongs to the Γ_8 irreducible representation of the O_h double group. Since $[\Gamma_8^2] = A_{1g} + E_g + T_{2g}$, the E_g and T_{2g} vibrations are JT active resulting in the $\Gamma_8 - (e + t_2)$ problem [quite similar to the $T - (e + t_2)$ problem]. The potential energy matrix has the same form as Eq. (36) for the $T - (e + t_2)$ problem with the same expressions for the $\mathbf{C}_\gamma$ matrices by the $\mathbf{S}_i$ spin matrices, but the latter, distinguished from the $T - (e + t_2)$ case, are 4 × 4 matrices of spin $S = 3/2$ (and can be expressed by Dirac matrices).

The eigenvalues of this matrix can be evaluated directly. They are two Kramers doublets with the following energies:

$$\epsilon_\pm = \tfrac{1}{2}(\omega_E^2\rho^2 + \omega_T^2Q^2) \pm \sqrt{(3V_E^2\rho^2 + 3V_T^2Q^2)^{1/2}} \tag{40}$$

where $\rho^2 = Q_\theta^2 + Q_\epsilon^2$, $Q^2 = Q_\xi^2 + Q_\eta^2 + Q_\zeta^2$. It means that in polar coordinates, $\epsilon_\pm$ does not depend on three rotation angles, and the equipotential cross sections of the surfaces are three-dimensional varieties. The lower sheet ϵ_- has two types of extrema points: tetragonal, $\rho_0 = |V_E|\sqrt{3}/\omega_E^2$, $Q_0 = 0$, $E_{\mathrm{JT}}(E) = 3V_E^2/2\omega_E^2$, and trigonal, $\rho_0 = 0$, $Q_0 = |V_T|\sqrt{3}/\omega_T^2$, $E_{\mathrm{JT}}(T) = 3V_T^2/2\omega_T^2$, the former being one-dimensional and the latter two-dimensional varieties. Depending on the $\eta = E_{\mathrm{JT}}(E)/E_{\mathrm{JT}}(T)$ value, either the tetragonal (when $\eta > 1$) or the trigonal ($\eta < 1$) extrema are absolute minima. If $\eta = 1$ the lower sheet of the AP surface has a four-dimensional variety of minima points. When the higher order terms of the vibronic interaction are taken into account the AP surface is warped and discrete extrema occur instead of the continuum (Dixon, 1977), quite similar to the $E - e$ (and other above-discussed) cases.

Electronic triplets and quadruplets are possible also in icosahedral systems. The AP of JT triplet, quadruplet, and quintet terms were considered by Khlopin *et al.* (1978).

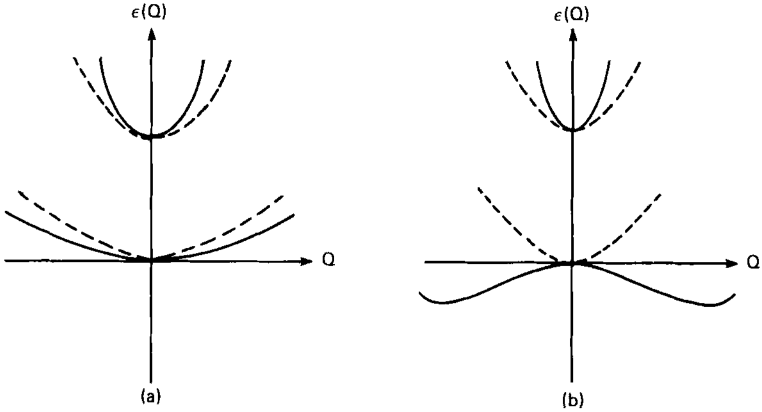
The most widespread vibronic situations are provided by the so-called quasi-degeneracy or pseudodegeneracy cases, when two or more electronic nondegenerate states are sufficiently strongly mixed by the vibronic interactions. By way of illustration, consider the simplest case of two energetically near-lying nondegenerate electronic states separated by the energy gap 2Δ, which are mixed by one nondegenerate vibration (Opik and Pryce, 1957). The potential energy matrix has the form:

$$U = \tfrac{1}{2}\omega^2 Q^2 \sigma_0 + \Delta\sigma_z + VQ\sigma_x \tag{41}$$

Its eigenvalues, the AP, can be derived directly (Fig. 8). Both sheets of the AP have an extremum at $Q = 0$, its curvature being $\omega^2 \pm V^2/\Delta$. It means that the vibronic coupling lowers the curvature of the $\epsilon_-(Q)$ sheet and increases the curvature of the upper sheet. If $\Delta < V^2/\omega^2$, the curvature of the lower sheet at $Q = 0$ becomes negative and two minima occur at $Q_\pm^{(0)} = \pm[V^2/\omega^4 - \Delta^2/V^2]^{1/2}$ with the curvature $\omega^2 - \omega^6\Delta^2/V^4$. The instability at the point $Q = 0$ (similar to the JT one) and its consequences are usually called the pseudo-Jahn-Teller effect (PJTE). If $\Delta \leq V^2/\omega^2$, the effect is considered strong, and for $\Delta > V^2/\omega^2$ it is called weak PJTE.

Note that the condition $\Delta \leq V^2/\omega^2$ correlates three parameters, and therefore it can be obeyed even when the energy gap between the mixing electronic states is relatively large. If under this condition the criterion of Eq. (9) is also valid, the nonadiabacity can be neglected and the AP $\epsilon_-(Q)$ acquires the physical meaning of nuclear potential energy. Then the negative curvature of the AP $\epsilon_-(Q)$ at the point $Q = 0$ can be interpreted as instability caused by vibronic mixing (see also Bersuker, 1980a,b).

One of the features of the PJTE, as distinguished from the JT effects, is that the vibronically mixing states $\psi_{\Gamma\gamma}(r)$ and $\psi_{\bar{\Gamma}\gamma}(r)$ may belong to different irreducible representations of the point group (whereas in the JT case, $\bar{\Gamma} = \Gamma$). This enlarges essentially the space of possible PJT active vibrations $\bar{\Gamma} \in \bar{\Gamma} \times \Gamma$. In particular, for systems having an inversion center Γ and $\bar{\Gamma}$ may have different parity. It means that in the PJTE odd-type nuclear displacements which take off the inversion center and lead to



(a) (b)

Fig. 8. The adiabatic potentials for two singlet electronic terms mixed by one singlet vibration in the case of weak (a) and strong (b) pseudo-Jahn–Teller effect. The same AP without taking into account the vibronic mixing are shown by dashed curves.

dipole moment formation can be JT active. If the PJTE is strong, this leads to the so-called dipolar instability: molecular systems having no proper dipole moments may have properties of rigid dipole molecules due to the dipole moments in the AP minima formed by the vibronic mixing with excited states (Bersuker, 1966a,b, 1969; Bersuker *et al.*, 1967).

There are many interesting applications of the idea of dipole instability (see the Bibliography Review, ed. Bersuker, 1982a) and among them the so-called vibronic theory of ferroelectricity (Bersuker, 1966; see also the review article of Bersuker and Vekhter, 1978). The idea of vibronic mixing of the ground state with near-lying excited states was also usefully employed in a series of chemical problems including elucidation of the origin of molecular dynamic instability (Bersuker, 1980a,b); of orbital symmetry rules in mechanisms of chemical reactions (Pearson, 1976); of vibronic chemical activation of molecular system by coordination in chemical reactions and catalysis (Bersuker, 1977, 1978a,b, 1980a,b).

D. Symmetry of JT Systems

Important results for the JT system properties can be obtained by means of group theory methods, including integrals of motion, and especially symmetry properties of the AP: the number of extrema points, the symmetry of the system at each of the extrema points, the symmetry group of equivalent extrema points, etc. It is known that analytical solutions of the Schrödinger equation require, first of all, separation of the variables, explicitly or implicitly based on additional symmetry of the Hamiltonian. Approximations used in these solutions are aimed at neglecting some of the Hamiltonian terms in order to increase their symmetry.

Consider the changes in symmetry owing to the above approximations in the solutions of the vibronic problem—to the limitation of the electronic spectrum by several states of the degenerate term and to the substitution of the operator of vibronic interaction $V(r, Q)$ by its expansion with respect to the nuclear displacements Q, including terms up to the quadratic one of Eq. (13). The vibronic Hamiltonian may be written in the form $\mathbf{H} = \mathbf{H}_{\mathrm{el}} + H_{\mathrm{v}} + \mathbf{V}$, where $\mathbf{H}_{\mathrm{el}} = E_{\Gamma}\mathbf{C}_A$ is the electronic Hamiltonian of the degenerate term with E_{Γ} energy, $\mathbf{C}_A$ being a unit $f_{\Gamma} \times f_{\Gamma}$ matrix (usually this part of $\mathbf{H}$ is excluded from consideration by a change of the energy read off to E_{Γ}), H_{v} is the vibrational Hamiltonian in the space of the JT active coordinates, and $\mathbf{V}$ is the operator of vibronic interactions.

The eigenfunctions of $\mathbf{H}_{\mathrm{el}} + H_{\mathrm{v}}$ have a multiplicative form $\Psi = \psi_{\Gamma\gamma}(r)\chi(Q)$, where $\psi_{\Gamma\gamma}$ and χ are the eigenfunctions of the $\mathbf{H}_{\mathrm{el}}$ and H_{v} Hamiltonians, respectively. The total symmetry group is thus a direct product $G_{\mathrm{el}} \times G_{\mathrm{v}}$, where G_{el} and G_{v} are the symmetry groups of the $\mathbf{H}_{\mathrm{el}}$ and H_{v} Hamiltonians. Since $\mathbf{H}_{\mathrm{el}}$ is multiple with the unit matrix $\mathbf{C}_A$ which does not change under unitary transformations in the space of the basic functions $\psi_{\bar{\Gamma}\gamma}(r) = |\bar{\Gamma}\gamma\rangle$, the G_{el} group coincides with the unitary group $U(f_{\bar{\Gamma}})$. The properties of the groups $U(n)$ are well known (Hamermesh, 1964). The number of parameters determining an arbitrary element of this group equals n^2. The set of n^2 elements $\mathbf{I}_{ij} = |i\rangle\langle j|$, $i, j = 1, 2, \ldots, n$, is complete with respect to the operation of commutation: $[\mathbf{I}_{ij}, \mathbf{I}_{kl}] = \mathbf{I}_{il}\,\delta_{kj} - \mathbf{I}_{kj}\,\delta_{il}$, i.e., they produce an algebra. It can be seen that they commute with the unit matrix which represents the electronic Hamiltonian of the n-fold degenerate term, and therefore these elements may be chosen as generators of the group.

The eigenfunctions of the Hamiltonian $\mathbf{H}_{\mathrm{el}}$ may be presented by column matrices (spinors). These functions can be regarded as describing different states (of a certain particle), which differ in the value of the projection of a vector S in an auxiliary "energy" space, formally analogous to the spin vector (energy spin or pseudospin). It follows that the unitary group $U(n)$ contains the group of rotations in the n-dimensional spin space $R(n)$ as a subgroup. With respect to these rotations the operators $\mathbf{I}_{ij} = \psi_i^\dagger \psi_j$ are components of a tensor of second rank, which can be linearly combined in order to transform after the irreducible representations $D^{(l)} \times D^{(l)}$, $2l + 1 = n$. The components of the appropriate irreducible tensors are determined by the following expressions:

$$\{\psi^{(l)} \times \psi^{(l)}\}^{(j)}_m = \sum_{p,q} \mathbf{I}_{pq}(lplq|jm) \tag{42}$$

where $(lplq|jm)$ are the Clebsh–Gordan coefficients of the group $R(n)$.

In particular, in the case of the linear $E - e$ problem the electronic Hamiltonian is described by the unitary group $U(2)$ with generators $\{\psi^{(1/2)} \times \psi^{(1/2)}\}^{(0)}_0 = \sigma_0$ and $\{\psi^{(1/2)} \times \psi^{(1/2)}\}^{(1)} = \boldsymbol{\sigma}$ ($\boldsymbol{\sigma} = \{\sigma_x, \sigma_y, \sigma_z\}$ are the Pauli matrices), the three operators σ_x, σ_y, and σ_z producing a complete algebra. An arbitrary operator of the $U(2)$ group is dependent on four $n^2 = 4$ parameters φ_0, φ_x, φ_y, φ_z and can be written in the form: $\mathbf{G} = \exp[i(\varphi_0\sigma_0 + \varphi_x\sigma_x + \varphi_y\sigma_y + \varphi_z\sigma_z)]$. It can be easily shown that the φ_0 parameter describes the trivial operation of multiplying the basis functions by a phase factor. Indeed, $\mathbf{G}(\varphi_0) = \exp(i\varphi_0\sigma_0) = \exp(i\varphi_0)\sigma_0$, and $\mathbf{G}(\varphi_0)\psi_\pm = \exp(i\varphi_0)\psi_\pm$. Excluding these trivial operations, we can limit ourselves to the three-parameter subgroup $SU(2)$ of the group $U(2)$, consisting of the unitary matrices $\mathbf{G} = \exp(i\boldsymbol{\varphi\sigma})$ having a determinant equal to unity.

The symmetry of the vibrational Hamiltonian is more convenient to consider within the presentation of secondary quantization. Let us introduce the following operators of creation and annihilation:

$$b^+_{\Gamma\gamma} = -\frac{i}{(2\hbar\omega_\Gamma)^{1/2}}(P_{\Gamma\gamma} + i\omega_\Gamma Q_{\Gamma\gamma}), \qquad b_{\Gamma\gamma} = \frac{i}{(2\hbar\omega_\Gamma)^{1/2}}(P_{\Gamma\gamma} - i\omega_\Gamma Q_{\Gamma\gamma}) \quad (43)$$

having the well-known commutation properties: $[b_{\Gamma\gamma}, b^+_{\bar{\Gamma}\bar{\gamma}}] = \delta_{\Gamma\bar{\Gamma}}\,\delta_{\gamma\bar{\gamma}}$. In these terms the vibrational operator $H_v = \hbar\omega_\Gamma \sum_\gamma (b^+_{\Gamma\gamma}b_{\Gamma\gamma} + \frac{1}{2})$ is invariant with respect to arbitrary unitary transformations in the space of $b_{\Gamma\gamma}$ operators not changing the commutation relations between $b_{\Gamma\gamma}$ and $b^+_{\Gamma\gamma}$ (Demkov, 1953).

In other words, the appropriate group for the n-dimensional oscillator is $U(n)$. The operators $F_{ij} = b_i^+ b_j$, $i, j = 1, 2, \ldots, n$, form a variety of n^2 elements, which is complete with respect to the operation of commutation $[F_{ij}, F_{kl}] = F_{il}\,\delta_{kj} - F_{kj}\,\delta_{il}$. It can be proved by direct verification that these elements commute with the Hamiltonian of an n-dimensional isotropic oscillator, and therefore they can be chosen as generators of the symmetry group. Similar to the above case, under the action of the operators of the $R(n)$ subgroup of the $U(n)$ group, the operators b_j transform as components of the n-dimensional vector, i.e., as components of the irreducible tensor $b^{(l)}$, $2l + 1 = n$. It follows that the operators $b_i^+ b_j$ transform as components of a tensor of second rank, which can be combined in irreducible [in the group $R(n)$] linear combinations (Judd, 1974):

$$\{b^{(l)} \times b^{(l)}\}^{(L)}_M = \sum_{m_1 m_2} b^+_{m_1} b^+_{m_2} (l m_1 l m_2 | LM) \qquad (44)$$

where $L = 0, 1, \ldots, 2l$; $m_1, m_2 = -l, -l + 1, \ldots, l$.

In particular, for a two-dimension oscillator ($n = 2$, $l = \frac{1}{2}$) it is convenient to use as generators of the group the following operators:

$$\begin{aligned} L_0 &= b^+_\theta b_\theta + b^+_\epsilon b_\epsilon, & L_x &= b^+_\theta b_\theta - b^+_\epsilon b_\epsilon \\ L_y &= b^+_\theta b_\epsilon + b^+_\epsilon b_\theta, & L_z &= -i(b^+_\theta b_\epsilon - b^+_\epsilon b_\theta) \end{aligned} \qquad (45)$$

Note that these tensor operators form a complete set with respect to the operation of commutation, and this is most convenient for reduction of the $U(2)$ group to subgroups. For instance, L_x, L_y, and L_z have the same commutative properties as the Pauli matrices σ_x, σ_y, σ_z, i.e., they produce an algebra. An arbitrary element of the four-parametrical group $U(2)$, describing the symmetry of the H_v Hamiltonian, may be written in the form: $G = \exp[i(\alpha_0 L_0 + \alpha_x L_x + \alpha_y L_y + \alpha_z L_z)]$, where α_i are real parameters. As above it can be shown that α_0 describes the trivial operation of multiplication of the wave functions with a phase factor, and hence the three-parametrical subgroup $SU(2)$ of the $U(2)$ group ($\alpha_0 = 0$) is sufficient to describe the vibrational subsystem.

Thus, without taking account of vibronic interactions the symmetry of the JT $E - e$ system is at least $SU(2) \times SU(2)$ and an arbitrary element of the group $\mathbf{G}(\boldsymbol{\alpha}, \boldsymbol{\varphi}) = \exp(i\boldsymbol{\alpha}\mathbf{L} + i\boldsymbol{\varphi}\boldsymbol{\sigma})$ depends on six parameters α_x, α_y, α_z, φ_x, φ_y, φ_z. The vibronic interaction lowers the symmetry of the system and the six parameters are no longer independent. The relations between them can be carried out from the condition that the operator $\mathbf{G}(\boldsymbol{\alpha}, \boldsymbol{\varphi})$ with interrelated values of α_i and φ_i commute with the total Hamiltonian, in particular, with the vibronic interaction. For small α_i and φ_i values $\mathbf{G} \approx 1 + i\boldsymbol{\alpha}\mathbf{L} + i\boldsymbol{\varphi}\boldsymbol{\sigma}$ and the condition of commutativity is $[(\boldsymbol{\alpha}\mathbf{L} + \boldsymbol{\varphi}\boldsymbol{\sigma}), (Q_\theta \sigma_x + Q_\epsilon \sigma_y)] = 0$. Inserting $Q_\gamma = (\hbar/2\omega_E)^{1/2}(b_\gamma^+ + b_\gamma)$ and calculating all the necessary commutative relations, we obtain

$$[(2\varphi_z - \alpha_z)Q_\epsilon + \omega_E^{-1}(-\alpha_x P_\theta + \alpha_y P_\epsilon)]\sigma_x + [(\alpha_z - 2\varphi_z)Q_\theta + \omega_E^{-1}(\alpha_x P_\epsilon + \alpha_y P_\theta)]\sigma_y - 2(\varphi_x Q_\epsilon - \varphi_y Q_\theta)\sigma_z = 0$$

Taking into account the linear independency of σ_i, Q_γ, and P_γ, we have $\alpha_x = \alpha_y = \varphi_x = \varphi_y = 0$, $\alpha_z = 2\varphi_z$, and

$$\mathbf{G} = \exp[i\alpha(L_z + \tfrac{1}{2}\sigma_z)] \tag{46}$$

It follows that as a result of the vibronic interaction the six-parameter group $SU(2) \times SU(2)$ is reduced to a one-parameter axial group C_∞. An arbitrary element of this group has the form of Eq. (46), and the appropriate infinitesimal operator (Moffit and Thorson, 1957),

$$\mathbf{J}_z = L_z + \tfrac{1}{2}\sigma_z \tag{47}$$

as can be easily proved, commutes with the total Hamiltonian, i.e., it is an integral of motion.

This result makes clear-cut physical sense. Without taking account of the vibronic interaction the motion of electrons is independent of that of the nuclei, and the energy spin $\frac{1}{2}\boldsymbol{\sigma}$ and vibrational moment $\mathbf{L}$ are preserved separately. The states of the electronic E term $\psi_\pm(r)$ having definite values of the projection of the energy spin on the z axis, are appropriate to the wave of electron density moving, say, in the case of the X_3 molecule, along its perimeter clockwise and counterclockwise, respectively. Similarly, the states corresponding to certain L_z values are appropriate to the wave of deformations of the equilateral triangle running clockwise and counterclockwise. The vibronic interaction results in a special coupling of the electronic and nuclear motions, due to which the vibrational moment $\mathbf{L}$ and energy spin $\frac{1}{2}\boldsymbol{\sigma}$ are no longer preserved separately; the energy of the system becomes dependent on the mutual orientations of $\mathbf{L}$ and $\frac{1}{2}\boldsymbol{\sigma}$, only the projection of the total moment $\mathbf{J} = \mathbf{L} + \frac{1}{2}\boldsymbol{\sigma}$ on the z axis being preserved. The above waves of electron density and nuclear configuration deformation are no longer running independently, but are correlated. The situation is similar to the coupling of orbital and spin motions in the LS scheme in atoms. On the other hand, the coherent rotations of the electron density and nuclear deformations are somewhat similar to solid-state polarons.

The operator L_z in the coordinate representation has the form: $L_z = \hbar^{-1}(Q_\theta P_\epsilon - Q_\epsilon P_\theta)$, or in polar coordinates, $L_z = -i\partial/\partial\varphi$. This explains the origin of the axial symmetry of the AP in the linear $E - e$ problem. In addition to arbitrary rotations around the z axis, the Hamiltonian of the linear $E - e$ problem is also invariant with respect to other independent operations (Leung and Kleiner, 1974): $\mathbf{P} = R_\epsilon\sigma_x$ and $\boldsymbol{\Theta} = K\sigma_x$, where $R_\epsilon = \exp(i\pi b_\epsilon^+ b_\epsilon)$ is the operator changing the sign of the Q_ϵ coordinate, and K is the operator of the complex conjugation; $\mathbf{P}$ and $\boldsymbol{\Theta}$ commute with the total Hamiltonian and obey the relations $\mathbf{P}^2 = 1, \boldsymbol{\Theta}^2 = 1, \mathbf{J}_z\mathbf{P} + \mathbf{P}\mathbf{J}_z = 0, \mathbf{J}_z\boldsymbol{\Theta} + \boldsymbol{\Theta}\mathbf{J}_z = 0, K\mathbf{P} = \mathbf{P}K$. The anticommutation of $\mathbf{P}$ and $\boldsymbol{\Theta}$ with $\mathbf{J}_z$ means that the energy does not change by the substitution $\mathbf{J}_z \to -\mathbf{J}_z$, and hence it depends only on $|j|$, where j is the eigenvalue of $\mathbf{J}_z$. Taking into account that according to Eq. (47) the quantum number j assumes only semi-integer values, $j = \pm 1/2, \pm 3/2, \ldots$, we come to the conclusion that all the vibronic energy levels of the linear $E - e$ problem are double degenerate. This proof is similar to that of the Kramers theorem for a "particle" with a semi-integer energy spin.

The axial symmetry of the linear $E - e$ problem emerges in fact from the coincidence of the E-type transformation properties in the trigonal and axial groups. The explicit form of the higher order terms in $Q_{E\gamma}$ in the vibronic interaction, i.e., the form of appropriate convolutions of the irreducible tensor operators, are determined by Clebsh–Gordan coefficients of the point group (but not the axial one), and therefore this axial symmetry of the linear $E - e$ problem is lowered when higher in $Q_{E\gamma}$ terms are taken into account.

The question of the lowest possible symmetry of the AP of a given electronic state in the space of normal coordinates $Q_{\Gamma\gamma}$ has been considered by Dagis and Levinson (1967). In the space of all normal coordinates the AP should be an invariant of the G_0 group of the initial (highest symmetry) nuclear configuration. However, for some of the elements of the G_0 group, the corresponding matrices of the Γ representation are unit matrices. Such elements leave the $Q_{\Gamma\gamma}$ coordinates unchanged. The set of such elements produce the so-called nucleus G_Γ of the representation Γ. The other elements of the G_0 group (including the identical one) form the factor group G_0/G_Γ. The latter is just the symmetry group of the AP in the space of the coordinate $Q_{\Gamma\gamma}$.

For instance, for an octahedral molecule ($G_0 = O_h$) the nucleus of the E_g representation of the JT active Q_θ and Q_ϵ coordinates is the D_{2h} group.

Hence the symmetry group of the AP in the two-dimensional space of these coordinates is the factor group O_h/D_{2h}, isomorphous to C_{3v}. This is just the symmetry of the AP in the case of the $E - e$ problem, which occurs if the quadratic terms of the vibronic interactions are taken into account. It means that as far as the symmetry of the AP in general is considered (but not the number of extrema points; see below), higher order terms in the $E - e$ problem may be neglected.

This result has a general meaning for the $E - e$ problem of any polyatomic system. Independent on the initial G_0 symmetry of different molecular groups (provided it contains E representation), the nontrivial transformations under the group elements are rotations around the third-order axis and reflections in the plane σ_v (if there are such elements in the G_0 group). Thus the factor group C_{3v} (or C_3) is the general symmetry group of the AP in the space of E displacements independent on the initial configuration and symmetry of the molecule. This result forms the foundation of the mathematical equivalency of all the $E - e$ problems independent of the origin of the electronic E term.

In the case of the $E - (b_1 + b_2)$ problem the factor group in the space of $B_1 + B_2$ vibrations and hence the symmetry of the AP is C_{2v} (cf. Fig. 5). For cubic systems with T terms the AP in the space of T_2 displacements has the symmetry $O \equiv T_d$ if $G_0 = 0$, O_h, and T_d and T if $G_0 = T$, T_h. The same symmetry of the AP remains also in the space of both E and T_2 vibrations.

These group-theoretical considerations also allow the solution of the question of the number of terms in the expansion of the vibronic interaction with respect to the nuclear displacements $Q_{\Gamma\gamma}$, which have to be retained in order to obtain, at least qualitatively, correct results. As mentioned above in the $E - e$ problem quadratic terms at least must be taken into consideration. In general, qualitatively correct results may be obtained by retaining those terms which give the lowest symmetry. The next terms change the results only quantitatively (and this may be important in the case of strong vibronic coupling). However, if the expansion equation (13) is broken too early, the symmetry of the AP becomes higher than the factor group, resulting in the "accidental" degeneracy of the vibronic energy levels.

In principle, the number of possible types of extrema points of the AP is determined by the number of different subgroups of the factor group G_0/G_Γ; depending on the position relative to the symmetry axes or planes, any point of the AP may pertain to a certain type. Under the influence of the symmetry elements of the factor group the initial point is transferred to another equivalent point. The variety of equivalent points forms a transitive set. In the case of the $E - e$ problem, for which the AP has C_{3v} symmetry, there are three transitive sets, three types of equivalent points. Six points of the first type are obtained by the action of all six elements of the C_{3v} group upon the initial point occupying a general position not coinciding with any symmetry axis or plane. Locally, the AP at this point has the lowest symmetry C_1. The symmetry of the nuclear configuration in this point is $C_1 \times D_{2h} = D_{2h}$. Three points of the second type lay on the symmetry planes of reflexion σ_v of the C_{3v} group with local symmetry C_s, the symmetry of the nuclear configuration being thus $C_s \times D_{2h} = D_{4h}$. The third type (one point) lies on the intersection of all the symmetry elements of the C_{3v} group having thus local C_{3v} symmetry, the molecular symmetry in this point being $C_{3v} \times D_{2h} = O_h$.

Thus the AP of an octahedral molecule in the space of E coordinates may have extrema points of three types: (1) six equivalent extrema points, in which the symmetry of the molecule is lowered to D_{2h}; (2) three extrema points with D_{4h} symmetry; and (3) one point with O_h symmetry. The latter can be the $E - e$ problem with zero vibronic interaction.

Note that in the above consideration of the number of extrema points the multiplicity of the degenerate electronic term is not involved. It means that the results are applicable to all the JT situations with given JT active coordinates. In particular, the above three types of extrema points obtained for the $E - e$ problem may be inherent in the $T - e$ problem and in singlet electronic terms vibronically coupled by E vibrations. The results obtained in this section are also applicable to the so-called multimode problems (Section III).

III. Solution of Vibronic Equations

The central problem of the theory of vibronic interaction is the determination of the energy spectrum and wave functions. In the limiting cases of weak and strong vibronic coupling this problem can be solved analytically (Section III,A). Special attention should be paid to the evaluation of the lowest vibronic states which demonstrate themselves mainly in various experimental situations. In the case of strong vibronic coupling the lowest energy levels result from the above-mentioned tunneling between the equivalent quasi-stationary states in the minima of the AP (Section III,A,2). In many cases physical magnitudes can be evaluated without solution of the vibronic equations using only the so-called vibronic reduction factors, provided these magnitudes are determined by pure electronic operators (independent of nuclear coordinates) and only by one (usually ground) vibronic energy term (Section III,C).

A. Analytical Solutions

In view of the great difficulties encountered in the solution of the system of coupled equations (4), and for general understanding of the expected JT effects, the analytical solutions for some limiting cases given below are of great importance.

1. *Weak Vibronic Coupling*

For zero vibronic coupling $V_\Gamma = 0$, $W_\Gamma = 0$ ($\Gamma \neq A_1$), the nuclear motions described by the Hamiltonian equation (23) are harmonic oscillations, and the energy spectrum consists of a superposition of equidistant energy levels spaced by $\hbar\omega_\Gamma$. The contribution of the linear vibronic coupling is roughly $\Delta E \sim V_\Gamma \bar{Q}_{\Gamma\gamma} \sim \hbar\omega_\Gamma(E_{JT}/\hbar\omega_\Gamma)^{1/2}$. Consider the case of weak vibronic coupling when $E_{JT} \ll \hbar\omega_\Gamma$ or $V_\Gamma^2/\hbar\omega_\Gamma^3 \ll 1$. In this case the perturbation theory can be employed considering the dimensionless vibronic coupling constant $k_\Gamma = (V_\Gamma^2/\hbar\omega_\Gamma^3)^{1/2}$ as a small parameter.

In the case of weak vibronic coupling the mean nuclear displacements $\bar{Q}_{\Gamma\gamma}$ are relatively small and the quadratic terms in $Q_{\Gamma\gamma}$ may be neglected, i.e., the calculations can be performed by the linear Hamiltonian equation (24). If the signs of V_Γ and all $Q_{\Gamma\gamma}$ magnitudes are changed simultaneously, the Hamiltonian remains unchanged. It means that all the observable magnitudes which are independent of the $Q_{\Gamma\gamma}$ values explicitly, if expanded in a series with respect to V_Γ, contain only even power of V_Γ, the second-order contribution being additive with respect to the index Γ. This allows us to consider the $E - (b_1 + b_2)$ problem as two separate ones, $E - b_1$ and $E - b_2$, the $T - (e + t_2)$ problem as $T - e$ plus $T - t_2$, the $\Gamma_8 - (e + t_2)$ problem as $\Gamma_8 - e$ and $\Gamma_8 - t_2$ separately, and so on, i.e., in each case when there is simultaneous vibronic coupling to different types of vibrations the results equal the second-order sum in the V_Γ contributions of each of these types of vibrations Γ.

Let us represent the Hamiltonian equation (24) as $\mathbf{H}_0 + \mathbf{V}$, where $\mathbf{H}_0$ is the oscillator Hamiltonian and $\mathbf{V}$ is the operator of linear vibronic coupling taken as a perturbation. The eigenfunctions of the $\mathbf{H}_0$ Hamiltonian are multiplicative with respect to electronic and vibrational variables, $\Psi^{(0)}(r, Q) = \psi_{\Gamma\gamma}(r)|\cdots n_{\Gamma\gamma}\cdots\rangle$, where $\Psi_{\Gamma\gamma}(r)$ are the initial electronic states of the degenerate term and $|\cdots n_{\Gamma\gamma}\cdots\rangle$ are the oscillator functions. The diagonal matrix elements of $\mathbf{V}$ with zero-order functions are zero, and thus the first nonzero contribution to the energy occurs only in the second-order perturbation theory. Therefore it is more convenient to perform unitary transformation to a new basis in which perturbation energy corrections already occur to first order. This can be done by means of the operator form of the perturbation theory (Tsukerblat *et al.*, 1975). The second-order vibronic Hamiltonian acquires the following form:

$$\mathbf{H}^{(2)} = \mathbf{H}_0 - \frac{1}{2}\sum_{\Gamma}\left(\frac{V_\Gamma}{\omega_\Gamma}\right)^2 \sum_{\gamma} \mathbf{C}^2_{\Gamma\gamma} + \mathbf{V}_2 \tag{48}$$

$$\mathbf{V}_2 = -\frac{i}{2\hbar}\sum_{\Gamma\gamma}\sum_{\bar{\Gamma}\bar{\gamma}} \frac{V_\Gamma V_{\bar{\Gamma}}}{\omega^2_\Gamma} Q_{\bar{\Gamma}\bar{\gamma}} P_{\Gamma\gamma}[\mathbf{C}_{\Gamma\gamma}, \mathbf{C}_{\bar{\Gamma}\bar{\gamma}}] \tag{49}$$

The second term in Eq. (48) can be excluded by means of an appropriate read-off, since $\Sigma_\gamma \mathbf{C}^2_{\Gamma\gamma}$ is a scalar of the symmetry point group proportional to the unit matrix, which mean that this term shifts all the energy levels by the same quantity. In Eq. (49), for $\mathbf{V}_2$ only the terms with $\Gamma = \bar{\Gamma}$ contribute to the secular matrix build-up by the degenerate-term wave functions and they should be retained (Bersuker and Polinger, 1982):

$$\mathbf{V}_2 = -\frac{i}{4\hbar}\sum_{\Gamma}\left(\frac{V_\Gamma}{\omega_\Gamma}\right)^2 \sum_{\gamma,\bar{\gamma}} (Q_{\Gamma\bar{\gamma}}P_{\Gamma\gamma} - Q_{\Gamma\gamma}P_{\Gamma\bar{\gamma}})[\mathbf{C}_{\Gamma\gamma}, \mathbf{C}_{\Gamma\bar{\gamma}}] \tag{50}$$

The operators $Q_{\Gamma\bar{\gamma}}P_{\Gamma\gamma} - Q_{\Gamma\gamma}P_{\Gamma\bar{\gamma}}$ transform as the lines of the antisymmetric production $\{\Gamma^2\}$ of the Γ representation and describe rotations in the subspace of the degenerate coordinates $Q_{\Gamma\gamma}$. Similarly, the $i[\mathbf{C}_{\Gamma\gamma}, \mathbf{C}_{\Gamma\bar{\gamma}}]$ possess the transformation properties of the representation $\{\Gamma^2\}$ and describe rotations in the space of degenerate electronic states. The sum of Eq. (50) is thus a scalar convolution of spin–orbital-coupling type in which there is the energy spin instead of the real one and the rotation of the deformation of the molecular framework instead of the orbital motions of the electrons.

These symmetry properties of the perturbation operator are very important and allow the construction of symmetry-adapted zero-order wave functions, which may be a difficult task, especially for highly degenerate excited vibrational energy levels. [Note that the nth level for E vibrations is $(n + 1)$-fold degenerate, and for T_2 vibration it is $(n + 1)(n + 2)/2$-fold degenerate, and these values must be multiplied by $f_{\bar{\Gamma}}$ in order to obtain the total multiplicity of the initial unperturbed energy levels.] As shown in Section II,D the symmetry of the unpertubed system is $SU(f_\Gamma) \times SU(f_{\bar{\Gamma}})$, and the vibronic interaction, if taken into account fully enough, lowers this symmetry to that of the point group of the nuclear framework. As seen from Eq. (50) in the second-order perturbation theory the symmetry of the system is still very high and equals the continuous group of rotations the group of the total momentum. It follows that the rotations of the energy spin and the deformation wave are no longer independent: the total momentum being equal the sum of the "orbital," and the "spin" ones is preserved. The symmetry-adapted zero-order functions can be obtained similar to those for the case of LS coupling of the orbital and spin motions in atoms, i.e., by means of the appropriate Clebsh–Gordan coefficients.

Let us illustrate the above results in the case of the $E - e$ problem as an example. The $\mathbf{C}_{E\gamma}$ operators determined by the basis electronic functions $\psi_{\pm}(r)$ are $\mathbf{C}_{E\theta} = \sigma_x$, $\mathbf{C}_{E\epsilon} = \sigma_y$ (Section II,C), and the second-order perturbation Hamiltonian is

$$\mathbf{H} = \mathbf{H}_0 - 2E_{\mathrm{JT}}\sigma_0 - 2E_{\mathrm{JT}}L_z\sigma_z \tag{51}$$

where E_{JT} and L_z are determined by Eqs. (29) and (45), respectively. Since the symmetry group of the two-dimensional oscillator is $SU(2) = R(3)$ and that for the electronic term is $SU(2) = R(3)$, the $\mathbf{H}_0$ Hamiltonian symmetry is $R(3) \times R(3)$. Its energy-level degeneracy is $2(n + 1)$ (due to two possible projections of the energy spin 1/2 and $n + 1$ values of the projection of the vibrational momentum), the corresponding quantum number l assuming the values $-n, -n + 2, \ldots, n$. The "spin–orbital" interaction $L_z\sigma_z$ partly removes this degeneracy since $\mathbf{L}$ and $\mathbf{S}$ are no longer preserved separately, and only the projection $\mathbf{J}_z = L_z + \frac{1}{2}\sigma_z$ with the quantum number $j = l \pm 1/2$ is preserved. Nevertheless, as often happens in perturbation theory, l and ± 1 still remain "good" quantum numbers for L_z and σ_z, respectively, and the appropriate operators in Eq. (51) can be substituted by their quantum numbers (Moffitt and Thorson, 1957):

$$\begin{aligned} E_{n,l,\pm 1,j} &= \hbar\omega_E(n + 1) - 2E_{\mathrm{JT}}(1 \pm l) \\ &= \hbar\omega_E(n + 1) - 2E_{\mathrm{JT}}(j^2 - l^2 + \tfrac{3}{4}) \end{aligned} \tag{52}$$

These energy levels remain twofold degenerate since for each state l there is an appropriate $(-l)$ state with the same energy. Thus, the vibronic interaction in the second-order perturbation theory splits the $2(n + 1)$-fold degenerate levels of the H_0 Hamiltonian into $n + 1$ equidistant twofold degenerate levels with energy intervals equal to $2E_{\mathrm{JT}}$. The energy interval between the limit doublets is $4nE_{\mathrm{JT}}$, i.e., it may be comparable to or larger than $\hbar\omega_E$, even for small V_E values. It follows that the perturbation theory is valid only for $4E_{\mathrm{JT}}/\hbar\omega_E \ll n^{-1}$.

As mentioned earlier, the twofold degeneracy of the energy levels has a Kramers-type origin (Section III,D). In particular, the ground state of the $\mathbf{H}_0$ Hamiltonian is not split by the vibronic interaction but shifted: $E_{0,0,\pm 1,\pm 1/2} = \hbar\omega_E - 2E_{\mathrm{JT}}$. Thus the initial twofold electronic degeneracy of the ground state is not removed by the vibronic interaction but transformed into twofold vibronic degeneracy.

The wave functions of the ground state are no longer multiplicative, $\Psi_{0,0,\pm 1,\pm 1/2} = \psi_{\pm}(r)|00\rangle - V_E\psi_{\mp}(r)(|10\rangle \pm i|01\rangle)(2\hbar\omega_E^3)^{-1/2}$, $V_E^2/2\hbar\omega_E^3 = E_{\mathrm{JT}}/\hbar\omega_E$ having the sense of the probability to find the JT system at $T = 0$ K in the "one-phonon" state $\Psi_+(r)|01\rangle$ or $\psi_-(r)|10\rangle$.

For the linear $T - t_2$ problem the operators $i[C_{T_2\gamma}, C_{T_2\bar{\gamma}}]$ can be represented by matrices of the energy spin $S = 1$. Taking into account the rules of quantization of the vibrational momentum, $l = n, n - 2, n - 4, \ldots, 1$ or 0, n being the number of the vibrational state, we have (Moffitt and Thorson, 1957)

$$E_{n,l,j} = \hbar\omega_T(n + \tfrac{3}{2}) + \tfrac{3}{16}E_{\mathrm{JT}}(T)[j(j + 1) - l(l + 1) - 6] \qquad (53)$$

where j is the quantum number of the operator $\mathbf{J}^2$ assuming the values $j = l, l \pm 1$ for $l \geq 1$, and $j = 1$ for $l = 0$, and $E_{\mathrm{JT}}(T)$ is the appropriate JT stabilization energy determined in Section II,C. The multiplicity of each of these energy levels is $2j + 1$. In particular, for the ground state $n = 0$, $l = 0, j = 1, 2j + 1 = 3$, i.e., the initial threefold degeneracy of the electronic term is preserved (transformed in vibronic degeneracy).

For the linear $\Gamma_8 - e$ problem the results obtained by the second-order perturbation theory formally coincide with Eq. (52) with the only difference that in addition to the twofold degeneracy due to the two signs of the j value all the energy levels are also twofold Kramers degenerate, in total fourfold degenerate. The Hamiltonian of the $\Gamma_8 - t_2$ problem is formally similar to that of the $T - t_2$ with 4×4 matrices of the energy spin $S = 3/2$ instead of $i[C_{T_2\gamma}, C_{T_2\bar{\gamma}}]$. The problem is thus reduced to the LS coupling of the appropriate momenta and results in the same energy-level scheme as in the $T - t_2$ problem given by Eq. (53), in which, however, the quantum number of the total momentum $j = l \pm 3/2$, $l \pm 1/2$ if $l > 1$, $j = 3/2 \pm 1$ if $l = 1$, and $j = 3/2$ if $l = 0$.

In the case of $E - b_1$, $E - b_2$, and $T - e$ problems all the $C_{\Gamma\gamma}$ matrices in the vibronic Hamiltonian are mutually commutative and hence all of them can be reduced to the diagonal form by means of a unitary transformation of the basis functions. The corresponding system of vibronic equations can be solved directly. The more complex $T - (e + t_2)$ problem with arbitrary coupling to E vibrations and weak coupling to t_2 vibrations has been solved by the perturbation theory (Bersuker and Polinger, 1973a). Vibronic states of Renner-type systems with weak vibronic coupling were considered analytically by Moffitt and Liehr (1957) and Pople (1960). The pseudo-JT effect for two nondegenerate states mixed by one vibration were considered by Witkowski (1961) and by Fulton and Gouterman (1961).

2. *Strong Vibronic Coupling*

Analytical solutions of the vibronic equations are also possible in the other limiting case of strong vibronic coupling, when $E_{\mathrm{JT}} \gg \hbar\omega_\Gamma$. In this case the inequality of Eq. (9) is also valid, and the AP in the regions near the minima points (and far from the point of degeneracy) have the physical sense of the potential energy of the nuclei, and the adiabatic approximation can be employed.

Our main interest is in the solving the equations of nuclear motion [Eq. (7)]. Here two different cases may be distinguished: (1) the lower sheet of the AP has an equipotential continuum of minima points (a trough), and (2) there are several minimum wells divided by potential barriers. Since the coordinates of the minima points are proportional to the vibronic coupling values, the quadratic terms of the vibronic interactions cannot be neglected in general. It means that case 1 above is exceptional. Nevertheless, taking into account its theoretical importance, we shall consider this case in more detail.

The simplest case with an AP trough is the linear $E - e$ problem. Using the adiabatic electronic basis functions which diagonalize the potential energy matrix [Eq. (27)] and neglecting the nonadiabacity contribution, we come to the Hamiltonian of the type shown in Eq. (7) for each of the AP sheets separately. As shown in Section II,D, the linear $E - e$ problem Hamiltonian has an integral of motion which in the adiabatic basis can be presented by the operator $L_z = -i\partial/\partial\varphi$. It means that its wave functions $\exp(ij\varphi)/(2\pi)^{1/2}$ are also eigenfunctions of the Hamiltonian as a whole. In other words, the angular and radial motions are separated, and the total wave function can be sought for in a multiplicative form: $\Psi = \exp(ij\varphi)\chi(\rho)/(2\pi\rho)^{1/2}$. Here the polar coordinates are used, and the factor $\rho^{-1/2}$ is singled out for convenience. The Hamiltonian for the radial motion is (Longuet-Higgins *et al.*, 1958):

$$H_{\pm} = -\frac{\hbar^2}{2}\frac{\partial^2}{\partial\rho^2} + \frac{\hbar^2 j^2}{2\rho^2} + \tfrac{1}{2}\omega_E^2\rho^2 \pm |V_E|\rho \tag{54}$$

The potential energy in Eq. (54) differs from the AP of Eq. (28) by the presence of the centrifugal energy $\hbar^2 j^2/2\rho^2$, the diagonal element Λ_{nn} in Eq. (7).

Note that the quantum number j can be only a semi-integer, $j = \pm 1/2$, $\pm 3/2$, . . . , and hence the contribution of the centrifugal term is never zero. It is especially large for small ρ values, in particular, for the lowest vibronic states of the upper AP sheet $\epsilon_+(\rho)$, which are localized in the vicinity of the minimum point at $\rho_0^{(+)} = (\hbar^2 j^2/|V_E|)^{1/3}$. This minimum point results from the mutual compensation of two dominant (in this range) forces: the JT force $(-|V_E|)$ and the centrifugal force $\hbar^2 j^2/\rho$. In the lower sheet and for the lowest vibronic states, the motion is localized near the bottom of the trough at a much greater distance ρ_0 from Eq. (29). Here the contribution of the centrifugal terms may be negligible. The lower sheet minima points, distinguished from those of the upper sheet, result from the compensation of the distorting JT force $|V_E|$ with that of the elastic force $-\omega_E^2\rho$. Accordingly, the equilibrium states of the lower sheet are sometimes called elastically stabilized, whereas those of the upper sheet are said to be centrifugally stabilized (Slonczewski, 1963).

For the lowest vibronic states using the harmonic approximation for the AP with respect to small displacements $r = \rho - \rho_0$ from the minima at ρ_0 and with an accuracy up to the terms $\sim V_E^{-2}$, we obtain oscillator solutions of Eq. (54) with energies (Longuet-Higgins *et al.*, 1958):

$$E_{nj}^{(-)} = \hbar\omega_E(n + \tfrac{1}{2}) + (\hbar^2 j^2/2\rho_0^2) - E_{\text{JT}} \tag{55}$$

Similarly, in the same approximation for the states of the upper sheet of the AP: $E_{nj}^{(+)} = \sqrt{3}(\hbar^2 V_E^2/|j|)^{1/3}(n + \tfrac{1}{2})$ (Slonczewski, 1963). However, for the upper sheet states the anharmonicity and the nonadiabatic mixing with the lower sheet states may change this result essentially.

The physical sense of the solution [Eq. (55)] is clear. Alongside the usual radial vibrations of the distorted (at $\rho = \rho_0$) molecular framework with the energy $E_{\text{vib}} = \hbar\omega_E(n + \tfrac{1}{2})$, there are free rotations of the deformation around the geometric center of the molecule (see Fig. 2) with a centrifugal contribution to the energy $E_{\text{rot}} = \hbar^2 j^2/2\rho_0^2$, and an appropriate deformation of the electronic distribution freely following the deformation of the framework, its energy being $E_{\text{el}} = -E_{\text{JT}}$. The energy gap between the two sheets of the AP at the minima points is proportional to V_E^2 (Section II,C), the vibrational energy spacing being $\Delta E_{\text{vib}} = \hbar\omega_E$, whereas the intervals between the rotational levels are $\Delta E_{\text{rot}} \sim V_E^{-2}$. Therefore for strong vibronic coupling $\Delta E_{\text{rot}} \ll \Delta E_{\text{vib}} \ll \Delta E_{\text{el}}$. This energy-level scheme, in which each electronic level is accompanied by its own equidistant vibrational spectrum, each of the levels of the latter having its own rotational structure, is quite similar to the usual cases of, say, a diatomic molecule. However, as stated above (Section II,C), these rotations are not real rotations of the molecule as a whole but pseudorotations in which each atom rotates around its own axis (Fig. 2).

The ground state with $n = 0, j = \pm 1/2$ after Eq. (55) is twofold degenerate and has the same transformation properties, as the initial electronic doublet.

Analogous results for the $T - (e + t_2)$ problem within the so-called d-mode model were obtained by O'Brien (1969, 1971). Here the "rotations" of the system correspond with its free displacements along the two-dimensional equipotential trough. The ground state is again of the same symmetry and multiplicity as the initial electronic term. The same ideas were used by Pooler and O'Brien (1977) for the solution of the $\Gamma_8 - (e + t_2)$ problem in the d-mode model.

In case 2, above, when instead of the equipotential trough there are several minima points divided by potential barriers, we start again with the simplest case of the quadratic $E - e$ problem with the potential energy matrix of Eq. (27). There is a continuous transition in the $E - e$ problem from case 1 to case 2 by a continuous change of the value of the quadratic vibronic constant W_E from zero to $|W_E| \lesssim \frac{1}{2}\omega_E^2$. For the sake of simplicity we consider first the case of weak quadratic coupling $|W_E| \ll \omega_E^2$. Here, again, if we pass to the adiabatic electronic basis, neglect the nonadiabacity mixing of different sheets of the AP (near the bottom of the trough $\rho \sim |V_E|/\omega_E^2$), expand the Hamiltonian of the lower sheet in a series with respect to the W_E/ω_E^2 values, and retain only the linear terms, we obtain (O'Brien, 1964):

$$H = -\frac{\hbar^2}{2}\frac{\partial^2}{\partial\rho^2} - \frac{\hbar^2}{2\rho^2}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{2}\omega_E^2\rho^2$$
$$-|V_E|\rho - W_E\rho^2\cos(3\varphi) \tag{56}$$

As above, the total wave function is $\Psi = \Phi/\sqrt{\rho}$ and Eq. (56) determines the factor Φ. If W_E is sufficiently small, the last term can be taken into account by means of the perturbation theory. Then the Hamiltonian and solutions—energies and wave functions—of the linear $E - e$ problem obtained above can be taken as a zero approximation. The perturbation operator is proportional to $\cos(3\varphi)$, and the matrix elements are nonzero for only $\Delta j = \pm 3$. It means that the ground state ($j = \pm\frac{1}{2}$) cannot be split by this perturbation (in any order of the W_E value). The same is true for all the excited states except those with $|j| = 3(2\nu + 1)/2$, $\nu = 0, 1, 2, \ldots$. The first excited level with $j = \pm 3/2$ is split in the first-order perturbation theory, the fourth level with $j = \pm 9/2$ is split in the third order, the seventh with $j = \pm 15/2$ is split in the fifth order, etc.

The splitting of the first excited state is $\Delta E_{0,\pm 3/2} \approx W_E\rho_0^2 = W_E V_E^2 \omega_E^{-4}$. This value should be much smaller than the spacing of the "rotational" levels of the linear $E - e$ problem $\Delta E_{\text{rot}} \sim \hbar^2\rho_0^{-2} \sim \hbar^2\omega_E^2/2E_{\text{JT}} : \omega_E^2/|W_E| \gg (2E_{\text{JT}}/\hbar\omega_E)^2$. The group-theoretical analysis shows that the twofold degenerate energy levels with $|j| = 3(2\nu + 1)/2$, which are split by the quadratic-term perturbation transform as $A_1 + A_2$ (i.e., they are "accidentally" degenerate), whereas the remaining levels with $|j| \neq 3(2\nu + 1)/2$, which do not split, transform as the twofold irreducible representation E.

If the inequality $\omega_E^2/|W_E| \gg (2E_{\text{JT}}/\hbar\omega_E)^2$ is not valid (but $\omega_E^2/|W_E| \gg 1$), the perturbation theory becomes inapplicable, although the Hamiltonian of Eq. (56) is still valid. In this case the separation of the ρ and φ variables can be carried out by means of the adiabatic approximation considering the radial and angular motions fast and slow, respectively. The Hamiltonian of the fast motion contains the angle φ as a parameter:

$$H(\rho) = -\frac{\hbar^2}{2}\frac{\partial^2}{\partial\rho^2} + \frac{1}{2}\omega_E^2\rho^2 - |V_E|\rho - W_E\rho^2\cos(3\varphi) \tag{57}$$

Neglecting the last term, which is of the order of $|W_E|/\omega_E^2 \ll 1$, we arrive at the simple harmonic oscillator equation, in fact the same as in the linear case.

The potential energy of the slow subsystem for the "rotational" states appropriate to the ground vibrational level of the radial motion can be obtained from Eq. (57) by its averaging with the ground-state vibrational function $\chi_0(\rho - \rho_0)$. The appropriate Hamiltonian is (O'Brien, 1964)

$$H(\varphi) = -\alpha(\partial^2/\partial\varphi^2) - \beta\cos(3\varphi) - E_{\mathrm{JT}} \tag{58}$$

where $\alpha = \hbar^2/2\rho_0^2 \approx \hbar^2\omega_E^2/4E_{\mathrm{JT}}$, $\beta = W_E\rho_0^2 \approx 2\Delta$, E_{JT} and Δ being determined by Eq. (32). The results of numerical solution of this equation obtained by O'Brien (1964) using the rotational states of the linear $E - e$ problem $\exp(ij\varphi)/\sqrt{2}\pi$, $j = \pm 1/2, \pm 3/2, \ldots$, as a basic set are presented in Fig. 9. Similar ideas have been employed by O'Brien (1969) in the solution of the linear $T - (e + t_2)$ problem.

It is obvious that if the potential barriers between the minima are high enough, the criterion of adiabatic separation of the φ and ρ variables in the Hamiltonian is invalid. In this case another approach based on the idea of tunneling splitting can be employed (Bersuker, 1961, 1962). In the

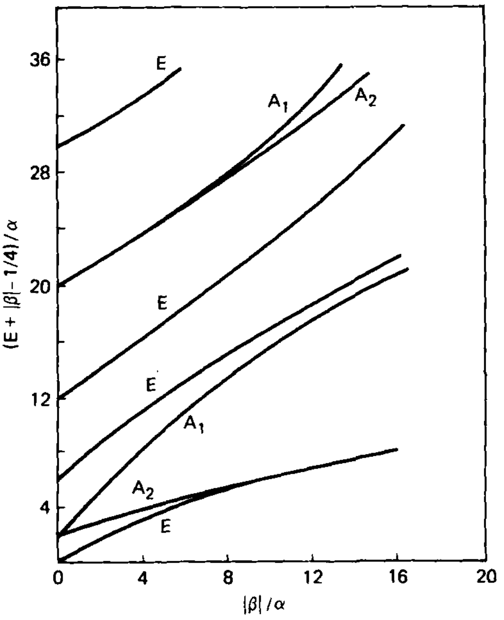


Fig. 9. The energy spectrum of hindered rotations in the quadratic $E - e$ problem; $\beta/\alpha = 2|W_E|V_E^4/\hbar^2\omega_E^8$ is the dimensionless quadratic vibronic constant, while $\epsilon/\alpha = 2EV_E^2/\hbar^2\omega_E^4$ is the dimensionless energy.

zero approximation the nuclear motion is assumed to be localized near the AP minima, and this assumption is equivalent to the supposition that the barrier height between the minima is infinite. Taking account of the finite dimensions of the barriers results in tunneling transitions of the system between the minima point configurations leading to appropriate splittings of the energy levels of the vibrational states of these configurations.

We denote the adiabatic approximation wave function of the system localized in the ith minimum of the AP by

$$\Psi_m^{(i)}(r, Q) = \psi_0(r, Q^{(i)})\Phi_m(Q - Q^{(i)}), \qquad i = 1, 2, \ldots, N \tag{59}$$

where $\psi_0(r, Q^{(i)})$ is the electronic wave function of the lower sheet of the AP taken at the point of the ith minimum $Q = Q^{(i)}$ (N is the number of equivalent minima points), and $\Phi_m(Q - Q^{(i)})$ is the wave function of the mth vibrational state in this minimum configuration. Note that for a more accurate calculation the adiabatic approximation wave function $\psi_0(r, Q)$ must be used instead of the $\psi_0(r, Q^{(i)})$ wave function of Born–Oppenheimer. If one neglects the tunneling transitions, the states described by Eq. (59) are N-fold degenerate due to the equivalency of the N minima configurations. The functions of Eq. (59) are not mutually orthogonal. In the case of weak tunneling one can look for the total wave function in the form of a linear combination of these functions taken as a basis set. For the ground state

$$\Psi = \sum_i c_i \Psi_0^{(i)}(r, Q) \tag{60}$$

The diagonalization of the Hamiltonian with Eq. (60) results in the following linear equations with respect to the energy E and the coefficients c_i:

$$\sum_i (H_{ki} - ES_{ki})c_i = 0 \tag{61}$$

where $S_{ki} = \langle \Psi_0^{(k)}(r, Q) | \Psi_0^{(i)}(r, Q) \rangle$ are the overlap integrals. The equation determining the energies is

$$\det(H_{ik} - ES_{ik}) = 0 \tag{62}$$

Its solution is straightforward. In particular, for the $E - e$ problem ($N = 3$), the threefold degeneracy of the zero-order problem is removed by the tunneling resulting in a singlet A doublet E:

$$E(A) = (H_{11} + 2H_{12})/(1 + 2S), \qquad E(E) = (H_{11} - H_{12})/(1 - S) \tag{63}$$

The tunneling splitting is thus equal to

$$\delta = E(A) - E(E) = 3\Gamma, \qquad \Gamma = (H_{12} - H_{11}S)/(1 + S - 2S^2) \tag{64}$$

and using the wave functions of Eq. (59) and the notation $p^2 = \tilde{\omega}_B^2/\tilde{\omega}_A^2 = 9|W_E|(\omega_E^2 - |W_E|)^{-1}$ ($\tilde{\omega}_A$ and $\tilde{\omega}_B$ are the two frequencies of the E vibrations split in the minimum configuration), we have:

$$\Gamma \approx E_{\mathrm{JT}} \frac{9 + 54p - 6p^3 - p^4}{2(g - p^2)(1 + 3p)^2} \left(\frac{16p}{3p^2 + 10p + 3}\right)^{1/2} \exp\left[-6 \frac{pE_{\mathrm{JT}}}{\hbar\tilde{\omega}_A(1 + 3p)}\right] \tag{65}$$

For $|W_E| \ll \omega_E^2$, i.e., for $p \ll 1$, $p^2 \approx 9|W_E|/\omega_E^2$,

$$\delta \approx 6E_{\mathrm{JT}} \left(\frac{p}{3}\right)^{1/2} \exp\left(-6p \frac{E_{\mathrm{JT}}}{\hbar\omega_E}\right) \tag{66}$$

It follows that $\delta > 0$ and hence the ground state is a vibronic doublet, quite similar to the case of the linear problem $E - e$. In the case of $T - t_2$ or $T - (e + t_2)$ problems, the localization of the nuclear motion in the four trigonal minima of the AP leads to a fourfold degeneracy, which is removed by the tunneling resulting in a singlet A and a triplet T, the latter being the ground state; as in other vibronic solutions it coincides with the initial electronic T term in multiplicity and transformation properties. In the case of six orthorombic minima of the quadratic $T - (e + t_2)$ problem, the tunneling splitting results in $T_1 + T_2$ (Bersuker and Polinger, 1973b, 1974). For more T-term details see Bersuker *et al.* (1975) and Bersuker (1975). Other cases of tunneling splitting were also considered by Bacci (1979) [tunneling between different types of minima of the quadratic $T - (e + t_2)$, when coexisting], Dixon (1977) (tunneling in the $\Gamma_8 - t_2$ problem with strong vibronic coupling), and others (see the Bibliography Review, Bersuker, 1982a).

The group-theoretical analysis of the possible tunneling splittings has been carried out by Martinenas and Dagis (1969) (see also Bersuker and Polinger, 1982). It is obvious that the tunneling approach is valid only if $\delta \ll \hbar\omega_E$ (or $\delta \ll \hbar\tilde{\omega}_A, \hbar\tilde{\omega}_B$). This inequality is obeyed even for $E_{\mathrm{JT}} \gtrsim \hbar\omega_E$. It means that if the JT stabilization energy is of the order of or greater than the magnitude of the appropriate vibrational quantum, there are tunneling splittings of the minimum configuration vibrational energy levels. Hence the tunneling splitting phenomenon is in principle quite general for JT systems with strong or moderate vibronic coupling. The same statement applies as well to systems with multiminimum AP of pseudo-JT origin.

Visually, the tunneling phenomenon may be presented as pulsating motions of the JT deformations when the system is performing many (at least several) vibrations in the distorted configuration of the AP minimum and then changes the direction of distortion to another one, which corresponds to another minimum, equivalent to the first one, and so on. The frequency of these pulsations of the deformation equals the tunneling splitting, and they are accompanied by appropriate redistributions of electron motions, adiabatically following the changes of the nuclear configuration.

However, from the quantitative point of view the results given by Eqs. (62)–(65) are not accurate enough, since they are based on a very poor basis set [Eq. (59)]. The magnitude of the tunneling splitting, as seen from the above equations, is sensitive to the behavior of the vibrational wave functions in the region within the potential barrier where the anharmonicity is important, and hence the use of harmonic oscillator functions in the calculations may be inadequate. This fault is only partly compensated by diagonalizing the total Hamiltonian. The results can be improved by either enlarging the number of minimum configuration vibrational functions used in the basis set, or by improving the behavior of these functions in the underbarrier region (say, by means of the variational principle). In principle, correct behavior of the wave functions in the classically forbidden underbarrier region can be reached also in the quasi-classical approximation considered in the next section.

3. *The Quasi-Classical Approximation*

The quasi-classical approximation can be very useful in solving vibronic problems, provided they can be reduced to one-dimensional ones. Consider again the two cases of vibronic problems: (1) the AP has an equipotential trough and (2) the AP has a discrete set of minima points. In case 1 the quasi-classical approximation can be applied to the description of radial motion after the separation of angular motion along the equipotential variety. In case 2, the angular motion cannot be separated. Nevertheless, the tunneling may be approximately reduced to the one-dimensional motion along the step slope curve from the saddle points to the minima points, the criterion of these separations is given below.

Let us consider the simplest JT system of the case 1 type, the linear $E - e$ problem (Voronin *et al.*, 1976; O'Brien, 1976). Neglecting the nonadiabatic mixing of the two sheets of the AP, the energies of the excited vibronic states can be obtained from the well-known Bohr–Sommerfeld condition of quantization:

$$S_{\pm}(E) = \oint \{2[E - E_{\pm}(\rho)]\}^{1/2}\, d\rho = 2\pi\hbar(n + \tfrac{1}{2}) \qquad (67)$$

where $E_{\pm}(\rho)$ is the potential energy from Eq. (54). The graphical solution of this equation is demonstrated in Fig. 10. The nearly linear function $S_{-}(E)$ displays that for the highly excited vibronic states of the lower sheet of the AP the energy spectrum is almost equidistant. It means that the result of Eq. (55) has in fact a larger range of validity than that determined by the criterion of the harmonic approximation used in its deduc-

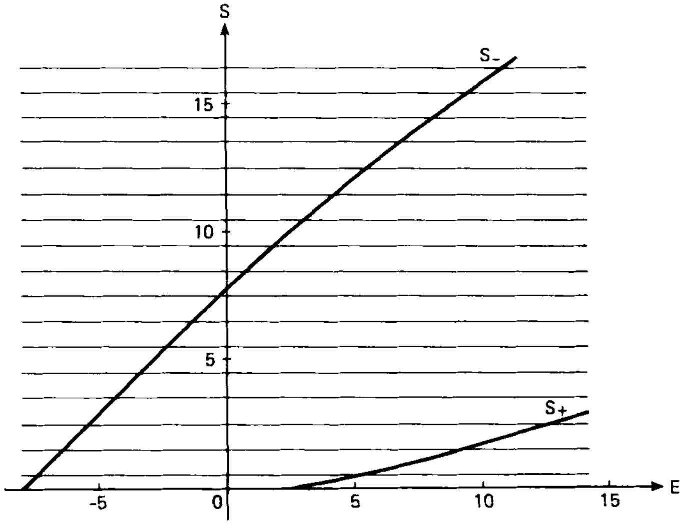


Fig. 10. Quantization of the radial motion in the linear $E - e$ problem after Bohr–Sommerfeld: the graphical solution of the transcendental equation $S_\pm(E) = 2\pi\hbar(n + \frac{1}{2})$. The energy and the action $S_\pm$ are plotted in $\hbar\omega_E$ and $\hbar$ units, respectively.

tion. The equidistant energy levels of the lower sheet in accordance with Eq. (55) are almost linearly decreasing with increasing V_E^2, while those of the upper sheet are increasing. For some of the V_E values some of the upper and lower sheet energy levels intersect, and an accidental degeneracy arises. At these points the nonadiabacity contribution $\Lambda_{+-} = \langle + | -\hbar^2 j\sigma_x/2\rho^2 | - \rangle$, removing this degeneracy becomes of first importance (Fig. 11).

Note that the quasi-classical approach is not necessarily limited by the adiabatic separation of the AP sheets or by the approximation of strong coupling. Indeed, Voronin *et al.* (1976) worked out a quasi-classical solution of the coupled system of vibronic equations arising from the Schrödinger equation with the Hamiltonian [Eq. (24)]. In particular, it follows from this work that with taking account of the nonadiabacity contribution Λ_{+-}, the condition of quantization equation (67) changes to $\cos(S_+/\hbar)\cos(S_-/\hbar) = \pm\bar{\Lambda}_{+-}/4$. A somewhat different approach to the problem has been developed by O'Brien (1976) by including the nonadiabacity operator in the potential energy matrix.

By way of example of case 2, let us consider the quadratic $E - e$ problem. Separating out the one-dimensional motion along the curve of steep slope [Eq. (33)] and joining together the quasi-classical solutions in the neighbor minima regions and in the classically forbidden region under

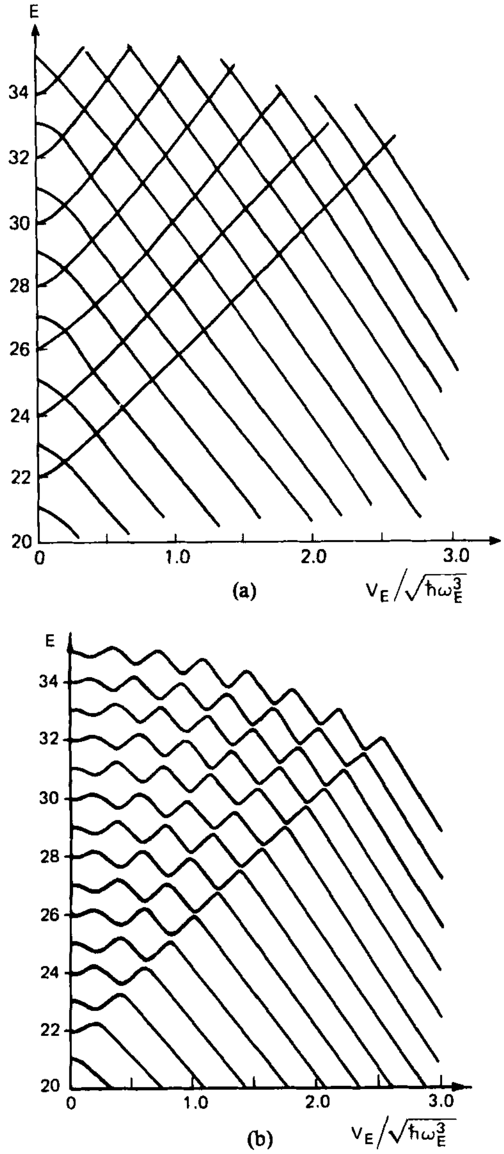


Fig. 11. The vibronic energy levels (in $\hbar\omega_E$ units) versus the dimensionless vibronic constant in the $E - e$ problem for $j = 41/2$ without (a) and with (b) taking nonadiabacity into account.

the potential barrier, we obtain for the tunneling splitting the following expression (Polinger, 1974):

$$\delta = 3\Gamma, \qquad \Gamma = \frac{\hbar\omega}{2\pi} \exp\left(- \frac{1}{\hbar} \int_a^b \{2\mu[\epsilon_-(q) - E_0]\}^{1/2}\, dq \right) \tag{68}$$

where $\epsilon_-(q)$ is the lower sheet of the AP; a and b are the points of classical return at the entrance and exit from the forbidden underbarrier area; respectively, ω is the frequency of vibrations in the AP minimum configuration along the steep slope line, and E_0 is the energy of the ground vibrational level. The integral in Eq. (68) is taken along the contour of Eq. (33). The direct evaluation of this integral in the case of $|W_E| \ll \omega_E^2$ gives

$$\delta \approx 3(\hbar\omega_E/2\pi)\, \exp[-0.6p(E_{\mathrm{JT}}/\hbar\omega_E)]$$

In the same paper (Polinger, 1974), quasi-classical estimations of the tunneling splitting for the case of trigonal minima of the $T - (e + t_2)$ problem were also obtained.

The above quasi-classical approach to the problem of tunneling splitting allows us in principle to obtain assymptotically exact results, provided that the vibronic coupling is sufficiently strong. The larger the V_Γ value is, the better the criterion of the quasi-classical approach obeyed and the less is the error introduced by neglecting the nonadiabacity contribution along the total curve of steep slope. Strictly speaking, the integral in Eq. (68) has to be taken along the stationary trajectory under the potential barrier (Baz' *et al.*, 1971). The use of the steep-slope curve instead of the stationary trajectory is equivalent to neglect of the centrifugal force (Karkach and Osherov, 1978). For sufficiently large vibronic coupling constants V_Γ, resulting in large radius of curvature of the trajectory, the contribution of the centrifugal term becomes negligible.

B. Numerical Solutions

Most vibronic problems $E_{\mathrm{JT}} \sim \hbar\omega_\Gamma$ and analytical solutions of the vibronic equations are inaccurate, at least from the point of view of quantitative results. Most numerical methods used in JT problem calculations are based either on the reduction of the problem to an algebraic one using an appropriate basis set, or on the use of classical variational methods.

The simplest basis set seems to be that of the weak vibronic coupling formed by the eigenfunctions of the zero-order Hamiltonian H_0 (Section III,A,1). The total wave functions of the Hamiltonian [Eq. (23)] may be sought for in the form of the following expansion:

$$\Psi = \sum_{\bar\gamma} \sum_{\cdots n_{\Gamma\gamma} \cdots} c_{\bar\gamma} \cdots n_{\Gamma\gamma} \cdots \psi_{\bar\Gamma\bar\gamma}(r) | \cdots n_{\Gamma\gamma} \cdots \rangle \tag{69}$$

This leads to the usual secular equation for the coefficients $c_{\bar{\gamma}} \cdots n_{\Gamma\gamma} \cdots$ and energies, its order being determined by the number of functions retained in the expansion of Eq. (69). This method gives acceptable results in the case of weak and, sometimes, moderate vibronic coupling, but it is invalid in the case of strong coupling. The larger the vibronic coupling is, the larger should be the number of terms in the expansion equation (69), and hence the dimension of the secular equation to be solved in order to get reasonable results. The upper limit of the vibronic constant values, for which the weak basis-set method is still applicable is thus limited by the computer's ability. On the other hand, the inaccuracy of the method is greater, the higher in energy is the vibronic state to be evaluated.

These limitations of the method may be lessened by means of symmetry considerations. As usual, the latter allow us to reduce the problem to numerical solutions of simplified equations resulting from the appropriate separation of variables, for which there are integrals of motion. For instance, in the case of the linear $E - e$ problem, only the equation of the radial motion has to be solved numerically. The separation of the angular variables should be carried out also for the basis functions. The two-dimensional oscillator wave functions $|n_\theta, n_\epsilon\rangle$ within the degenerate set with a fixed number of phonons $n = n_\theta + n_\epsilon$ can be transformed to the linear combinations $\sim\exp(il\varphi)\chi_{nl}(\rho)$, $l = -n, -n + 2, \ldots, n$. This can be done by means of the matrices of irreducible representations of the appropriate chain of subgroups $SU(2) \equiv R(3) \rightarrow C_\infty$ [see the discussion following Eq. (51)]. Thus the radial functions $\chi_{nl}(\rho)$ of the two-dimensional oscillator (in the representation where $L_z = -i\partial/\partial\varphi$ is diagonal) can be taken as a basis set. For this latter the matrix of the Hamiltonian has a tridiagonal form (Moffitt and Thorson, 1958; Longuet-Higgins *et al.*, 1958). The solutions of the appropriate $E - e$ problem have been also obtained by Struck and Herzfeld (1966), Uehara (1968), and Muramatsu and Sakomoto (1978). The energy-level dependence on the vibronic constant value is illustrated in Fig. 12. For small V_E values the energies are close to those obtained in Eq. (52) by means of the perturbation theory. For large V_E values the vibronic levels have the vibrational–rotational structure well described by the formulas of strong vibronic coupling [Eq. (55)].

The solution of the problem carried out separately for each j value is equivalent to the decomposition of the matrix of the total Hamiltonian in blocks labeled by the irreducible representations of the axial group $E_{|j|}$. This enlarges essentially the computer abilities allowing us to take into account a greater number of terms in the expansion [Eq. (69)]. Here the classification of the basis functions on the irreducible representations of

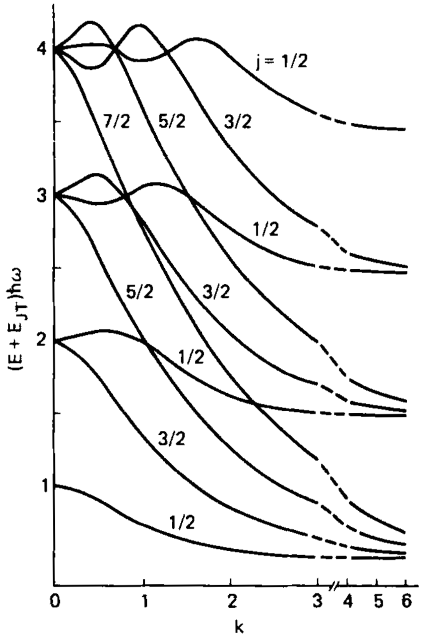


Fig. 12. Vibronic energy levels in the $E - e$ problem versus $k = |V_E|/(\hbar\omega_E^3)^{1/2}$ obtained by numerical calculations (after Muramatsu and Sakamoto, 1978).

the chain of subgroups

$$U(f_{\Gamma}) \to SU(f_{\Gamma}) \to R(f_{\Gamma}) \to R(3) \to G_0 \qquad (70)$$

where f_{Γ} is the multiplicity of the degenerate term, may be very useful. It is important that the consequent reduction of the symmetry on the order of Eq. (70) and the appropriate reduction of the irreducible representations as a rule does not result in repeating irreducible representation. This makes the construction of symmetry-adapted basis functions and their labeling with genealogic quantum numbers easier. The Hamiltonian is a scalar of the G_0 group, but transforms as nontotally symmetric representations of the higher symmetry groups. The application of the Wigner–Eckart theorem to the nontotally symmetric tensor operators of the Hamiltonian simplifies the procedure of block separation of the matrix Hamiltonian; for more details see the review article by Judd (1974).

The above method of group genealogy is most efficient when the G_0 group of the vibronic Hamiltonian is one of the irreducible Lee groups, as in the case of the linear $E - e$ problem. But even if this is not the case, the genealogic quantum numbers still simplify the solution of the vibronic problem. For instance, they have been successfully used by Caner and Englman (1966) in the solution of the linear $T - t_2$ problem. Linear combination Φ_{lm} belonging to the irreducible representations $D^{(l)}$ of the $R(3)$ group (eigenfunction of the vibrational momentum operator L) have been constructed by the wave functions $|n_\xi n_\eta n_\zeta\rangle$ of the three-dimensional isotropic oscillator of the T_2 vibrations. Then, taking into account the fact that the electronic functions of the T-term transform as $D^{(1)}$ of the $R(3)$ group (the energy spin $S = 1$), the wave functions of the total momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ were built up according to the rules of the addition of momenta. These functions are the weak-coupling basis set. The further reduction $R(3) \rightarrow O_h$ results in repeating representations mixed by the operator of vibronic interactions.

The result of diagonalization of the appropriate matrix by the weak coupling basis, cut at the state $J = 13$, is given in Fig. 13. Note that in agreement with the results of perturbation theory in the case of weak coupling (the left-hand side of the Fig. 13), the spectrum consists of

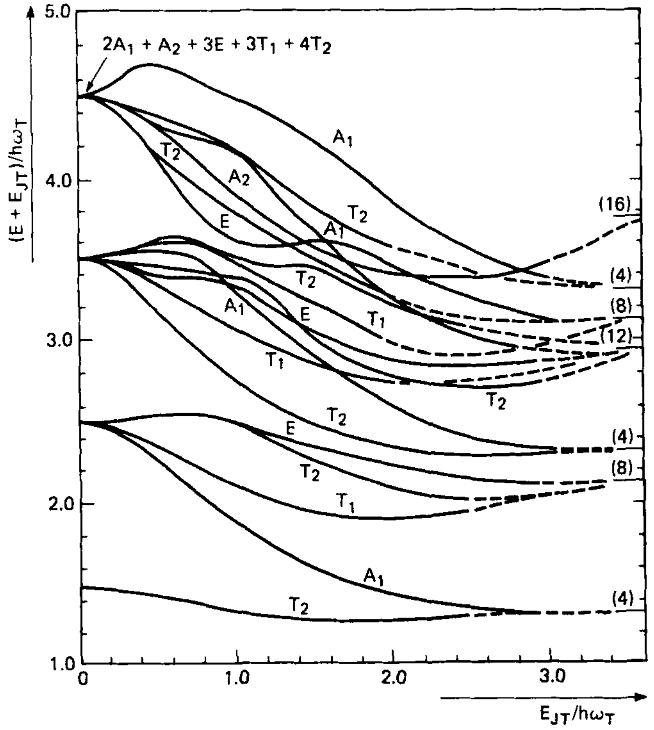


Fig. 13. Vibronic energy levels in the $T - t_2$ problem versus the JT stabilization energy (after Caner and Englman, 1966).

equidistant levels (with a spacing equal to $\hbar\omega_T$) weakly split by vibronic interaction. In the strong coupling limit there are two equidistant sets of energy levels with $\hbar\omega_T$ and $\hbar\omega_T\sqrt{2/3}$ spacings, respectively, describing the appropriate harmonic vibrations in the trigonal minima.

For more complicated cases when the symmetry of the vibronic Hamiltonian cannot be described by a Lee group, the computational possibilities may be enlarged by using special algorithms. One of them is the so-called method of minimal iterations, the Lancozs method (Faddeev and Faddeeva, 1963). It has been used by Muramatsu and Sakamoto (1978) to solve the $E - (b_1 + b_2)$ problem by diagonalizing a 231 × 231 matrix, which corresponds to the mixing of all the vibrational states with $n_1 + n_2 \leq 20$. In the case of $\omega_1 = \omega_2$ and $V_1 = V_2$, this solution corresponds to the $E - e$ problem. For the latter the results of the diagonalization of the 200 × 200 matrix for the state $j = 1/2$ corresponding to the mixing of the vibrational states with $n_\theta + n_\epsilon \leq 199$ have been obtained.

The number of mixing basis states to be retained in the expansion equation (69) depends also on the number of degrees of freedom of the JT active coordinates. The multiplicity of the nth vibrational level of an $s$fold isotropic oscillator is $\sim f_\Gamma n^{s-1}/(S - 1)!$, where f_Γ is the multiplicity of the electronic term. For instance, for the $T - (e + t_2)$ problem ($f_T = 3$, $S = 5$), and if the mixing of the vibrational states up to the $N = 8$ is taken into account, $n_\theta + n_\epsilon + n_\xi + n_\eta + n_\zeta \leq 8$, the matrix to be solved has the dimension 3861 × 3861. If symmetry-adapted functions are used, the dimension of each block of this matrix is reduced by an order of magnitude. But even then the diagonalization of the matrix is at the upper limit of the computer abilities. On the other hand, mixing of the vibrational states up to $N = 8$ allows us to obtain satisfactory results only for moderate vibronic coupling with $E_{\mathrm{JT}} \lesssim 2\hbar\omega_\Gamma$ and only for the lowest vibronic states. The present status in the calculations of the vibronic spectrum of the linear $^{2S+1}T - (e + t_2)$ problem is illustrated schematically in Fig. 14.

The solution of the $\Gamma_8 - t_2$ problem was carried out by Thorson and Moffitt (1958) and by Judd (1977) (Fig. 15). With the variation of the vibronic constant, the excited states oscillate near the average values $\hbar\omega_T(n + \frac{3}{2}) - E_{\mathrm{JT}}$, at some points forming accidentally degenerate multiplets. Similar results for the $E - e$ problem were obtained by Muramatsu and Sakomoto (1978). A more refined calculation shows that the intersections of different levels have a small dispersion. The origin of the effect as a whole was discussed by Judd (1977). Numerical solutions of the $\Gamma_8 - (e + t_2)$ problem in the case of the d-mode model ($\omega_E = \omega_T$, $V_E = V_T$) were obtained by Pooler and O'Brien (1977).

There is a large class of vibronic systems with pseudodegenerate terms for which if $\Delta \sim \hbar\omega$, the solution can be carried out but numerically. This

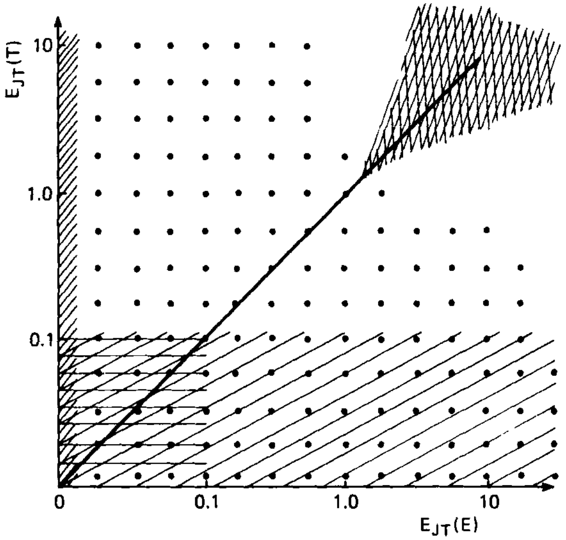


Fig. 14. Present status of the vibronic spectra calculations in the $T - (e + t_2)$ problem. The tetragonal $E_{JT}(E)$ and trigonal $E_{JT}(T)$ JT stabilization energies are plotted on the axis in $\hbar\omega_E = \hbar\omega_T = \hbar\omega$ units in a logarithmic scale. The area of possible parameter values in this scheme is divided into domains of applicability of the perturbation theory of Moffitt and Thorson (1957) (horizontal shading), the numerical results of Caner and Englman (1966) (inclined thick shading), the perturbation theory of Bersuker and Polinger (1973a) (inclined thin shading), the d-mode model, $E_{JT}(E) = E_{JT}(T)$, of O'Brien (1971) (inclined line), the qualitative results of O'Brien (1969) (double shading), the numerical calculations of Muramatsu and Sakamoto (1978) and Boldyrev *et al.* (1981) (marked by points).

also concerns the case when the group of near-lying electronic terms originates from the spin–orbit splitting. If the latter occurs in the first-order perturbation theory, the splitting is usually not small and must be taken into account alongside and simultaneously with the vibronic interaction. The cubic polyatomic system in triplet electronic states are typical examples of this kind. They lead to the one of the most difficult computational $^{2S+1}T - (e + t_2)$ problem with taking account of the spin–orbit interaction and low-symmetry crystal fields (or other low-symmetry perturbations). The latter lower the symmetry of the system thus making the group-theoretical classification more difficult. In addition to the large number of mixing electronic states $f = 3(2S + 1)$ and of the vibrational degrees of freedom (in addition to the five JT active E and T_2 coordinates, the electronic states may be mixed by other coordinates, too), there are a large number of free parameters (two vibrational frequencies, three spin–orbit constants, at least two vibronic constants, and one or more low-symmetry perturbation parameters). All this increases enormously

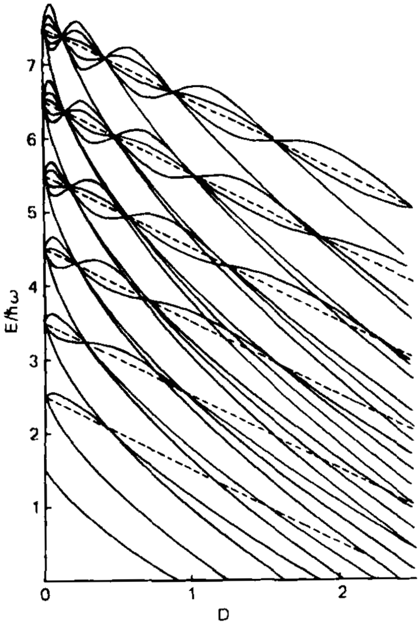


Fig. 15. The vibronic energy levels of the $\Gamma_8 - t_2$ problem in $\hbar\omega_T$ units versus $D = E_{JT}/\hbar\omega_T$.

the dimension of the secular matrix to be solved and requires its repeating solution. For instance, for the $^4T - (e + t_2)$ problem with the number of mixing vibrational basis states $\Sigma_\gamma n_\gamma \leq 8$ and without additional complications, the matrix dimension is 15444 × 15444. One of the ways to overcome these difficulties by using the so-called method of coordinate relaxation based on consequent minimization of the functional of the energy for each of the coordinates $c_\gamma \cdots n_{\Gamma\gamma} \cdots$ of the function [Eq. (69)] was suggested recently by Boldyrev *et al.*, 1981.

Note that in all of the iteration methods based on the variational principle the transformation properties of the probe function are preserved during the minimization process. This means that if the probe function $\Psi_{\Gamma\gamma}^{(0)}$ was chosen transforming as the γ line of the Γ representation the minimization procedure results in the lowest energy function $\Psi_{\Gamma\gamma}$ with the same transformation properties. One of the advantages of the method of coordinate relaxation is that it is not necessary to retain in the computer memory the whole matrix to be diagonalized. If, as in the case under consideration, the matrix elements are sufficiently simple, they can be recalculated when necessary, and then only the calculated eigenvectors have to be retained in the memory. In this case the occupied memory volume is proportional to the dimension of the basis set M, but not M^2 as in the usual methods. The results for the ${}^3T - (e + t_2)$ problem, taking account of the spin–orbit interaction and the trigonal field splittings, were obtained by Boldyrev *et al.* (1981).

Another method based on the variational principle is the method of canonical transformations. As a result of the shift transformation $\mathbf{U} = \exp(\lambda \mathbf{S})$, where the operator $\mathbf{S}$ may be taken, for instance, as a combination of $\partial/\partial Q_{\Gamma\gamma}$ and $\mathbf{C}_{\Gamma\gamma}$ magnitudes, the vibronic Hamiltonian can be reduced to the form $\tilde{\mathbf{H}}_0 + \tilde{\mathbf{V}}$, where $\tilde{\mathbf{H}}_0$ is sufficiently simple. The parameter λ can be obtained from the condition of energy minimum in the ground state of the $\tilde{\mathbf{H}}_0$ Hamiltonian. As a result of this shift transformation the operator of vibronic coupling becomes proportional to the so-called renormalized coupling constant $V_\Gamma \exp[-\alpha E_{\mathrm{JT}}/(\hbar\omega)]$, where α is a numerical coefficient. This renormalized constant can serve as a small parameter of the perturbation theory for both limit cases $V_\Gamma \rightarrow 0$ and $V_\Gamma \rightarrow \infty$. It may be expected that such a perturbation theory gives acceptable results also for intermediate values of V_Γ (Wagner, 1972; Barentzen and Polansky, 1978; Barentzen *et al.*, 1981). The method gives good results for the ground state of the system, and this is quite understandable in view of its variational nature.

C. Vibronic Reduction Factors

Some general properties of the ground vibronic state can be elucidated using group-theoretical considerations. In all the vibronic problems considered so far the ground vibronic term has the same multiplicity and transformation properties as the initial degenerate electronic term $\bar{\Gamma}$. But until now nobody proved the theorem evidencing that this is a general fact and the ground vibronic state remains $\bar{\Gamma}$ independent of the vibronic parameters of the system. Nevertheless, as far as nobody proved the contrary, the vibronic ground state may be assumed to be $\bar{\Gamma}$.

Consider the properties of the system determined by the ground vibronic state. In the presence of small perturbations described by the operator $F_{\Gamma\gamma}$ the perturbation matrix determining the observable properties can be evaluated by means of the Wigner–Eckart theorem. The problem simplifies when $F_{\Gamma\gamma}$ depend on either electronic or nuclear coordinates (and not on both). Suppose, first, that the former case is realized, $F_{\Gamma\gamma} = F_{\Gamma\gamma}(r)$. The vibronic wave function of the ground state can be presented in the form of a tensor convolution:

$$\Psi_{\bar{\Gamma}\bar{\gamma}}(r, Q) = \sum_{\Gamma\gamma\gamma_1,\gamma_2} \chi_{\Gamma_1\gamma_1}(Q)\psi_{\bar{\Gamma}\gamma_2}(r)\langle\Gamma_1\gamma_1\bar{\Gamma}\gamma_2|\bar{\Gamma}\bar{\gamma}\rangle \tag{70}$$

where Γ_1 obeys the condition: $\bar{\Gamma} \in \Gamma_1 \times \bar{\Gamma}$. Calculating the matrix elements of the operator $F_{\Gamma\gamma}(r)$ with the wave functions [Eq. (70)], we have (Englman *et al.*, 1970; Englman, 1972; Bersuker and Polinger, 1973a)

$$\langle \Psi_{\bar{\Gamma}\gamma_1}(r, Q)|F_{\Gamma\gamma}(r)|\Psi_{\bar{\Gamma}\gamma_2}(r, Q)\rangle = K(\Gamma)\langle \Psi_{\bar{\Gamma}\gamma_1}(r)|F_{\Gamma\gamma}(r)|\psi_{\bar{\Gamma}\gamma_2}(r)\rangle \tag{71}$$

where

$$K(\Gamma) = f_{\bar{\Gamma}} \sum_{\Gamma_1} (-1)^{j(\Gamma_1)} \begin{Bmatrix} \bar{\Gamma} & \Gamma & \bar{\Gamma} \\ \bar{\Gamma} & \Gamma_1 & \bar{\Gamma} \end{Bmatrix} \langle \chi^2_{\Gamma_1} \rangle \tag{72}$$

Here $\{:::\}$ is the 6Γ – symbol for the G_0 group; $j\ (\Gamma_1)$ is the fictitious moment of the Γ_1 representation; and the $\langle \chi^2_\Gamma \rangle$ values are determined by the following equations:

$$\langle \chi_{\Gamma_1\gamma_1}|\chi_{\Gamma_2\gamma_2}\rangle = \langle \chi^2_{\Gamma_1}\rangle\, \delta_{\Gamma_1\Gamma_2}\, \delta_{\gamma_1\gamma_2} \tag{73}$$

For instance, for the $E - e$ problem of a trigonal or cubic system, we have:

$$\begin{aligned} K(A_1) &= 1 = \langle \chi^2_{A_1}\rangle + \langle \chi^2_{A_2}\rangle + \langle \chi^2_E\rangle \\ K(A_2) &= p = \langle \chi^2_{A_1}\rangle + \langle \chi^2_{A_2}\rangle - \langle \chi^2_E\rangle \\ K(E) &= q = \langle \chi^2_{A_1}\rangle - \langle \chi^2_{A_2}\rangle \end{aligned} \tag{74}$$

Since $\langle \chi^2_\Gamma \rangle \geq 0$ for all the Γ values and their sum equals a unity, $K(\Gamma) \leq 1$ for all the $\Gamma \neq A_1$. Thus for the ground-state properties the vibronic interaction reduces the matrix elements of electronic operators $K(\Gamma)$ times. This effect is called vibronic reduction, and $K(\Gamma)$ values are called vibronic reduction factors.

In the cases when the symmetry of the problem becomes "accidentally" higher than G_0, some of the irreducible representations Γ of the G_0 group unite in irreducible representations of higher dimension. It means that some of the $\langle \chi^2_\Gamma \rangle$ values are interrelated, resulting in some relations between the appropriate vibronic reduction factors $K(\Gamma)$. Let us consider the linear $E - e$ problem which is "accidentally" axially symmetric. Since the wave functions $\Psi_\theta(r, Q)$, $\Psi_\epsilon(r, Q)$, $\psi_\theta(r)$, $\psi_\epsilon(r)$, and the normal coordinates Q_θ and Q_ϵ are real, the functions $\chi_{\Gamma\gamma}(Q)$ in Eq. (70) are also real. On the other hand, using the energy spin functions $\psi_{\pm 1/2}(r)$ and $\Psi_{\pm 1/2}(r, Q)$,

$$\psi_{\pm 1/2}(r) = \frac{1}{\sqrt{2}}\,[\psi_\theta(r) \pm i\psi_\epsilon(r)], \quad \Psi_{\pm 1/2}(r, Q) = \frac{1}{\sqrt{2}}[\Psi_\theta(r, Q) \pm i\Psi_\epsilon(r, Q)] \tag{75}$$

we can rewrite Eq. (70) in the following form:

$$\Psi_{1/2} = \chi_0\psi_{1/2} + \chi_1\psi_{-1/2}, \qquad \Psi_{-1/2} = \chi_1^*\psi_{1/2} + \chi_0^*\psi_{-1/2} \tag{76}$$

where in polar coordinates $\chi_j(Q) = f_j(\rho)\exp(ij\varphi)$, $j = 0, \pm 1/2, \pm 1$, and $f_j(\rho)$ is a real function. By comparison of Eqs. (76) and (70), one obtains (Leung and Kleiner, 1974):

$$\chi_{A_1} = \operatorname{Re}\chi_0, \quad \chi_{A_2} = -\operatorname{Im}\chi_0, \quad \chi_{E\theta} = \sqrt{2}\operatorname{Re}\chi_1, \quad \chi_{E\epsilon} = -\sqrt{2}/\operatorname{Im}\chi_1 \tag{77}$$

Since $\chi_0 = f_0(\rho)$ is real, $\chi_{A_2} = 0$ and (Ham, 1968) $K(A_2) + 1 = 2K(E)$, or

$$2q - p = 1 \tag{78}$$

This is an exact relation, provided the ideal linear $E - e$ problem is considered. For real systems it becomes approximate, the deviations being due to the contribution of quadratic terms, to mixing with excited states, to the multimode nature of the vibronic coupling (Section IV), etc. In general, $\langle\chi^2_{A\varphi}\rangle \geq 0$ and $2q - p = 1 - 4\langle\chi^2_{A_2}\rangle \leq 1$.

Similarly, for the linear $T - \mathrm{d}$ problem, the Hamiltonian is "accidentally" of higher (than G_0) symmetry $R(3)$, and the irreducible representations E_g and T_{2g} are unite in the representation $D^{(2)}$ of the three-dimensional group of rotations. It means that $K(E) = K(T)$. By means of considerations similar to those used above in the linear $E - e$ case, it can be shown that in the linear $T - \mathrm{d}$ problem the tensor convolution, Eq. (70) does not contain terms $\sim\chi_{T_1\gamma}(Q)$. Accordingly, $\langle\chi^2_{T_1}\rangle = 0$ in Eq. (72). Together with the equation $K(E) = K(T_2)$, it leads the following relation (O'Brien, 1971; Romestain and D'Aubigne, 1971):

$$K(E) = K(T_2) = \tfrac{2}{5} + \tfrac{3}{5}K(T_1) \tag{79}$$

In general, $\langle\chi^2_{T_1}\rangle \geq 0$ and

$$K(E) + \tfrac{3}{2}[K(T_2) - K(T_1)] = 1 - 3\langle\chi^2_{T_1}\rangle \leq 1 \tag{80}$$

Analytical expressions for the vibronic reduction factors as functions of the vibronic parameters can be obtained, but for the limiting cases of weak and strong coupling, for which the wave functions are known explicitly. Following Eq. (71), the $K(\Gamma)$ values can be calculated as the relation between the matrix elements $\langle\Psi_{\bar{\Gamma}\gamma}(r, Q)|F_{\Gamma\gamma}(r)|\Psi_{\bar{\Gamma}\gamma_2}(r, Q)\rangle$ and $\langle\psi_{\bar{\Gamma}\gamma_1}(r)|F_{\Gamma\gamma}(r)|\psi_{\bar{\Gamma}\gamma_2}(r)\rangle$. For instance, in the linear $E - e$ problem in the second-order perturbation theory approximation with respect to the vibronic constant V_E, we have $q = 1 - 2E_{\mathrm{JT}}/\hbar\omega_E$, $p = 1 - 4E_{\mathrm{JT}}/\hbar\omega_E$. In the case of strong vibronic coupling using the adiabatic states [Eq. (49)], one obtains $q \approx 1/2$, $p = 0$.

Similar results for the $T - (e + t_2)$ problem and its particular cases, the $T - e$ and $T - t_2$ problems, were obtained by Ham (1965, 1972) and

Englman *et al.* (1970). In the case of weak coupling, $K(E) + \frac{3}{2}[K(T_2) - K(T_1)] = 1$. It follows from the comparison with Eq. (80) that $\langle \chi^2_{T_1} \rangle = 0$. A more accurate calculation shows that this relation is valid only up to fourth order in the V_T value and slightly breaks in the range of moderate coupling, while in the strong coupling limit it becomes again exactly valid (Leung and Kleiner, 1974).

The general feature of all the vibronic reduction factors is their strong dependence on the $E_{JT}/\hbar\omega$ value, due to which, even for moderate vibronic coupling, the vibronic reduction of physical magnitudes may be very strong (reaching several orders of magnitudes). This was first noted by Bersuker and Vekhter (1963) by calculating the spin–orbit splitting of the $^2T_2$ term with taking account of vibronic interactions. Ham (1965, 1968) generalized this idea, proving its applicability to all cases of physical magnitudes dependent on only electronic variables (the effect is sometimes called the Ham effect).

In the second-order perturbation theory the influence of the operator $F_{\Gamma\gamma}(r)$ can be taken into account by means of the following tensor convolution:

$$\mathscr{F}^{(2)}_{\bar{\Gamma}\bar{\gamma}}(r, Q) = \sum_{\gamma_1\gamma_2} F_{\Gamma\gamma_1}(r)\,\mathscr{D}(r, Q)F_{\Gamma\gamma_2}(r)\,\langle \Gamma\gamma_1\Gamma\gamma_2|\bar{\Gamma}\bar{\gamma}\rangle \tag{81}$$

where the Green's function $\mathscr{D}(r, Q)$ is

$$\mathscr{D}(r, Q) = \sum_{\Gamma\gamma n}{}' \frac{|\Psi_{\Gamma\gamma n}(r, Q)\rangle\langle\Psi_{\Gamma\gamma n}(r, Q)|}{E_0 - E_{\Gamma n}} \tag{82}$$

Here the summation is performed over all the excited states $\Psi_{\Gamma\gamma n}(r, Q)$ (E_0 being the energy of the ground state). Without vibronic interactions the $\Psi_{\Gamma\gamma n}$ function can be factorized into electronic and vibrational functions, the latter being excluded due to their mutual orthogonality. Then

$$\mathscr{F}^{2}_{\bar{\Gamma}\bar{\gamma}}(r) = \sum_{\Gamma\gamma,\gamma_1,\gamma_2} F_{\Gamma\gamma_1}(r)\left\{\frac{|\psi_{\Gamma\gamma}(r)\rangle\langle\psi_{\Gamma\gamma}(r)|}{E_0 - E_\Gamma}\right\} F_{\Gamma\gamma_2}(r)\langle\Gamma\gamma_1\Gamma\gamma_2|\overline{\Gamma\gamma}\rangle \tag{83}$$

becomes independent on nuclear coordinates. When the vibronic interactions are taken into account two implications arise. First, the excited vibronic states of the electronic term under consideration may be envolved as intermediate states due to the nonorthogonality of the vibrational states. This possibility was considered by Ham (1965) in the case of the $T - e$ problem with spin–orbit interaction λLS taken into account as a perturbation. In the limiting case of strong vibronic coupling, $E_{\mathrm{JT}}(E) \gg \hbar\omega_E$, the appropriate perturbation operator takes the form:

$$\mathbf{H}^{(2)}_{\mathrm{SO}} = -\frac{\lambda^2}{3E_{\mathrm{JT}}(E)}\left(L^2_x\mathbf{S}^2_x + L^2_y\mathbf{S}^2_y + L^2_z\mathbf{S}^2_z\right) \tag{84}$$

The physical sense of this result becomes clear if one takes into account that in the case of strong vibronic coupling $3E_{\mathrm{JT}}(E)$ is just the energy gap between the AP sheets at the point $Q_1^{(0)}$ of the AP minimum configuration. It means that in the limit case of strong vibronic coupling the JT distortion is equivalent to the appropriate static tetragonal crystal field, and the correct result can be obtained from Eq. (83), where the summation is carried out over the upper sheets of the AP in the configuration of the AP minimum at $Q = Q_1^{(0)}$.

Another source of influence of the vibronic interactions on the second-order splitting is due to the contribution of the excited electronic states. Owing to the same transformation properties of the operator $\mathscr{F}^{(2)}_{\bar{\Gamma}\bar{\gamma}}(r, Q)$ after Eq. (81) and $\mathscr{F}^{(2)}_{\bar{\Gamma}\bar{\gamma}}(r)$ after Eq. (83), the difference in their matrix elements can be taken into account by means of second-order vibronic reductions factors $K^{(2)}(\bar{\Gamma})$ (Vekhter, 1973). If only one excited electronic term at an energy distance Δ is taken into account and the energy difference $E_{\Gamma n} - E_{\Gamma m}$ between its vibronic states is neglected as compared with Δ, $\Delta \gg |E_{\Gamma n} - E_{\Gamma m}|$, then $K^{(2)}(\bar{\Gamma}) \approx K(\bar{\Gamma})$. In general, however, the higher order vibronic reduction factors are not reduced to that of the first-order $K(\Gamma)$. This is true also in the cases when there is more than one excited term mixed with the ground-state term by the perturbation, provided that not for all of them $\Delta \gg |E_{\Gamma n} - E_{\Gamma m}|$.

The idea of vibronic reduction factors can be generalized to arbitrary matrix elements of not only the ground-state term. Let us denote the vibronic factor (in the case under consideration it is not necessarily a reduction factor) by

$$K(\Gamma_1|\Gamma|\Gamma_2) = \frac{\langle\Psi_{\Gamma_1}\|F_\Gamma\|\Psi_{\Gamma_2}\rangle}{\langle\psi_{\bar{\Gamma}}\|F_\Gamma\|\psi_{\bar{\gamma}}\rangle} \tag{85}$$

This vibronic factor may be especially useful when, as in the case of strong vibronic coupling, there are near-lying vibronic states which are necessarily mixed by the perturbation. For instance, in the quadratic $E - e$ problem these are the two tunneling energy levels E and A, which are mixed by electronic operators of E symmetry. In this case the matrix elements $\langle\Psi_A|F_{E\gamma}|\Psi_{E\gamma}\rangle$ can be reduced to the vibronic factor $r = K(A|E|E)$. In the strong-coupling limit the r value can be calculated by means of tunneling functions Eq. (49), resulting in $r = \pm\sqrt{2}/2$ (Ham, 1972).

Consider now as a perturbation the operator $F_{\Gamma\gamma}(Q)$, which is a function of nuclear coordinates Q. The case of the $F_{\Gamma\gamma} = A_{\Gamma\gamma}Q_{\Gamma\gamma}$ perturbation and its change under the vibronic interaction influence is of practical interest, say, in the analysis of the quadrupole splittings in the ESR and acoustic nuclear resonance spectra. In these problems $A_{\Gamma\gamma}$ are functions of the nuclear spin of the JT center. The influence of the $Q_{\Gamma\gamma}$ operator on the vibrational subsystem through the vibronic coupling affects also the electronic subsystem. If this influence is sufficiently small and can be taken into account as a perturbation splitting the ground state, the matrix elements of the perturbation can be expressed by the vibronic reduction factors. On the other hand, this same splitting determined directly is proportional to the reduced-matrix element $\langle \Psi_\Gamma \| Q_\Gamma \| \Psi_\Gamma \rangle$. It follows that $\langle \Psi_{\bar{\Gamma}} \| Q_\Gamma \| \Psi_{\bar{\Gamma}} \rangle = -V_\Gamma K(\Gamma)/\omega_\Gamma^2$ (Ham, 1972), i.e., the matrix elements of JT normal coordinates increase with the vibronic constant V_Γ. This "vibronic amplification" of the splittings caused by nuclear coordinate operators may manifest itself not only in the quadrupole splitting, but also in other effects, in particular in the Stark effect in systems without inversion symmetry.

IV. The Multimode JT Effect

The vibronic problems considered above are called ideal problems in the sense that the number of JT active coordinates with given symmetry is taken minimal. Meanwhile in real polyatomic systems there are more than one vibration of a given type. For instance, even in the simple tetrahedral ML_4 molecule there are two sets of T_2-type vibrations both JT active, and therefore the vibronic problem for a T term of this molecule is not $T - (e + t_2)$, but $T - (e + t_2' + t_2'')$, including thus eight vibrational degrees of freedom instead of five in the ideal case. The greater the number of atoms, the greater the number of JT active modes of the same type, provided that systems with the same symmetry are compared. The multimode JT problems are thus more widespread than the ideal ones, the former including also the problems of impurity centers in crystals.

For the multimode problem the notion of vibronic coupling must be specified. For large systems the assumption that the degenerate term under consideration lies far away in energy from the other terms means that the appropriate electronic states are localized near a small group of atoms (usually called the JT center), and the vibronic coupling is essentially nonzero only for the interaction with the displacements of these atoms. This does not mean that there is no coupling to all the JT modes. Indeed, the local displacements contain all the JT modes, since owing to elastic interactions the displacements of all the atoms including the local ones are mixed. However, the local nature of the coupling allows the reduction of essentially the number of vibronic coupling constants employed in the calculations.

In the multimode problems the ideas employed for simplification of the calculations are similar to those used above for ideal problems: analytical solutions are obtained in the limiting cases of weak and strong coupling, many qualitative results can be deduced from the shape of the AP without completely solving the vibronic equations.

A. Adiabatic Potentials of Multimode JT Systems

The extrema properties of the AP of multimode JT systems are qualitatively the same as for ideal vibronic systems, i.e., all the qualitative results obtained for the AP in Sections II,C and II,D are valid also for appropriate multimode systems (Bersuker and Polinger, 1982).

In general, the potential energy matrix of a multimode system in the case of the linear JT effect has the form:

$$\mathbf{U} = \sum_{\Gamma\gamma} \sum_{n=1}^{N(\Gamma)} [\tfrac{1}{2}\omega_n^2(\Gamma) Q_{n\Gamma\gamma}^2 \mathbf{C}_A + V_n(\Gamma) Q_{n\Gamma\gamma} \mathbf{C}_{\Gamma\gamma}] \tag{86}$$

where $\omega_n(\Gamma)$ and $V_n(\Gamma)$ are the frequency and linear vibronic coupling constant for the vibrational coordinate $Q_{n\Gamma\gamma}$, n numbering the $N(\Gamma)$ irreducible representations of the same type Γ. This expression can be transformed by means of a scale transformation:

$$\bar{q}_{n\Gamma\gamma} = \omega_n(\Gamma) Q_{n\Gamma\gamma} \tag{87}$$

and a rotation in the subspace of each group of $N(\Gamma)$ coordinates transforming as the same line of the same irreducible representation Γ in such a way as one of the directions of the transformed coordinate system coincides with $q_{1\Gamma\gamma}$,

$$q_{1\Gamma\gamma} = \frac{\sum_{n=1}^{N(\Gamma)} [V_n(\Gamma)/\omega_n(\Gamma)] \bar{q}_{n\Gamma\gamma}}{\left(\sum_{n=1}^{N(\Gamma)} [V_n^2(\Gamma)/\omega_n^2(\Gamma)]\right)^{1/2}} \tag{88}$$

In these new coordinates we have

$$\mathbf{U} = \mathbf{U}_{\mathrm{JT}}(q_1) + \frac{1}{2} \sum_{\Gamma\gamma} \sum_{n=2}^{N(\Gamma)} q_{n\Gamma\gamma}^2 \mathbf{C}_A \tag{89}$$

where

$$\begin{aligned} \mathbf{U}_{\mathrm{JT}}(q_1) &= \frac{1}{2} \sum_{\Gamma\gamma} q_{1\Gamma\gamma}^2 \mathbf{C}_A + \sum_{\Gamma\gamma} \mathcal{V}_\Gamma q_{1\Gamma\gamma} \mathbf{C}_{\Gamma\gamma} \\ \mathcal{V}_\Gamma &= \left(\sum_{n=1}^{N(\Gamma)} [V_n^2(\Gamma)/\omega_n^2(\Gamma)] \right)^{1/2} \end{aligned} \tag{90}$$

and the normalizing factor $\mathcal{V}_\Gamma^{-1}$ is introduced for preserving the orthogonality of the transformation

$$q_{1\Gamma_\gamma} = \sum_{n=1}^{N(\Gamma)} R_{1n} \bar{q}_{n\Gamma_\gamma}, \qquad \sum_{n=1}^{N(\Gamma)} R_{1n}^2 = 1 \tag{91}$$

The matrix U after Eq. (89) consists of two commutative terms: the first, $\mathbf{U}_{\mathrm{JT}}$, corresponds to an ideal vibronic system, whereas the second, containing the unit matrix C_A, depends on all the other non-JT coordinates. Its eigenvalues are

$$\epsilon_j(\cdots q_{n\Gamma_\gamma}\cdots) = \epsilon_j^{(\mathrm{JT})}(q_1) + \frac{1}{2}\sum_{n=2}^{N(\Gamma)} q^2_{n\Gamma_\gamma} \tag{92}$$

where $\epsilon_j^{(\mathrm{JT})}(q_1)$ is the eigenvalue of the matrix $\mathbf{U}_{\mathrm{JT}}(q_1)$. Therefore the number of extrema points, their characteristics, as well as the JT stabilization energies are determined by only the $\epsilon_j^{(\mathrm{JT})}(q_1)$ term describing an ideal vibronic system with JT active modes $q_{1\Gamma_\gamma}$. The coordinates of the extrema points are thus

$$q^{(0)}_{1\Gamma_\gamma} \neq 0, \qquad q^{(0)}_{1\Gamma_\gamma} = 0, \qquad n \neq 1 \tag{93}$$

The inverse transformation from the $q_{n\Gamma_\gamma}$ coordinates to $\tilde{q}_{n\Gamma_\gamma}$ requires the knowledge of all the matrix elements of the transformation matrix, while Eq. (88) provides only the first line of this matrix. It means that in the inverse transformation only the first column is known:

$$\tilde{q}_{n\Gamma_\gamma} = \mathscr{V}_\Gamma^{-1}[V_n(\Gamma)/\omega_n(\Gamma)]q_{1\Gamma_\gamma} + \sum_{m=2}^{N(\Gamma)} R_{nm}q_{m\Gamma_\gamma} \tag{94}$$

However, taking into account that all the $q^{(0)}_{m\Gamma_\gamma}$ are zero, except that for $m = 1$, we obtain

$$\tilde{q}^{(0)}_{n\Gamma_\gamma} = \mathscr{V}_\Gamma^{-1}[V_n(\Gamma)/\omega_n(\Gamma)]q^{(0)}_{1\Gamma_\gamma} \tag{95}$$

and for the initial normal coordinates $Q_{n\Gamma_\gamma} = \tilde{q}_{n\Gamma_\gamma}/\omega_n(\Gamma)$, we obtain:

$$Q^{(0)}_{n\Gamma\gamma} = \frac{V_n(\Gamma)q^{(0)}_{1\Gamma\gamma}}{\mathscr{V}_\Gamma\,\omega_n^2(\Gamma)} \tag{96}$$

Thus, the extrema-point coordinates $Q^{(0)}_{n\Gamma\gamma}$ of the AP of a multimode system are expressed by the coordinates $q^{(0)}_{1\Gamma\gamma}$ of the extrema points of the AP of an ideal vibronic system, the JT stabilization energy remaining the same as for an ideal system with the effective vibronic constants determined by Eq. (90). For instance, in the case of the linear multimode $E - (e_1 + e_2 + \cdots)$ problem, taking $q_{1\theta} = \rho\cos\varphi$, and $q_{1\epsilon} = \rho\sin\varphi$, we have

$$\begin{gathered} Q^{(0)}_{n\theta} = [V_n(E)/\omega_n^2(E)]\cos\varphi, \qquad Q^{(0)}_{n\epsilon} = [V_n(E)/\omega_n^2(E)]\sin\varphi \\ E_{\mathrm{JT}} = \tfrac{1}{2}\mathscr{V}^2 = \frac{1}{2}\sum_{n=1}^{N(E)} \frac{V_n^2(E)}{\omega_n^2(E)} \end{gathered} \tag{97}$$

From here it follows that the AP of the multimode $E - (e_1 + e_2 + \cdots)$ problem has a continuum of minima points forming a one-dimensional trough, quite similar to the ideal $E - e$ problem. If the nuclear motions are localized in this trough they are like a wave of distortions of the nuclear framework running around the JT center. The amplitude of this wave is rapidly decreasing by going from the JT center to the peripheral atoms.

B. Solutions of the Multimode Problem

In spite of its complexity the multimode problem can be solved analytically in the limiting cases of weak and strong vibronic coupling. The appropriate ideas are illustrated below by considering the multimode $E - (e_1 + e_2 + \cdots)$ problem for a JT center of a small radius, i.e., when the electrons forming the degenerate electronic term are coupled essentially to the displacements of the atoms of the first coordination sphere only. These kinds of systems are widespread among coordination compounds of transition metals and rare-earth elements with localized d and f electrons, as well as dielectric and large-gap semiconductor crystals with point defects (small radius impurity centers, some F-centers, etc.).

The Hamiltonian of a small radius JT center with a multimode $E - (e_1 + e_2 + \cdots)$ problem may be written in the following form:

$$\mathbf{H} = \tfrac{1}{2} \sum_{n\gamma} (P_{n\gamma}^2 + \omega_n^2 Q_{n\gamma}^2) + V(X_{1\theta}\sigma_x + X_{1\epsilon}\sigma_y) \tag{98}$$

where V is the linear vibronic constant and $X_{n\Gamma\gamma}$ ($\Gamma = E$, $\delta \in \Gamma$) are the symmetrized displacements of the atoms of different coordination spheres labeled by the index n. The $X_{n\Gamma\gamma}$ magnitudes are related to the normal coordinates $Q_{n\Gamma\gamma}$ by the orthogonal transformation

$$X_{n\Gamma\gamma} = \sum_m a_{nm}(\Gamma\gamma) Q_{m\Gamma\gamma} \tag{99}$$

Expressions for the a_{nm} coefficients for some particular cases are given by Steggles (1977). Substituting $X_{1\theta}$ and $X_{1\epsilon}$ obtained from Eq. (99) into Eq. (98), one can obtain the Hamiltonian containing the potential energy matrix in Eq. (86).

After the orthogonal transformation of Eq. (99) we obtain, instead of Eq. (98),

$$\begin{aligned} \mathbf{H} = \tfrac{1}{2} \sum_{n\gamma} P_{n\gamma}^2 + \tfrac{1}{2} \sum_{n,m,\gamma} X_{n\gamma}(\omega^2)_{nm} X_{m\gamma} \\ + V(X_{1\theta}\sigma_x + X_{1\epsilon}\sigma_y) \end{aligned} \tag{100}$$

where n and m number both different coordination spheres and different E representations within the vibrational representation of each coordination sphere, and $(\omega^2)_{nm} = \sum_k a_{nk}(E\gamma)a_{km}(E\gamma)\omega_k^2$. Let us present the JT center of a small radius as two interacting subsystems. The first subsystem includes the JT ion plus the first coordination sphere, while the second contains all the other vibrational degrees of freedom of the polyatomic system. The Hamiltonian [Eq. (100)] can be presented as the sum $\mathbf{H}_{\mathrm{JT}} + H_{\mathrm{v}}' + H_{\mathrm{int}}$, where $\mathbf{H}_{\mathrm{JT}}$ is the vibronic Hamiltonian of the first coordination sphere having the form of Eq. (23) with the force constant $\omega_E^2 = (\omega^2)_{11}$, H_{v}' is the Hamiltonian of harmonic oscillations of the remaining atoms, and

$$H_{\mathrm{int}} = \sum_{n \neq 1} (\omega^2)_{n1}\rho_n\rho_1 \cos(\varphi_n - \varphi_1) \tag{101}$$

is the operator of interaction of the "JT modes" ("interacting" modes) $X_{1\theta}$ and $X_{1\epsilon}$ with the remaining part of the polyatomic system (here, the polar coordinates $X_{n\theta} = \rho_n \cos\varphi_n$ and $X_{n\epsilon} = \rho_n \sin\varphi_n$ are used).

Owing to the factor $\cos(\varphi_n - \varphi_1)$ the deformations of all the coordination spheres are involved in the coherent rotation of the electron density and the wave of deformation of the first coordination sphere, resulting in a wave of deformation which covers the total polyatomic system. In general, this collective rotation is stationary, since the appropriate momentum $\mathbf{J}_z = L_z + \frac{1}{2}\sigma_z$, $L_z = \sum_n(-i\partial/\partial\varphi_n)$, is an integral of motion (Section II,D). Besides, the oscillations of the magnitude of the deformation of the first coordination sphere owing to the term $\rho_n\rho_1$ are transmitted to the next spheres and propagate in the form of diverging (from the JT center) waves.

1. *The Case of Weak Coupling*

The simultaneous change of sign of both $V_n(\Gamma)$ and $Q_{n\Gamma\gamma}$ in Eq. (86) does not change the Hamiltonian. This means that the observable magnitudes expanded in series with respect to the $V_n(\Gamma)$ values contain only even powers. The quadratic contributions to $V_n(\Gamma)$ are additive with regard the index Γ, allowing us to consider the multimode problems for each type of vibration separately ($E - e$, $T - e$, $T - t_2$, $\Gamma_8 - e$, $\Gamma_8 - t_2$, and $E - b_1$, $E - b_2$) and to summarize the results if there is simultaneous coupling to different types of vibrations.

The Hamiltonian of the second-order perturbation theory for these "separated" problems has a higher symmetry than the initial one G_0 (Sections II,D and III,A,1) and the operators $F_{\Gamma\gamma}$ in the Green's function $\langle\langle F_{\Gamma\gamma}^+ | F_{\Gamma\gamma}\rangle\rangle$ have to be classified after the irreducible representations of the enlarged group. This allows us to choose the $F_{\Gamma\gamma}$ operators in such a way as to be able to determine separately the energy spectra of states having different transformation properties: at $T = 0$ K the contribution to the poles of the Green's functions are nonzero only for the vibronic states $|\bar{\Gamma}\bar{\gamma}\rangle$ which have nonzero matrix elements $\langle\bar{\Gamma}\bar{\gamma}|F_{\Gamma\gamma}|0\rangle$ with the ground state $|0\rangle$.

The difficulties arising due to the electronic degeneracy of the ground state can be overcome by employing the idea of quasi-averaged values (Bogolubov, 1961). In so doing a low-symmetry term λA removing the degeneracy of the ground state must be added to the Hamiltonian, and then one has to assume $\lambda = 0$ after taking $T \rightarrow 0$ K. For instance, for the $E - e$ problem described by the Hamiltonian [Eq. (98)], the term to be added is $\lambda\sigma_z$, which removes the degeneracy of the ground state $j = \pm 1/2$, preserving the axial symmetry (Section II,D). If $\lambda > 0$ the ground state is $j = -1/2$, and the Green's function $\langle\langle X_0|X_-\rangle\rangle$ ($X_\pm = (X_{1\theta} \pm iX_{1\epsilon})/\sqrt{2}$) takes into account only excited states with $j = -3/2$. Since the X_+ operators change the oscillator quantum numbers of the unperturbed system by unity, it is clear that the first nonzero corrections to this Green's function contain the information about the excited vibronic states arising from the first excited vibrational state with transformation properties $j = -3/2$. If $\lambda < 0$, the ground state is $j = 1/2$, and the above Green's function describes the states with $j = -1/2$ arising also from the first excited vibrational state. Complex conjugated states are described by the Green's function $\langle\langle X_-|X_+\rangle\rangle$.

If the Hamiltonian of the system can be presented in the form of the sum $H_\text{v} + \mathbf{V}(X_1)$, where H_v is the Hamiltonian of harmonic vibrations and $\mathbf{V}(X_1)$ is the perturbation caused by the local displacements of the atoms of the first coordination sphere, the following integral equations of motion are valid ($t \geq 0$):

$$\begin{aligned} X_{1\Gamma\gamma}(t) &= X^{(0)}_{1\Gamma\gamma}(t) - \int_0^t G^{(0)}_\Gamma(t - \tau)\, \frac{\partial \mathbf{V}(X_1(\tau))}{\partial X_{1\Gamma\gamma}}\, d\tau \\ \mathbf{C}_{\Gamma\gamma}(t) &= \mathbf{C}_{\Gamma\gamma} + \frac{i}{\hbar} \int_0^t [\mathbf{V}(X_1(\tau)), \mathbf{C}_{\Gamma\gamma}(\tau)]\, d\tau \end{aligned} \tag{102}$$

Here, as usual, the time dependence of the operators is determined by the Heisenberg representation with the total Hamiltonian $\mathbf{H} = H_\text{v} + \mathbf{V}(X_1)$, except $X^{(0)}_{1\Gamma\gamma}(t)$ for which the zero Hamiltonian H_v is taken instead of $\mathbf{H}$ and $G^{(0)}_\Gamma(t) = -i\hbar^{-1}\theta(t)\langle[X^{(0)}_{1\Gamma\gamma}(t), X_{1\Gamma\gamma}]\rangle$ is the retarded zero Green's function,

$$G^{(0)}_\Gamma(t) = -\frac{i}{\hbar}\,\theta(t) \sum_n \frac{|a_{1n}(\Gamma_\gamma)|^2}{\omega_n(\Gamma)} \sin(\omega_n(\Gamma)t) \tag{103}$$

Substituting Eqs. (101) and (102) (written for the $E - e$ problem) into the expressions for retarded Green's functions $G = \langle\langle X_+|X_-\rangle\rangle$ and

$\mathcal{D} = \langle\langle\sigma_+|X_-\rangle\rangle$, and assuming the decoupling $\langle\langle\sigma_z, X_+|X_-\rangle\rangle \approx \langle\sigma_z\rangle\langle\langle X_+|X_-\rangle\rangle$, one can obtain (Rozenfeld and Polinger, 1976) the following:

$$G(\omega) = G_E^{(0)}(\omega)[1 - (4\pi/\hbar\omega)\langle\sigma_z\rangle V^2 G_E^{(0)}(\omega)]^{-1} \tag{104}$$

(Here the presentation of functions by Fourier integrals and the well-known theorem of convolution are also used.) The spectrum of one-quantum excitations is determined by the Green function poles, i.e., by the roots of the following transcendental equation:

$$4\pi\langle\sigma_z\rangle V^2 G_E^{(0)}(\omega) = \hbar\omega \tag{105}$$

As mentioned previously, at $T = 0$ K, $\lambda = +0$, one has $\langle\sigma_z\rangle = -1$ and the Eq. (105) describes the spectrum of vibronic states with $j = -3/2$. At $\lambda = -0$, $\langle\sigma_z\rangle = 1$, and Eq. (105) determines the energy levels with $j = -1/2$. In the particular case of the ideal vibronic system when $\omega_n = \omega_E$ for all n values, Eq. (105) can be solved directly resulting in solutions obtained in Section III,A,I.

In particular, for a JT impurity center in crystals the spectral density $\rho(\omega) = 2\,\mathrm{Im}\,G(\omega + i\epsilon)$, $\epsilon = +0$, determining the observable magnitudes is of special interest. It happens that $\rho(\omega)$ is a function of the "priming" density of states $\rho_\Gamma^{(0)}(\omega) = 2\,\mathrm{Im}\,G_\Gamma^{(0)}(\omega + i\epsilon)$, $\epsilon = +0$, and its Gilbert transform

$$r_\Gamma^{(0)}(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{2z\rho_\Gamma^{(0)}(z)}{z^2 - \omega^2}\,dz \tag{106}$$

Taking into account Eq. (104), it can be shown that in the vicinity of those roots ω_α of the transcendental equation $4\pi\langle\sigma_z\rangle V^2 r_E^{(0)}(\omega) = \hbar\omega$, for which the "priming" density of states $\rho_E^{(0)}(\omega)$ is small, the redetermined spectral density $\rho(\omega)$ has a Lorentz shape with a semiwidth $\gamma_\alpha = \rho_E^{(0)}(\omega_\alpha)[\partial r_E^{(0)}(\omega_\alpha)/\partial\omega_\alpha]^{-1}$. If the root ω_α falls into the forbidden zone where $\rho_E^{(0)}(\omega_\alpha) = 0$, then $\gamma_\alpha = 0$ and the Lorenzian changes to a δ function.

Thus, even the weak vibronic coupling may lead to the essential redetermination of the energy spectrum, in particular, to the occurrence of local and pseudolocal new vibronic states.

This result may be given a clear-cut visual interpretation. Without taking account of the vibronic interactions the spectrum of the system corresponds to infinite motions of free phonons. The vibronic interaction breaks the multiplicative form of the wave function of the ground state with respect to electronic and vibrational variables, mixing them by one-phonon excited states. The descrete local states which occur due to the vibronic coupling correspond to the finite motion of the impurity-phonon system, to the bonding of the phonon to the JT center. In other words, owing to the vibronic interaction the free-rotating low-symmetry electron-density distribution involves in its motion one phonon seized into a stationary orbit.

The above qualitative deductions about the vibronic structure of the density of states of a multimode JT system are valid also in more complicated situations. Thus, coupled states of the phonon with the impurity center arise also in the case of the pseudo-JT effect, considered by Kogan and Suris (1966) (local states) and Aminov and Kochelaev (1969) (pseudolocal states). The general theory of such bounded states concerned impurity centers in crystals is given in the review article by Levinson and Rashba (1973).

2. *Strong Vibronic Coupling*

As for ideal problems, in the multimode vibronic problems with strong vibronic coupling two cases have to be distinguished. In the first case the lower sheet of the AP has a continuum of equipotential minima points forming a trough, while in the second case there is a finite number of absolute minima divided by potential barriers. In the simplest linear $E - (e_1 + e_2 + \cdots)$ problem the lower sheet of the AP has a continuum of equipotential minima points forming a circular trough. In the adiabatic approximation the operator of the potential energy (including centrifugal energy) is

$$E_{\pm}(\cdots Q_{n\gamma}\cdots) = \frac{\hbar^2 j^2}{2I} + \frac{1}{2}\sum_{n\gamma} \omega_n^2 Q_{n\gamma}^2 \pm |V|(X_{1\theta}^2 + X_{1\epsilon}^{2'})^{1/2} \quad (107)$$

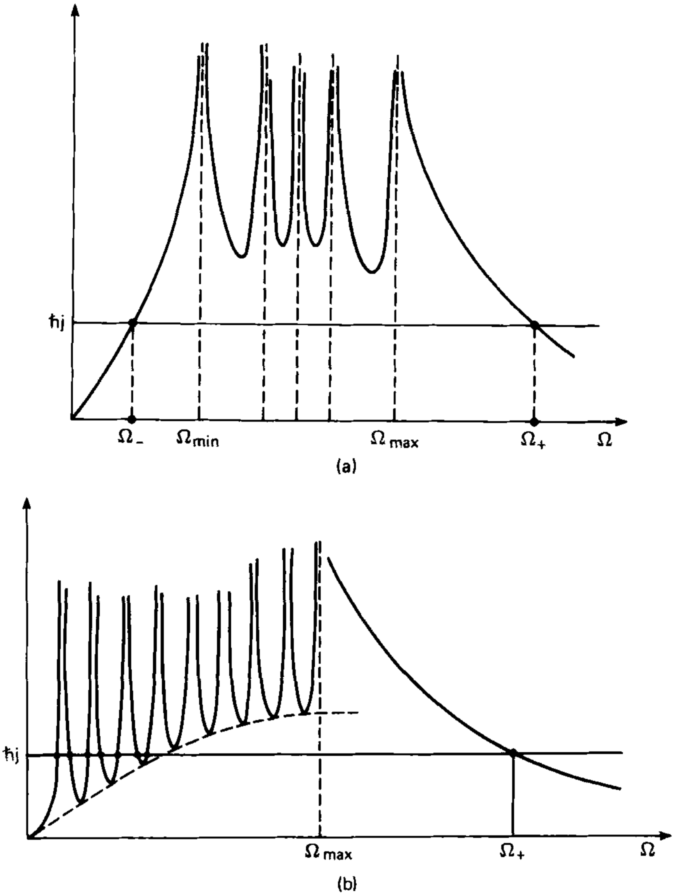
where $I = \Sigma_{n\gamma} Q_{n\gamma}^2$ is the momentum of inertia of cooperative rotations. Equalizing the first derivatives $\partial E_{\pm}/\partial Q_{n\gamma}$ to zero, we find

$$Q_{n\theta}^{(0)} = \mp \frac{|V| a_{1n}(\theta)}{\omega_n^2 - \Omega^2}\cos\varphi, \qquad Q_{n\epsilon}^{(0)} = \mp \frac{|V| a_{1n}(\epsilon)}{\omega_n^2 - \Omega^2}\sin\varphi \quad (108)$$

where $\Omega = \hbar j/I_0$ is the angular frequency of the cooperative rotation of the deformation, $I_0 = \Sigma_{n\gamma} Q_{n\gamma}^{(0)2}$ is the momentum of inertia for the motions along the trough at its bottom, $\varphi = \arctan(X_{1\epsilon}/X_{1\theta})$ is the angle determining the orientation of the deformation in the first coordination sphere. Substituting the $Q_{n\gamma}^{(0)}$ values from Eq. (108) into the expression for I_0, we have

$$V^2\Omega \sum_n [a_{1n}^2(\gamma)/(\omega_n^2 - \Omega^2)^2] = \hbar j \quad (109)$$

Graphical solutions of this equation are illustrated schematically in Fig. 16.



(a)

(b)

Fig. 16. Graphic solution of the transcendental Eq. (109). (a) The molecular multimode case. The dashed lines are the asymptotes of the left-hand side of the equation crossing the points $\Omega = \omega_n$. In the case of strong vibronic coupling only two solutions Ω_+ and Ω_- remain. (b) The case of a JT (impurity) center in crystals. The inclined dashed line is the envelope of the minima points of the left-hand side of Eq. (109) in the region of small frequencies.

In the case of molecular JT systems (Fig. 16a) with strong enough vibronic coupling all the minima of the left-hand side of Eq. (109) situated in between the singularities at $\Omega = \omega_n$ lie over the line $\hbar j$. It means that Eq. (109) has only two solutions, Ω_+, Ω_-, which obey the inequalities $0 < \Omega_- < \omega_{\min}$ and $\Omega_+ > \omega_{\max}$, where $\omega_{\min}$ and $\omega_{\max}$ are the smallest and the largest ω_n frequencies, respectively. It can be seen from Eq. (108) that Ω_- determines the points of the trough of the lower sheet, whereas Ω_+ pertains to the upper sheet.

For impurity centers in crystals the situation is essentially different from the molecular case, since in this case $\omega_{\mathrm{min}} = 0$. The envelope of the minima points situated in between the singularities $\Omega = \omega_n$ (the dashed line in Fig. 16b) in the range of small Ω values is described by the linear dependence $V^2\overline{\omega^{-4}}\Omega$, where

$$\overline{\omega^n} = \sum_k |a_{1k}(\gamma)|^2\omega_k^n \tag{110}$$

It is obvious that Eq. (109) has an infinite number of roots in the range of small Ω values (for any V values), the absolute minimum corresponding to $\Omega_- = 0$. This value of the angular frequency is appropriate to the infinite moment of inertia $I_0 = \hbar_j/\Omega_-$. This result can be understood as follows. As stated above the minima of the lower sheet of the AP result from the compensation of the destabilizing JT and centrifugal force by the elastic ones $\sim\omega_n^2 Q_{n\gamma}$. For low-frequency acoustic vibrations with $\omega_n \to 0$, the stabilization by the elastic force can be reached only at infinite values of $Q_{n\gamma}^{(0)}$. This is the reason for the devergency of the I_0 value first noted by Slonczewski (1963).

This result means that in general stationary rotation of the wave of deformations covering the whole crystal is impossible because of the infinite value of the moment of inertia. Nevertheless, quasi-stationary rotations are possible without participation of the long-wave acoustic phonons, the interaction with the latter causing the weak decay of these rotations. Owing to the very small density of the long-wave acoustic phonons, this interaction is also very small.

To summarize, in the space of the "radial" degrees of freedom which are orthogonal to the angular displacement along the trough, the potential energy E_- from Eq. (107) has an infinity-approaching narrowing well with a warped bottom. Because of this narrowing of the well the JT stabilization energy $E_{\mathrm{JT}} = \frac{1}{2}V^2\overline{\omega^{-2}}$ is difficult to attain. As a result quasi-stationary rotations with a finite value of the moment of inertia occur in the system. Accordingly, some well-defined rotational resonances have to be present in the vibronic density of states.

The mathematical realization of the above physical considerations was carried out by Polinger and Bersuker (1979a). In higher orders, with respect to the V^{-1} value, the equilibrium positions $Q_{n\gamma}^{(0)}$ are not infinite. The Hamiltonian of the lower sheet of the AP in the harmonic approximation takes the form $H = H_{\mathrm{vib}} + H_{\mathrm{rot}} + H_{\mathrm{el}}$, where H_{vib} is the Hamiltonian of small vibrations near the bottom of the trough in the "radial" directions,

$$H_{\mathrm{rot}} = \hbar^2 j^2/2I_0, \qquad H_{\mathrm{el}} = -E_{\mathrm{JT}} = -\tfrac{1}{2}V^2\overline{\omega^{-2}} \tag{111}$$

$I_0 = V^2\overline{\omega^{-4}}$ is the moment of inertia corresponding to the quasi-stationary cooperative rotation. A part of the variables in the Hamiltonian H_{vib}

which are not changed by the separation of the angular variable φ_1 gives the initial contribution to the phonon dispersion law. The spectrum for the remaining variables is essentially changed and can be found by means of Green's functions. (Polinger and Bersuker, 1979a). Since the evaluated equilibrium values of the coordinates $Q_{n\gamma}^{(0)}$ are not exact, the Hamiltonian also contains small (with respect to V^{-1}) terms linear in $Q_{n\gamma}$, which cause the relaxation of the rotational levels described by H_{rot}.

The vibrational states of the Hamiltonian H_{vib} may be expanded in the series with respect to the complete set of vibrational states of the system without vibronic interactions. In the case of strong vibronic interaction this expansion contains multiphonon states. From this point of view the rotational states can be interpreted as describing the motion of a multiphonon electron-vibrational formation of polaron type localized on the degenerate quasi-stationary orbits near the JT center. When the vibronic constant increases, the lifetime of this quasi-polaron also increases and, accordingly, the width of the rotational resonances decreases. Mathematically, by increasing the V value, the spacing of the rotational structure of the energy spectrum decreases, and the rotational energy levels fall into a lower frequency spectral range, where the density of states and hence the probability of direct decay is smaller.

The vibronic spectrum of the upper sheet of the AP can be found by considering the H_{int} value from Eq. (101) as a perturbation. In the initial approximation the JT "interacting" modes $X_{1\gamma}$ are separated from the others, and in the centrifugal stabilized states of the upper sheet they give a discrete energy spectrum which is sunken in the vibrational spectrum of the remaining degrees of freedom. The spacing $\Delta E_{\text{rot}}^{(+)}$ of the rotational levels of the upper sheet is $\sim V^{2/3}$, and for strong enough coupling it may be larger than the quantum of the highest frequency vibrations. In this case direct decay processes are forbidden by the energy-preservation law. The decay of rotational states hence may take place only in the second or higher order perturbations with respect to H_{int}. Taking into account the fact that the probability of second-order processes is $\sim H_{\text{int}}/\Delta E_{\text{rot}}^{(+)}$, we come to the conclusion that the stronger the vibronic coupling, the less the width of the appropriate resonances in the vibronic density of states, and this confirms the validity of the perturbation theory in these cases. [The quasi-stationary states of the upper sheet of the AP are usually called Slonczewski resonances (Slonczewski, 1963).] However, the width of the Slonczewski resonances are determined not so much by the rotational–vibrational relaxation processes within the upper sheet of the AP, but by the nonadiabatic relaxation to the lower sheet of the AP (Slonczewski and Moruzzi, 1967).

For the states of the lower sheet of the AP the H_{int} term in Eq. (101) can be taken into account by means of the perturbation theory only in the cases when the elastic interaction of the displacements of the first coordination sphere atoms with the others is sufficiently small, and when in the zero approximation the coupled motion of the electrons of the JT center and the deformation of the first coordination sphere can be assumed to be independent of the vibrations of the atoms of the other coordination spheres. This is the so-called quasi-molecular or cluster model of the problem; it was suggested by O'Brien (1972). The development of the cluster approach to the multimode vibronic problems is presented in the review article by Englman and Halperin (1978). The solution of the multimode $E - e$ problem with strong vibronic coupling given in present article follows the works of Slonczewski (1963) and Polinger and Bersuker (1979a), and is not limited by the frames of the cluster model. A similar approach to the $\Gamma_8 - (e + t_2)$ problem[3] with strong linear vibronic coupling was used by Fang Li-Zhi and Ou Zhi (1966a,b).

Let us now discuss the case of multimode problems, in which the lower sheet of the AP has several absolute minima points divided by potential barriers. In the simplest case of the quadratic $E - e$ problem, the Hamiltonian differs from that of Eq. (98) by an additional term $W[(X_{1\theta}^2 - X_{1\epsilon}^2)\sigma_x - 2X_{1\theta}X_{1\epsilon}\sigma_y]$ [*cf.* Eq. (30)], or $W\rho_1^2 \cos(3\varphi_1)$, which does not allow to separate the angular motion along the φ_1 coordinate. If, however, the spacing of the energy spectrum corresponding to the motion along φ_1 is small with regard to the energy spacing in the vibrational subsystem, then the appropriate motions can be separated in the adiabatic approximation, quite similar to the ideal vibronic problem case (Section II,A,2). The spectrum of the fast subsystem can be obtained by excluding the terms with $\partial/\partial\varphi_1$ from the Hamiltonian. For the lowest vibronic states the motion along all the other degrees of freedom can be reduced to harmonic oscillations near the new equilibrium positions. Considerations similar to those used in the deduction of Eq. (111) lead to results (Bersuker and Polinger, 1981), some of which are briefly mentioned below.

The vibrational Hamiltonian of the fast subsystem can be presented as a sum of two commutative parts, $H_A + H_B$ appropriate to the decomposition of the E_g representation of the O_h group into two representations A_{1g} and B_{1g} in the configuration of the AP minimum of D_{4h} symmetry. The Hamiltonian H_B and its appropriate density of states have the same form, as H_{vib} in Eq. (111) in which only the linear vibronic coupling is taken into account. The Hamiltonian H_A describes radial vibrations (in the minima

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[3] It is interesting to note that the interaction of a nucleon with the field of mesons (in the charged pseudoscalar model) is described by the Hamiltonian which is formally similar to that of the multimode $\Gamma_8 - t_2$ problem, its first solution having been obtained about 40 years ago (Pauli and Dancoff, 1942).

configurations) weakly changed by the quadratic vibronic coupling. These changes are similar to those expected when taking into account the changes in the force constants in the vicinity of the JT center due to the impurity defect.

To consider the slow subsystem, i.e., the rotations along the bottom of the AP trough warped by the quadratic terms of vibronic interactions, one has to average the Hamiltonian with the ground vibrational state of the fast subsystem. Keeping only the first terms in V^{-1} and W, we obtain the Hamiltonian [Eq. (58)] with $\alpha = \hbar^2 V^{-2}(\overline{\omega^{-2}})^{-2}/2$ and $\beta = V^2 W(\overline{\omega^{-2}})^2$. Thus, the spectrum of hindered rotations in the multimode $E - e$ problem formally coincides with that of the appropriate ideal problem (Section II,A,2), but the α and β parameters depend on all the frequencies ω_n (or their averaged values).

The hindered rotations in the multimode JT system under consideration may be interpreted as the motion of the above-discussed multiphonon formation of polaron type which suffers reflections from the potential barrier. If β is great enough the minima wells of the AP are separated by high potential barriers. In this case the motion of the quasi-polaron is similar to the pulsating motions in the ideal case and can be reduced to tunneling through the barrier.

The energy levels of the motion of the slow subsystem (hindered rotations or tunneling between the minima configurations) are sunken in the vibrational energy spectrum of the fast subsystem. If the vibronic coupling is strong enough the spacing of the energy spectrum of the slow subsystem is exponentially small, its excitations falling in the spectral range of very small frequencies the densities of which are also very small. Owing to this circumstance the nonadiabacity corrections to the adiabatic separation of the radial and angular motions are small. The adiabatic separation of motions also causes limitations for the possible value of the quadratic vibronic constant W, namely $|W|\overline{\omega^{-2}} \ll 1$. Analytic expressions based on the quasi-classical approach for the tunneling splitting magnitude, free of this limitation, are given in the book by Bersuker and Polinger (1982). The multimode $T - (e + t_2)$ problem with predominant coupling to E vibrations was solved by Polinger (1979).

C. Vibronic Reduction Factors in Multimode Problems

As in the case of ideal problems the ground vibronic state wave function $\Psi_{\bar{\Gamma}\bar{\gamma}}(r, Q)$ has the same multiplicity and transformation properties as that for the ground electronic $\psi_{\bar{\Gamma}\bar{\gamma}}(r)$. Therefore, similar to the ideal case, multimode vibronic reduction factors can be introduced in order to determine matrix elements of electronic operators with vibronic states by calculating those with electronic states. All the previously mentioned (Section III,C) ideal systems up to Eq. (77) are also valid for multimode systems. However, the relation $2q - p = 1$ for the $E - e$ problem does not hold in the multimode case. This is due to the fact that in the multimode problem there are complex scalars χ_0 of the axial group such as $\chi_{A_2} = -\mathrm{Im}\,\chi_0 \neq 0$ [cf. Eq. (77)]. For instance, in the two-mode $E - e$ problem such a scalar may take the form of a series $\chi_0 = \sum_j f_j(\rho_1, \rho_2)e^{ij(\varphi_1 - \varphi_2)}$. As follows from Eq. (74) in the multimode linear $E - e$ problem, $2q - p < 1$. However, this inequality cannot serve as an absolute criterion of the multimode nature of the JT problem since, as mentioned in Section III,C, there are other contributions to this inequality (quadratic vibronic coupling, second-order effects, etc.). In the case of weak vibronic coupling the breakdown of the relation $2q - p = 1$ begins at the fourth-order perturbation theory (Gautheir and Walker, 1973; Halperin and Englman, 1973):

$$p = 1 - \frac{2V^2}{\hbar}\overline{\omega^{-3}} + \frac{4V^4}{\hbar^2}\left(\overline{\omega^{-3}}\right)^2$$

$$q = \tfrac{1}{2}(1 + p) - \frac{1}{2}\frac{V^4}{\hbar^2}\sum_{n,m}\frac{a_{1n}^2(\gamma)a_{1m}^2(\gamma)}{\omega_n^3\omega_m^3}\left(\frac{\omega_n - \omega_m}{\omega_n + \omega_m}\right)^2$$

In the case of strong vibronic coupling in the multimode $E - e$ problem with linear coupling $p = 0$ (this is a result due to the adiabatic separation of the two sheets of the AP), whereas for q we obtain (Polinger and Bersuker, 1979b), $q = \frac{1}{2}\exp(-M/2)$ where $M \sim V^{-2}$. In the particular case of the two-mode $E - e$ problem

$$M = \frac{\hbar}{2V^2}\frac{\left(\overline{\omega^{-2}}\right)^2 - \overline{\omega^{-4}}\Big)^2}{\omega_1^2\omega_2^2\left(\overline{\omega^{-4}}\,\overline{\omega^{-2}}\right)^{3/2}}$$

The numerical investigation of the vibronic reduction factors in the two-mode $E - e$ problem (Evangelou *et al.*, 1980) shows that the difference between $2q - p$ and unity is relatively small for any values of the vibronic constants and ω_n frequencies.

V. Concluding Remarks

In this review article on the theory of vibronic interactions in polyatomic systems, the latest achievements for ideal and multimode JT problems are considered. As mentioned in Section II, the discussion of numerous applications of the theory to concrete systems, now the subject of separate monographs (Bersuker, 1982b), is beyond the aim of this article. Also, the important problems of cooperative JT and pseudo-JT effects in crystals are not considered here.

One of the important problems of the general theory of the JT effect, the determination of vibronic constants, remains unsolved. The main parameters of the vibronic Hamiltonian (Section II) are the vibronic constants V_Γ and the vibrational frequencies ω_Γ. While the latter are well known (either empirically or from direct calculations), the vibronic constants occur only in the vibronic interaction scheme, the possibility of their evaluation being studied very little. On the other hand, all the applied aspects of the theory are determined by the V_Γ value (Bersuker, 1982b).

The difficulties arising in the calculations of the vibronic constants are due first of all to the lack of sufficiently precise wave function for the initial configuration of the system Q_0 determined in Section II. For the pseudo-JT effect and for the JT effect of an excited degenerate term the appropriate excited-state wave functions are also needed. But the lack of wave functions does not exhaust the above difficulties. Indeed, the total wave function of the system employed in the calculation of the vibronic constants, strictly speaking, includes also the states of the inner strongly bound electrons. Some of the observable magnitudes calculated with these V_Γ values (e.g., the AP curvature, or the vibrational frequencies in the AP minima configurations), occur as a small difference of two large numbers, resulting thus in a very low accuracy of the calculated values. Liehr (1958) suggested using in these cases the so-called "floating" basis set. However, in so doing the problem of the number of electronic states to be considered by "floating" orbitals occurs.

One of the possible ways to overcome the difficulties with this and other problems is provided by the so-called orbital vibronic constants determined as one-electron matrix elements of the vibronic interaction operators (Bersuker, 1977, 1978b, 1982b). The latter are one-electron operators, and therefore in the approximation without configuration interaction the vibronic constants for the JT effect (and in the approximation of "frozen" orbitals also for the pseudo-JT effect) are equal to the sum of orbital vibronic constants. Empirical schemes have been proposed for their evaluation. The description of the vibronic coupling by means of orbital vibronic constants also allows the consideration of some interesting applied problems, in particular, the influence of one molecular system upon another by their weak coordination (e.g., in catalysis), which leads to the change of the orbital occupation numbers and hence to the change of the orbital contributions to the vibronic constants (Bersuker, 1977, 1978, 1982b).

There have been also some suggestions to use semiempirical methods for vibronic constant calculations (Obert and Bersuker, 1978; Bacci, 1979; Nikiforov *et al.*, 1980, etc.), but the problem as a whole is still unsolved, remaining one of the most interesting in the vibronic theory under consideration.

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Electronic Structure of Polymers*

MIKLÓS KERTÉSZ†
Central Research Institute for Chemistry
Hungarian Academy of Sciences
Budapest, Hungary

I. Introduction

Since the discovery of the high conductivity of doped polyacetylene (Chiang *et al.*, 1977), increasing attention has been directed toward the development of microscopic models of the electronic structure of polymers in general and of conjugated organic polymers in particular. The underlying physical model, namely the one-particle picture, is being widely used in this field and is considered basically correct. On a practical level, this means that periodic models are usually constructed which justify

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* Dedicated to the memory of Professor Andrej Ažman.

† Present address: Department of Chemistry, Cornell University, Ithaca, New York, 14853.

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using the terminology of energy-band theory (e.g., Callaway, 1964). With refinements of calculational tools, self-consistent calculations at even the *ab initio* level have become widespread. In this article, wherever possible we shall cite the most refined *ab initio* calculations, although a number of important effects such as the Peierls distortion or the Hartree–Fock (HF) instabilities can be understood at a very simple level of sophistication [e.g., the Hückel or Pariser–Parr–Pople (PPP) models], which can be useful in interpreting the results of more sophisticated calculations. The prototype of conjugated polymers is as mentioned, polyacetylene (PA) or $(CH)_x$ (Fig. 1), and we shall discuss its "bond-length alternation problem" in detail below. The electronic structure of the prototype of the saturated polymers, polyethylene $(CH_2)_x$, has been adequately discussed in this serial publication in a previous article (André, 1980), so we shall not focus on it here (see also Fabish, 1979). Another interesting group of polymers may be obtained by regularly replacing H atoms of $(CH_2)_x$ by large pendant groups such as $—C_6H_5$. These pendant-group polymers have many interesting spectroscopic properties which can be understood on the basis of localized electronic states (Duke and Fabish, 1976; for a review see Fabish, 1979; Duke, 1981) and thus are not within the scope of this article. Inorganic quasi-one-dimensional (1D) crystals (e.g., chains of tetracyanoplatinate ions; Whangbo and Hoffmann, 1978) can be considered polymer-like systems having many features in common with such polymers as PA (e.g., the Peierls theorem of 1955). However, we do not discuss these inorganic systems here since a good review has already appeared (Whangbo, 1981); we also neglect the large and important field of the electronic structure theory of biopolymers (for good reviews see Ladik, 1973, 1978).

In this article we focus on methodological problems related to the

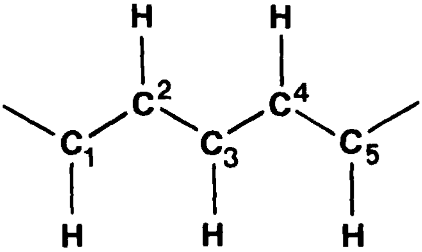


Fig. 1. Polyacetylene (PA) or $(CH)_x$ in all-trans configuration.

treatment of the electronic structure of polymers, such as the boundary conditions and problems related to the large size of these systems, *ab initio* techniques, and a symmetry dilemma connected with the quasi-degeneracy of partially filled bands. The results of the application of these and semiempirical techniques to the carbon atomic chain to $(CH)_x$ and a series of related polymers, polydiacetylene (PDA), and some further conjugated polymers, are compared with experimental results. Most of the discussion is based on 1D models.

II. Quantum Chemical Methods for Treatment of the Electronic Structure of Periodic Polymers

A. On the Boundary Conditions

It is customary to impose periodic boundary conditions (BC) (Born and von Kármán, 1912) on a chemically periodic polymer in order to be able to treat practically the large number of electronic degrees of freedom and to take the infinite-size limit of the resulting equations. We shall take this course below, but before doing so we would like to discuss this point critically. There are a number of important phenomena in which end effects are basically important. In performing band-structure calculations one focuses on properties independent of the BC, i.e., on the bulk properties. In principle, bulk properties can be obtained from infinite clusters by definition independent of the BC. One is justified in asking to what extent the periodic BC results in the infinite-size limit can be obtained from calculations done on a finite, small fragment or cluster of the chain. As it turns out, there are cases when a cluster of polyethylene as small as five CH_2 units gives excellent results when compared with those based on periodic BC (see Table I). Differences are much smaller here than for changes due to the inclusion of a larger basis set. Similarly, Brédas *et al.* (1980) find that conformational preferences of polyethylene can be very accurately decided on the basis of clusters as small as C_6H_{10}. In more polar chains (e.g., hydrogen bonded), however, results on clusters are not as close to the periodic BC results (Table II).

On the other hand, the energy band structure and the density of states (DOS) are in principle more sensitive to the size of the cluster, partly because of the van Hove singularities (e.g., Callaway, 1964), especially pronounced in 1D calculations. Nevertheless, a rough idea on the band structure can be obtained from small clusters, as done, e.g., by Duke and Paton (1981) in their CNDO study of the UV photoemission spectra of $(CH)_x$. They find that by increasing the number of (CH) units to over 16,

TABLE I

COMPARISON OF CLUSTER CALCULATIONS[a] AND PERIODIC BOUNDARY CONDITION CALCULATIONS[b] ON POLYETHYLENE USING STO-3G BASIS SET

	Cluster[a]	Periodic BC[b]
Equilibrium C—C distance (bohr)	2.916	2.924
C—H distance (bohr)	2.058	2.058
HCH (deg)	107.1	107.0
CCC (deg)	112.4	112.6
Longitudinal elastic modulus (GPa)	405	406

[a] Crist *et al.* (1979).

[b] Karpfen (1981a).

the theoretical valence DOS does not change on the scale of ~0.7 eV (width of the supposed resolution). Due to finite resolution, the van Hove singularities are smeared, thus permitting cluster calculations for DOS in polymers. The problem of the finiteness of the cluster within the periodic BC situation can be discussed on an analytical example based on the π-electron Hückel (1931) study of a model for PA. As shown by Longuet-Higgins and Salem (1959) the eigenvalues of a Hückel model with periodic BC of $4n + 2$ C atoms can be given as

TABLE II

BINDING ENERGY PER HYDROGEN BOND IN HYDROGEN FLUORIDE AND HYDROGEN CYANIDE CLUSTERS AND INFINITE CHAINS (IN kJ/mol)

System	Clusters				Periodic BC
	$n = 2$	$n = 3$	$n = 4$	$n = 8$	
$(\mathrm{HF})_n^a$	23	—	32	38	43
$(\mathrm{HF})_n^b$	40	46	50	55	67
$(\mathrm{HCN})_n^c$	15	34	—	—	41

[a] Kertész *et al.* (1975), *ab initio*, STO-3G.

[b] Karpfen *et al.* (1974), CNDO/2.

[c] Kertész *et al.* (1976a), *ab initio*, STO-3G.

$$\begin{aligned}\epsilon_j^{\pm} = \pm\{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \\ \times \cos[2\pi j/(2n+1)]\}^{1/2}\end{aligned} \tag{1}$$

where β_1 and β_2 are the two different resonance integrals and $j = 0, \pm 1, \pm 2, \ldots, \pm n$. From this, the forbidden energy gap (E_g) is

$$E_g = \epsilon_n^{+} - \epsilon_n^{-} \tag{2}$$

In the usual solid-state limit $n \to \infty$ and $E_g = 2|\beta_1 - \beta_2|$. For large n, expansion in $1/n$ gives at lowest order of $1/n$,

$$\begin{aligned}E_g = 2|\beta_1 - \beta_2| \\ - \beta_1\beta_2/(4n^2|\beta_1 - \beta_2|)\end{aligned} \tag{3}$$

without a $1/n$ term. Expansion of the band at $j = n/2$ for n even gives

$$\begin{aligned}\varepsilon_{j=n/2} = (\beta_1^2 + \beta_2^2)^{1/2} \\ \times\left(1 - \frac{\beta_1\beta_2}{\beta_1^2 + \beta_2^2}\frac{1}{2n} + \cdots\right)\end{aligned} \tag{4}$$

We note that for the metallic case ($\beta_1 = \beta_2$) the gap approaches zero as $1/n$, thus the system is never exactly degenerate for finite n. In general, energy values of a finite cluster are expected to differ at most up to the order of $1/n$ from those of an infinite chain except for a few finite levels (nonbulk or localized states).

It is not only the superiority of the bulk results in this sense which justifies the use of periodic BC, but primarily the numerical work is greatly simplified. Through the introduction of the reciprocal **k** space, instead of one large matrix problem, a set of **k**-vector-dependent small problems arise. Furthermore, use of **k** vectors and Brillouin zones (BZ) brings order into the large number of states. It should be mentioned that use of periodic BC leads to results independent of the choice of the elementary cell [although self-consistent field (SCF) procedures do not always converge independently of this choice]. This fact can be used to test numerical procedures and computer programs (Kertész, 1976a; Kertész *et al.*, 1980d; Piela and Stolarczyk, 1981).

B. Bloch Functions and Wannier Functions

The overwhelming majority of the polymer quantum chemical calculations are based on the linear combination of atomic orbitals (LCAO) expansion. The LCAO crystal orbital ansatz for the one-electron wave functions in solids is due to Bloch (1928):

$$\psi_{\mathbf{k}} = (N^{-1/2}) \sum_{\mathbf{R}} e^{i\mathbf{kR}}\chi(\mathbf{r} - \mathbf{R}) \tag{5a}$$

where N is the number of unit cells in the crystal ($N \rightarrow \infty$) and $\mathbf{R}$ runs over the crystal lattice. In a 1D case, $\mathbf{R} = j\mathbf{a}$ ($j = 0, 1, 2, \ldots, N - 1$) and $\mathbf{k} = [2\pi/(N - 1)](\mathbf{a}l/|\mathbf{a}|^2)$, $l = 0, 1, 2, \ldots, N - 1$. In higher dimensions reciprocal lattice vectors are used (e.g., Callaway, 1964). The above Bloch functions are symmetry orbitals which transform according to the irreducible representations of the translation operations of the crystal lattice. In case there are m atomic orbitals (AO) in the unit cells, the symmetry orbitals [Bloch functions (BF)] will have besides $\mathbf{k}$ the index of the AO in question

$$\psi_{\alpha\mathbf{k}} = (N^{-1/2}) \sum_{\mathbf{R}} e^{i\mathbf{kR}}\chi_\alpha(\mathbf{r} - \mathbf{R}) \tag{5b}$$

Then, as usual, BFs with the same $\mathbf{k}$ can mix to form one-electron functions of the more complex systems (e.g., Koutecký and Zahradnik, 1961; Ladik, 1965):

$$\begin{aligned} \varphi_{n\mathbf{k}} &= \sum_{\alpha=1}^{m} C_{n\alpha}(\mathbf{k})\psi_{\alpha\mathbf{k}} \\ &= (N^{-1/2}) \sum_{\mathbf{R}} \sum_{\alpha=1}^{m} e^{i\mathbf{kR}} C_{n\alpha}(\mathbf{k})\chi_\alpha(\mathbf{r} - \mathbf{R}) \end{aligned} \tag{6}$$

where n is the band index. The $C_{n\alpha}(\mathbf{k})$ mixing coefficients are to be determined from a secular equation depending on the model Hamiltonian (see Section II,B).

Bloch functions are delocalized over the entire infinite crystal; however, they can be localized to Wannier functions (WF) (Wannier, 1937), leaving the many-electron Slater determinant unchanged

$$w_n(\mathbf{r} - \mathbf{R}) = N^{-1} \sum_{\mathbf{k}} e^{-i\mathbf{kR}}\varphi_{n\mathbf{k}}(\mathbf{r}) \tag{7}$$

In the LCAO case,

$$w_n(\mathbf{r}) = \sum_{\mathbf{R}'} \sum_{\alpha=1}^{m} W_{n\alpha}(\mathbf{R}' - \mathbf{R})\chi_\alpha(\mathbf{r} - \mathbf{R}') \tag{8a}$$

where

$$W_{n\alpha}(\mathbf{R}) = N^{-1} \sum_{\mathbf{k}} e^{i\mathbf{kR}} C_{n\alpha}(\mathbf{k}) \tag{8b}$$

It is a well-known property of Eqs. (8a) and (8b) that in the specific case of one orbital per cell ($m = 1$) and orthonormal $\chi_\alpha(\mathbf{r} - \mathbf{R}) - s$, $C_{n\alpha}(\mathbf{k})$ can be taken as 1 and then the Wannier function becomes identical with the AO: $w(\mathbf{r}) = \chi(\mathbf{r})$.

If the AOs are not orthonormal, $\langle \chi(\mathbf{r}) | \chi(\mathbf{r} - \mathbf{R}) \rangle = S(\mathbf{R})$. Then $\langle \varphi_{\mathbf{k}} | \varphi_{\mathbf{k}'} \rangle = \delta_{\mathbf{k},\mathbf{k}'} S_{\mathbf{k}}$ with $S_{\mathbf{k}} = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} S(\mathbf{R})$. As a consequence the norm is **k** dependent even for this simple case. Therefore the WFs extend over more than one AO. In fact, since the WFs form an orthonormal set they are a possible choice of well-localized orthogonalized orbitals (Löwdin, 1956).

We mention an interesting asymptotic property of the WFs: In the limit of weak interaction of the elementary cells the WFs become equal to molecular orbitals (MO) of the isolated cell. [This follows from the **k** independence of the $C_{n\alpha}(\mathbf{k})$ in this limit.] Thus while the WFs approach the MOs, the BFs remain unphysically delocalized over the whole infinite crystal. This asymptotic property has led to the idea (Kertész *et al.*, 1979e), of localizing the WFs further within the elementary cell by combining WFs from different occupied bands, as is usual in the calculation for localized orbitals in molecules. These further localized functions are very similar to localized orbitals in molecules and can be assigned to lone pairs, σ-bonding orbitals, etc. Actual transformation of BFs to WFs is inhibited by the difficulty of determining the free phase factor of the BFs in an optimal way. [The transformation $\varphi_{n\mathbf{k}} \rightarrow \varphi_{n\mathbf{k}} \exp(i\omega_{n\mathbf{k}})$ leaves the BFs invariant but not the WFs.] Some progress has been achieved by deriving a variational equation for $\omega_{\mathbf{k}}$ (Kertész and Biczó, 1973). Other restrictions can lead to symmetrical WFs (Van Boehm and Calais, 1979). Some applications on numerically available *ab initio* BFs have also been made (Kertész *et al.*, 1979a,e; Suhai, 1980a). Thus it is realistic to hope that numerical WFs can be used in local perturbation and correlation problems in the near future.

C. Hartree–Fock–Roothaan Theory for Polymers. The SCF Crystal Orbital Equations

The Hartree–Fock–Roothaan (HFR) formalism (Roothaan, 1951) is well known in molecular quantum chemistry. Its crystal orbital (CO) version constitutes one of the most important theoretical tools for the study of the electronic structure of polymers. Some notable differences of this CO scheme as compared to the MO scheme (**k**-space integration, lattice sums) are also discussed in this section.

1. *General Formalism*

In the 1960s the molecular HFR method was extended by several authors to encompass periodic solids within different semiempirical schemes (Peacock and McWeeney, 1959; Ladik and Appel, 1964; Popov and Shustorovich, 1965; André and Leroy, 1967; Imamura, 1970;

Morokuma, 1970; Evarestov *et al.*, 1976), taking the density matrix dependence of the Hamiltonian into account as required by the HF scheme. The general HFR CO equations have been derived by Del Re *et al.* (1967) and independently by André *et al.* (1967). The derivation is omitted here; we merely mention that the key step is to use the Bloch form of Eq. (6) as a trial function. As a consequence, a set of **k**-dependent $m \times m$ matrix equations arise, which we summarize here to enable the further discussion

$$\mathbf{H}(\mathbf{k})\mathbf{C}_n(\mathbf{k}) = \epsilon_n(\mathbf{k})\mathbf{S}(\mathbf{k})\mathbf{C}_n(\mathbf{k}) \tag{9}$$

These complex pseudoeigenvalue equations can be solved directly for a set of **k** points by the computer program of Zakrajsek and Zupan (1975). The **k**-dependent matrix elements are Fourier lattice sums of the direct-space matrix elements. In 1D,

$$\mathbf{F}(\mathbf{k}) = \sum_{j=-\infty}^{\infty} \exp(i\mathbf{k}j\mathbf{a})\mathbf{F}(j) \tag{10}$$

$$\mathbf{S}(\mathbf{k}) = \sum_{j=-\infty}^{\infty} \exp(i\mathbf{k}j\mathbf{a})\mathbf{S}(j) \tag{11}$$

The direct-space Fock and overlap matrix elements are defined by use of integrals over AOs as follows

$$S_{\alpha\beta}(j) = \langle \chi_\alpha(\mathbf{r}) | \chi_\beta(\mathbf{r} - j\mathbf{a}) \rangle = \langle {}^{0}_{\alpha} | {}^{j}_{\beta} \rangle \tag{12}$$

$$h_{\alpha\beta}(j) = \langle {}^{0}_{\alpha} | -\tfrac{1}{2}\Delta | {}^{j}_{\beta} \rangle - A_{\alpha\beta}(j) \tag{13}$$

$$A_{\alpha\beta}(j) = \sum_{h=-\infty}^{\infty} \sum_{I}^{(\mathrm{nuc})} \left\langle {}^{0}_{\alpha} \left| \frac{Z_I}{|\mathbf{r} - \mathbf{X}_{h,I}|} \right| {}^{j}_{\beta} \right\rangle \tag{14}$$

where Z_I is the charge of nucleus I at position $\mathbf{X}_{h,I}$ in the nuclear attraction term $A_{\alpha\beta}(j)$. Summation over I includes all nuclei in the unit cell h. The Fock matrix elements also include the two-electron integrals $\langle {}^{0j}_{\alpha\beta} | {}^{hl}_{\gamma\delta} \rangle$ with the ⟨11/22⟩ index convention. (In Section II,E the ⟨12/12⟩ convention is used because of the complex nature of BFs.) The density matrix elements contain a sum convertible to an integral over the doubly occupied part of the BZ

$$D_{\gamma\delta}(j) = \frac{2}{N} \sum_{\mathbf{k}} \sum_{n} (\mathrm{occ}) \exp(i\mathbf{k}j\mathbf{a}) C^{*}_{n\gamma}(\mathbf{k}) C_{n\delta}(\mathbf{k}) \tag{15}$$

The Coulomb term

$$V_{\alpha\beta}(j) = \sum_{h,l=-\infty}^{\infty} \sum_{\gamma,\delta=1}^{m} D_{\gamma\delta}(h - l) \langle {}^{0j}_{\alpha\beta} | {}^{lh}_{\delta\gamma} \rangle \tag{16}$$

and the exchange term

$$X_{\alpha\beta}(j) = \frac{1}{2} \sum_{h,l=-\infty}^{\infty} \sum_{\gamma,\delta=1}^{m} D_{\gamma\delta}(h - l) \langle {}^{0h}_{\alpha\gamma} | {}^{lj}_{\delta\beta} \rangle \tag{17}$$

contribute to the Fock matrix in the usual way

$$F_{\alpha\beta}(j) = h_{\alpha\beta}(j) + V_{\alpha\beta}(j) - X_{\alpha\beta}(j) \tag{18}$$

The total energy per cell is

$$E_{\text{tot}} = E/N = N^{-1} \sum_{\mathbf{k}} \sum_{n} (\text{occ})\epsilon_n(\mathbf{k}) + \sum_{j=-\infty}^{\infty} \operatorname{Tr}(\mathbf{h}(j)\mathbf{D}(j)) + NR \tag{19a}$$

$$NR = \sum_{j>l=-\infty}^{\infty} \sum_{I,J}{}' \frac{Z_I Z_J}{|\mathbf{X}_{j,J} - \mathbf{X}_{l,I}|} \tag{19b}$$

where the prime on the sum indicates omission of the term with zero denominator. Expectation values of one-particle operators $\hat{\mathcal{O}} = \Sigma$ (all electrons)$\hat{\mathcal{O}}(\mathbf{r}_i)$ can be expressed through the density matrix as (Kertész *et al.*, 1979c)

$$\overline{\mathcal{O}} = N \sum_{j=-\infty}^{\infty} \sum_{\alpha,\beta} D_{\alpha\beta}(j) \langle {}^{0}_{\alpha} | \hat{\mathcal{O}} | {}^{j}_{\beta} \rangle \tag{20}$$

Mulliken populations can be defined in terms of sums over products of density matrix elements and overlaps, e.g., the atomic populations for atom A are

$$q_A = \sum_{j=-\infty}^{\infty} \sum_{\alpha,\beta}^{A} D_{\alpha\beta}(j) \langle {}^{0}_{\alpha} | {}^{j}_{\beta} \rangle \tag{21}$$

As usual, the Mulliken population analysis is a subdivision of the total electronic charge. The total electronic charge of the unit cell is

$$\sum_{j=-\infty}^{\infty} \sum_{\alpha,\beta} D_{\alpha\beta}(j) \langle {}^{0}_{\alpha} | {}^{j}_{\beta} \rangle = n_0 \tag{22}$$

2. *Semiempirical Formalisms*

As in molecular quantum chemistry, semiempirical versions of the LCAO crystal orbital formalism have found widespread applications. These can be derived by, e.g., substituting into the general formalism the corresponding Hamiltonian matrix elements. Usually, the range of their applicability is very similar to that of the original molecular methods. The simple π-electrons-only methods as that of Hückel (1931) and PPP (Pariser and Parr, 1953; Pople, 1953) have found widespread applications to conjugated chains or other polymers (e.g., Lennard-Jones, 1937;

Ooshika, 1957; Longuet-Higgins and Salem, 1959; Koutecký and Zahradnik, 1961; Salem, 1961; Popov and Shustorovich, 1965; Ladik, 1965, 1973; André and Leroy, 1967; Kertész *et al.*, 1974; Wilson, 1975; Yarkony and Silbey, 1977; Kertész, 1979; Balasubramanian and Yarkony, 1980). Next in sophistication, and perhaps most popular is the extended Hückel theory (EHT; Hoffmann, 1963), especially for the band structure itself, because it is free from the tendency of the HF methods to predict forbidden energy gaps too large. Applications of EHT to saturated polymers have been reviewed by André (1980); results on conjugated polymers (Whangbo *et al.*, 1979) are discussed together with results of other methods in Section III.

Self-consistent field methods such as the different variations of neglect of the differential overlap (NDO) (Pople *et al.*, 1965) have also been used for polymers (for a review on saturated polymers see André, 1980). Some available calculations on conjugated systems are discussed in Section III, and the nice agreement between CNDO/2 and *ab initio* STO-3G calculations is generally noteworthy. Some other techniques, e.g., the simultated *ab initio* methods (Duke and O'Leary, 1973; Delhalle *et al.*, 1977) can be considered as non-SCF one-electron methods based on pattern molecules. Thus they are very closely related to EHT. The same remark holds for the nonempirical effective potential approach of Nicolas *et al.* (1980).

The quality of the results of semiempirical methods has been found to be the same as for smaller molecules, of course. Computationally, however, they are at least one order of magnitude cheaper than their *ab initio* counterpart with a minimal basis set, not to mention large sets. Furthermore, there is a severe technical limitation for the full geometry optimization of periodic polymers related to the low-frequency phonon modes. Namely, one may enlarge the unit cell in order to include several chemical repeat units. Such an increase of geometry freedom permits the formation of "secondary" (or higher order) structures through the formation of weak bonds among units being "far," measured along the main chain but geometrically rather close. These higher order structures are of primary importance in the physics and chemistry of polymers and their biological functioning, but usually the physical repeat unit is too large in such a case to permit *ab initio* treatment. The role of this problem should not be underestimated and it will be one major reason to continue with semiempirical polymeric electronic structure calculations.

D. Computational Aspects

In addition to the convergency problems familiar from MO calculations (convergency with respect to the density matrix to self-consistency and convergency with respect to basis set), in CO calculations one has to

TABLE III

FUNCTION OF ENERGY GAPS ON THE FINITE-NEIGHBOR APPROXIMATION AND BASIS SET

System	Basis set	Number of neighbors included	Gap (a.u.)	Reference
$(C_2)_x$	STO-3G	2^a	0.3647	Karpfen (1979)[c]
		4^b	0.408	Kertész *et al.* (1978a)
		3^a	0.3758	Karpfen (1979)
		4^a	0.3828	Karpfen (1979)
		6^a	0.3853	Karpfen (1979)
	(7,3)	2^a	0.2553	Karpfen (1979)
		4^a	0.2885	Karpfen (1979)
	(7,3,1)	2^a	0.2679	Karpfen (1979)
$(CH)_x$	STO-3G	2^a	0.3109	Karpfen (1979)
		4^b	0.2660	Kertész *et al.* (1977a)
		4^a	0.2958	Karpfen (1979)
	8s4p/4s	2^a	0.2116	Karpfen (1979)

[a] In unit cells.
[b] Atomic neighbors along main chain.
[c] Personal communication.

consider convergency with respect to (1) the number of points in the **k** mesh representing integrals in Eqs. (15) and (19); (2) the number of included neighbors in the lattice sums of Eqs. (10), (11), (14), (16), (17), (19), and (20); and (3) the shape of the Fermi surface (FS) in systems with partially filled band(s) (Kertész, 1976a). Aside from the FS problem, it has been the general experience (see Table III) to assess the relative importance of the various convergence problems by the simplified relations (Kertész, 1976a; Karpfen, 1978, 1981a; Kertész *et al.*, 1980d) basis set > lattice sums > **k**-point integration. An exception is the case of the metallic (partially filled band) situation, where the lattice sum of the exchange term [Eq. (17)] is slowly convergent (Ukrainskii, 1975; Kertész, 1976a; Monkhorst and Kertész, 1981).

1. **k**-*Space Integration*

No difficulty is posed by **k**-space integration in 1D. Even though finite **k**-mesh is used, a strict correspondence with a periodic cluster is usually lost, because the $\pm\pi/a$ point is not included in the latter [see Eq. (1) for $j = n$]. The number of **k** points should be sufficiently large to ensure the reliability of the density submatrices for large j in Eq. (15).

2. *Finite-Neighbor Approximation*

It is desirable to evaluate the long-range Coulomb terms (Löwdin, 1956), however, in practical computer realizations the integrals over AOs in Eqs. (12)–(19) can be evaluated explicitly over a finite range only. We shall designate this the finite-neighbor approximation. Coulomb integrals fall off slowly, asymptotically as

$$\left\langle \begin{matrix} 0 \\ \alpha \end{matrix} \middle| \frac{Z}{|\mathbf{X} - \mathbf{r}|} \middle| \begin{matrix} 0 \\ \alpha \end{matrix} \right\rangle \sim \frac{Z}{|\mathbf{X}|} \tag{23}$$

$$\left\langle \begin{matrix} 00 \\ \alpha\alpha \end{matrix} \middle| \begin{matrix} RR \\ \beta\beta \end{matrix} \right\rangle \sim \frac{1}{|R|} \tag{24}$$

Because of electrical neutrality of the crystals, however, an approximate cancellation of the Coulomb terms enables the finite neighbor approximation to give meaningful results. Several alternatives for the choice of the cutoff region are possible. The four different cutoff methods discussed below in fact represent different constructions of model Hamiltonians, possessing somewhat different properties, the differences going to zero as the cutoff region increases. In practice, this limit can be reached by using the special techniques of long-range lattice sums (see Sections II,D,3 and 4).

Method 1. Cellular Mth-neighbor approximation (André and Leroy, 1971; Karpfen and Schuster, 1976; Karpfen, 1981b). Integrals are calculated for a cluster with $M + 1$ elementary cells, and those are kept which involve at least one orbital from the reference (zeroth) cell. (Beyer and Karpfen, 1982 have successfully used a multipole expansion technique combined with this method.) It is easy to write the code of a computer program for this scheme based on existing MO programs, however, small artificial asymmetries in the resulting density matrices are introduced. These are avoided by method 2.

Method 2. Symmetric Mth-neighbor approximation (Kertész, 1976a; Kertész *et al.*, 1980d). This uses a similar scheme, but further integrals are neglected on symmetry grounds within the $M + 1$ cell cluster, namely those which are equivalent by translation symmetry to another formally $M + 1$-st neighbor integral: if interaction C_2–C_5 is neglected (on Fig. 1), then the same type of integral involving atoms C_1–C_4 cannot be retained. This symmetric cutoff is achieved practically by means of a distance parameter ρ (ρ-cut procedure, Kertész, 1976a). This procedure had some role in clarifying the (sometimes important) consequences of the small inaccuracies of method 1 (Kertész *et al.*, 1977a, 1980d) especially for total energies and band structures of chains with a near-metallic state.

Method 3. A more involved finite-neighbor approximation is being used by the Namur group in connection with their techniques using long-range lattice summations (Delhalle *et al.*, 1978; Piela and Delhalle, 1978; Brédas, 1980). In the finite-neighbor part their limit for h in Eqs. (14) and (16) is $-M$ to M as in methods 1 and 2. However, in contrast to those, the summation over l in Eq. (16) do not go from $-M$ to M but from $h - M$ to $h + M$. This method, together with the next one, has the advantage that the charge distributions $d_{\alpha\beta}^{hl} = \chi_\alpha(\mathbf{r} - h\mathbf{a})\chi_\beta(\mathbf{r} - l\mathbf{a})$ also contain contributions when h approaches M for values of l larger than M. This justifies the different limits in the l and h summation. A similar scheme has been used by Euwema *et al.* (1973) and Wilhite and Euwema (1974) in their "charge-conserving integral approximation." In method 3, e.g., an integral $\langle {}^{0M}_{\alpha\beta} | {}^{M2M}_{\gamma\delta} \rangle$ is retained although it is neglected in methods 1 and 2. Such an integral occurs in a cluster containing at least $2M + 1$ unit cells. On the other hand, a much larger integral from the $2M + 1$ cell region $\langle {}^{00}_{\alpha\alpha} | {}^{2M2M}_{\beta\,\beta} \rangle$ is neglected (or approximated by a classical term) in this approach. Thus method 3 corresponds to an intermediate case between Mth- and $2M$th-neighbor approximation in the sense of methods 1 and 2. This method has been used in connection with the long-range summation methods with considerable success.

Method 4. Two-cutoff parameters approximation. Suhai (1980a) has recently used a scheme which can be considered a refinement of method 3. In Suhai's scheme the summation over l is extended from $h - M'$ to $h + M'$, not as in method 3 from $h - M$ to $h + M$. The introduction of the new parameter M' is justified by the high degree of localization of the overlap charge distribution $d_{\alpha\beta}^{hl}$. This scheme is intermediate between the Mth and $M + M'$th-neighbor approximation in cellular sense and might be more economical in practical calculations because M' can be chosen significantly smaller than M. Somewhat surprisingly, however, in actual calculations based on this method the total energy converges slowly as M increases; e.g., even for M as large as 20, the total energy per cell differs by ~ 1 eV from the $M \to \infty$ extrapolated value.

Unfortunately, since no calculations using these four methods have been performed on the same polymer, a critical comparison is not possible. Nonetheless, it is satisfying to note that results on H chains using methods 1 and 2 converge to the same numbers (Kertész *et al.*, 1976a; Karpfen, 1979a,b). Results on LiH chains (Delhalle *et al.*, 1980) established agreement between methods 1 and 3. While these findings prove that all these methods should lead to the same results if M is sufficiently large, in actual calculations considerable differences occur due to computer limitations in choosing M sufficiently large. A way out of this problem is provided by the analytical treatment of the long-range parts of the summations.

3. *Long-Range Lattice Sums. Coulomb Terms*

Considerable progress has been achieved (Delhalle *et al.*, 1978; Piela and Delhalle, 1978; André *et al.*, 1978; Brédas, 1980; Piela, 1980) in treating the sum of the two (individually divergent) Coulomb sums, the nuclear attraction and electron repulsion terms in the expression of the Fock matrix elements

$$W_{\alpha\beta}(j) = -A_{\alpha\beta}(j) + V_{\alpha\beta}(j) = \sum_{h=-\infty}^{\infty} \left(-\sum_{I} \left\langle {}^{0}_{\alpha} \left| \frac{Z_I}{|\mathbf{r} - \mathbf{X}_{h,I}|} \right| {}^{j}_{\beta} \right\rangle \right.$$
$$\left. + \sum_{l=-\infty}^{\infty} \sum_{\gamma,\delta=1}^{m} D_{\gamma\delta}(h-l) \left\langle {}^{0\,j}_{\alpha\beta} \middle| {}^{lh}_{\gamma\delta} \right\rangle \right) \tag{25}$$

as well as an analogous term in the total energy per cell

$$E_C = \sum_{h=-\infty}^{\infty} \left[\sum_I \sum_J \frac{Z_I Z_J}{|\mathbf{X}_{0,J} - \mathbf{X}_{h,I}|} - \sum_{j=-\infty}^{\infty} \sum_I \sum_{\alpha,\beta} D_{\alpha\beta}(j) \right.$$
$$\left. \times \left\langle {}^{0}_{\alpha} \left| \frac{Z_1}{|\mathbf{r} - \mathbf{X}_{h,I}|} \right| {}^{j}_{\beta} \right\rangle \right] \tag{26}$$

resulting from nuclear repulsion and electron nuclear attraction. In both cases terms with large h are Coulombic in character, and due to the neutrality of the elementary cell these converge in the same way as do usual Madelung sums. For large h terms with $|l - h| \ll |h|$, $|j| \ll |h|$ are significant due to the fast decrease of the overlap charge densities $\chi_\alpha(\mathbf{r} - h\mathbf{a})\chi_\beta(r \pm (l - h)\mathbf{a})$ and $\chi_\alpha(\mathbf{r})\chi_\beta(\mathbf{r} - j\mathbf{a})$, respectively. Then a multipole expansion can be applied to the Coulomb interactions (Piela and Delhalle, 1978; Piela, 1980), which is easy to perform as only one-particle matrix elements are to be calculated. Numerical experience has shown that this procedure is very effective even in the case of a $(\mathrm{LiH})_x$ chain with large long-range (LR) contributions for both the Fock matrix elements (Piela and Delhalle, 1978) and the total energy (Delhalle *et al.*, 1980). An alternative approach (André *et al.*, 1978; Fripiat and Delhalle, 1979) based on the Fourier transform technique of Harris and Monkhorst (1970) gives equally excellent results but it is restricted at present to Gaussian basis sets. By the use of this latter method Brédas *et al.* (1980) have demonstrated that the LR terms may have a dramatic effect on the total energy differences of chain conformations. The energy difference of the T and G conformations of polyethylene per $(\mathrm{CH_2})$ unit was found to be $E_\mathrm{T} - E_\mathrm{G} = 0.02672$ a.u. without LR terms. The correct value with LR corrections is -0.00464

a.u., thus even the sign may be wrong. Most remarkable is, however, that up to seven significant figures for the same total energies and up to all significant figures for the same energy differences resulted from small-cluster (C_5H_{12}, C_6H_{14}) calculations as well. While this confirms the correctness of the procedure, it also sheds some light on the nature of the LR corrections which are rather more mathematical than physical in character in that case.

Finally in this section on LR Coulomb sums we mention an attractive and very simple approach. Piela and Stolarczyk (1982) and Stolarczyk and Piela (1982) have proposed to use the freedom in the definition of the elementary cell to supplement it by point charges having the following properties: (1) they are placed at the boundaries, (2) pairwise opposite in sign and equal in magnitude so that they cancel due to translational symmetry, and (3) are chosen in such a way as to make the dipole, quadruple, etc., moments zero if possible. This ensures a very fast direct-space convergence, as demonstrated by numerical examples (L. Piela, 1981, personal communication). This scheme, which is a generalization of the Madelung summation method of Calara and Miller (1976) is very promising due to its simplicity especially in 3D, while for polymers it is limited to chains with the dipole moment parallel to the chain.

4. *Long-Range Lattice Sums. Density Matrix and Exchange*

The exchange term in the Fock matrix [Eq. (17)] contains the LR term

$$\sum_{|l|\gg 1} \sum_{\gamma,\delta} D_{\gamma\delta}(l)\left(\begin{smallmatrix} 0 & 0 \\ \alpha & \delta \end{smallmatrix}\middle|\begin{smallmatrix} l & l \\ \gamma & \beta \end{smallmatrix}\right) \tag{27}$$

giving a contribution to the $F_{\alpha\beta}(l)$ direct-space Fock matrix element. The behavior of this sum is strongly influenced by the asymptotics of $D_{\gamma\delta}(l)$ for large l. In the case of a metallic chain with one orbital per unit cell ($m = 1$, so AO indices may be omitted) in the Hückel model $C(\mathbf{k}) = 1$. Substituting this into Eq. (16) we obtain for the density matrix elements ($l \neq 0$)

$$D(l) = \frac{2}{N} \sum_{\mathbf{k}} (\text{occ}) \exp(i\mathbf{k}l\mathbf{a}) = \frac{1}{\pi} \int_{-\pi/2}^{\pi/2} dk e^{ikl} = \frac{2}{\pi|l|} \sin\left(\frac{\pi}{2} l\right) \tag{28}$$

$D(l)$ has a very slow ($|l|^{-1}$) decay, producing an $|l|^{-2}$ decay of terms in the sum (27). A similarly slow decrease results for any partial filling of the band, while for the fully filled band $D(l) = 2\delta_{l,0}$, thus within this simple model no LR term occurs.

The problem of the slow convergence of this exchange sum has been shown to lead to inaccuracies in band and total energies (Kertész, 1976a;

Piela *et al.*, 1981). The first attempt to understand this slow convergence is due to Ukrainskii (1975), who studied the nonalternating PA (effectively one electron per unit cell). He found that in accordance with Eq. (28) the terms in the sum (27) fall off like $(-1)^l l^{-2}$ leading to zero DOS at the Fermi level (FL). This nonphysical result of LR exchange in HF theory was long known for the free-electron gas and was proven recently by Monkhorst (1979) for any half-filled band system in any number of dimensions.

More recently, Piela *et al.* (1981), as well as Monkhorst and Kertész (1981), have attempted to analyze the behavior of the LR exchange term in polymer quantum calculations. Both groups concluded that in a system with nonzero energy gap this sum converges much faster than in the metallic case. The faster decay of the density matrix elements could be anticipated on the basis of well-known results of Kohn (1959) and Des Cloizeaux (1964) related to the proof of existence of exponentially decaying Wannier functions. The density matrix elements can be expressed in terms of the WFs LCAO coefficients [Eq. (8b)], as

$$D_{\alpha\beta}(j) = \sum_{n}^{\text{occ}} \sum_{h=-\infty}^{\infty} W_{n\alpha}(j-h) W_{n\beta}(h) \tag{29}$$

provided no partially filled band is present. Since all $W_{n\alpha}(l) - s$ decay exponentially, so does $D_{\alpha\beta}(j)$ for large j, with the rate of the slowest decaying WF from the occupied set. Monkhorst and Kertész (1981) have studied analytically two-band models and established a relationship between this exponential behavior and the energy gaps and bandwidths of the polymer. It was possible to show (Salem, 1961; Monkhorst and Kertész, 1981) that

$$\lim_{l\to\infty} D_{\alpha\beta}(n+1)/D_{\alpha\beta}(n) = -\rho \tag{30}$$

where the dimensionless $\rho < 1$ is a complicated function, but it can usually be approximated by

$$\bar{\rho} = [1 + \delta/(1+\gamma)^2]^{-1} \tag{31}$$

where δ is the band gap/bandwidth ratio and γ is the largest overlap of neighboring orbitals in the chain. This connection of the band parameter δ and the localization parameter ρ may be used to discriminate differently localizable (π, σ, core) electrons (Kertész *et al.*, 1982c). In the metallic limit $\delta \to 0$ ($\rho \to 1$), and thus the exponential decay disappears in agreement with Ukrainskii's (1975) result.

It is expected that for the general case ρ can be approximated by

$$[1 + \delta_{\min}/(1+\gamma)^2]^{-1} \tag{32}$$

where $\delta_{\min}$ is the smallest bandgap/bandwidth ratio. Then the convergence of the exchange sum (27) can be monitored by evaluating the asymptotic term as (for $\rho < 1$)

$$X_{\text{asy}} = \sum_{l>M} D(l)/l \approx \sum_{l>M} (-)^{l} l^{\alpha} \tag{33}$$

where α is less than $-3/2$. For large M, $X_{\text{asy}} \approx (-\rho)^{M} M^{\alpha}$. Numerical experience on different chains at *ab initio* level (Kertész *et al.*, 1982c) has shown that the asymptotic region is reached as fast as 4–5 neighbors. We may thus conclude that the LR exchange sums are under control for systems with nonzero gap.

It is instructive to relate the LR behavior of the density matrix to elements of the Hamiltonian matrix. A recent analysis (Surján *et al.*, 1982) has shown that starting from strictly localized orbitals, the asymptotic tails of the WFs (and thus those of the density matrix) have two kinds of contributions: (1) "through-space" terms arising from a delocalization correction over large distance and much larger (2) "through m-bond" delocalization terms resulting from successive perturbations of "through 1, 2, . . . , $m - 1$ bond" delocalization corrections to the strictly localized orbitals. This leads to an exponential decay, too, with a rate analogous to that of Eq. (30). These latter, through m-bond delocalization tails of the WFs do not change in first order if bond length and bond angles are fixed. Consequently, although these dominate the LR decay of the density matrix, the smaller through-space terms may control conformational potential curves.

E. Instabilities in the Case of Partially Filled Bands

Instability of HF wave functions appears in cases of near degeneracy or degeneracy (Ooshika, 1957; Overhauser, 1960; Thouless, 1961; Čižek and Paldus, 1967; Fukutome, 1968; Paldus and Čižek, 1970) which leads to the occurrence of lower lying symmetry-breaking solutions. Such broken symmetry (BS) solutions are essentially of two types (according to terminology of Čižek and Paldus, 1967):

(1) singlet instability (in the case of doubly filled Slater determinant, space-unrestricted HF), and

(2) nonsinglet instability (if the double-occupancy restriction is released, spin-unrestricted HF, UHF).

Such problems are of particular importance in discussing the electronic structure of polymers with partly filled energy bands having zero energy gaps.

Another related but different problem is whether the presence of the

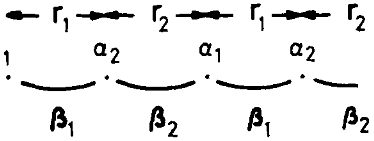


Fig. 2. Hückel model of a simple two-atom-per-elementary-cell chain; α_1 and α_2 are the Coulomb integrals, β_1 and β_2 the resonance (or hopping) integrals, respectively: $r = \frac{1}{2}(r_1 + r_2)$; $\Delta r = r_1 - r_2$; $\Delta = \beta_1 - \beta_2$.

HF instability is driving the lattice to distort or not. Although there are indications that these two effects are closely connected, in the absence of detailed knowledge about electron correlation effects some caution is in order (Calais, 1977). In the remaining part of this section we shall discuss the electronic instability problem in polymer calculations (which is essentially a manifestation of the "symmetry dilemma"; Löwdin, 1969) and its relation to the lattice instability (Peierls, 1955). This is connected to the study of the potential energy curve of the nuclei around the equidistant configuration. A classification is already possible with a very simple two-atom two-electron per unit cell (Hückel) model (Kertész *et al.*, 1980a), illustrated in Fig. 2. Here the r_i bond lengths, the β_i hopping (resonance), and the α_i on-site (Coulomb integrals alternate. The metallic state corresponds to parameters $\alpha_1 = \alpha_2$ and $\beta_1 = \beta_2$. A relation of the type $\beta_i = a \exp(-br_i)$ is assumed, ensuring coupling of the geometry and the electronic parameters. The total energy as function of $\Delta = \beta_1 - \beta_2$ around $\Delta r = r_1 - r_2 = 0$,

$$\alpha_1 = \alpha_2, \qquad E_{\text{tot}}/N = x_1|\Delta r|\ln|\Delta r| + y_1(\Delta r)^2 + \cdots \tag{34a}$$

$$\alpha_1 \neq \alpha_2, \qquad E_{\text{tot}}/N = -x_2(\Delta r^2) + y_2(\Delta r)^2 + \cdots \tag{34b}$$

where x_i are parameters; y_i are related to the other (frozen core) electrons not taken into account explicitly in this model. Thus, the metallic state (34a) always distorts independently of the elastic part (Peierls, 1955). This is due to the one-dimensionality of the system because an appreciable fraction of the states in the BZ reach stabilization due to the distortion, as illustrated in Fig. 3. The magnitude of the distortion is limited by the elastic constant y_1. The heteroatomic chain (34b) may or may not distort, depending on the relation of Δ and Δr as well as on the magnitude of x_2 and y_2. For completeness we mention that the total energy per cell can be expanded around other points of the curve, too, yielding

$$E_{\text{tot}}/N = -x_3(\Delta r) + y_3(\Delta r)^2 \tag{34c}$$

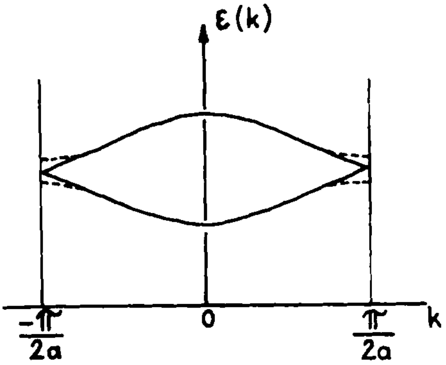


Fig. 3. Simple argument to illustrate the Peierls distortion. Upon distortion of the lattice (bond-length alternation in PA), a forbidden energy gap occurs. Since only the lower branch is filled with electrons, a stabilization of the electronic energy term occurs. Distortion is limited by elastic forces of the lattice (2a is the translation of the distorted chain).

Equation (34c) describes the potential energy curve around a nonequidistant point ($r_1 \neq r_2$) and is thus not applicable to the study of the behavior of the curve around $r_1 = r_2$ within the Hückel Hamiltonian. However, if Coulomb interactions are included, this case will be realized by the bond-order alternation-wave ground state (the three possibilities are illustrated in Fig. 4).

1. *The Singlet Instabilities. Charge-Density Waves and Bond-Order Alternation Waves*

We shall use as an example a one-electron-per-atom chain. This corresponds to the above model with $r_1 = r_2$, $\beta_1 = \beta_2$, and $\alpha_1 = \alpha_2$, and describes a half-filled-band metallic chain. Then the Bloch functions

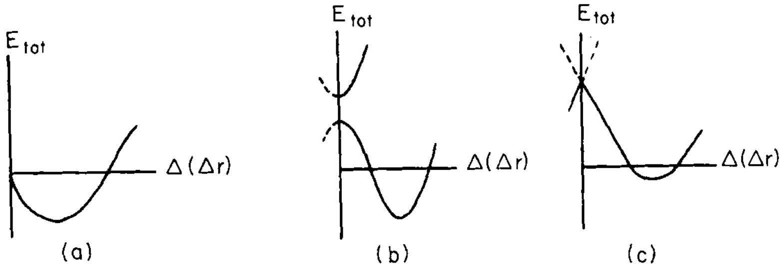


Fig. 4. Three possible dependencies of the total energy as function of the asymmetric distortion of the lattice: (a) Peierls case, Eq. (34a); (b) diagonal charge-density wave, Eq. (34b); (c) off-diagonal CDW, Eq. (34c).

[Eq. (6)] having no variational freedom can be reduced to [Eq. (5)]. Energy gain is possible, however, by breaking the symmetry (Löwdin, 1969), using lower symmetry Bloch functions

$$\varphi_k^e = \frac{\sqrt{2}}{\sqrt{N}} \sum_j (\text{even}) \exp(ikja)\chi(r - ja) \tag{35}$$

$$\varphi_k^o = \frac{\sqrt{2}}{\sqrt{N}} \exp\left(\frac{ik}{2}\right) \sum_j (\text{odd}) \exp(ikja)\chi(r - ja) \tag{36}$$

In this way it is possible to introduce new degrees of variational freedom in the now already broken symmetry (BS) wave function in several ways; e.g.,

$$\varphi_k^{\text{BS}} = e^{i\omega_k} \cos f_k \varphi_k^e + \sin f_k \varphi_k^o \tag{37}$$

The symmetric function is a special case of this when $f_k = \pi/4$ and $\omega_k = 0$. If this restriction is released, the function φ_k^{BS} has a lower symmetry than before, corresponding to a doubling of the elementary cell because the coefficients of the odd and even sublattices are no longer related by symmetry. Thus, effectively, we have a two-electron–two-orbital unit cell. The corresponding densities describe different kinds of charge waves, as is apparent from Table IV. With charge density waves (CDW), the charges alternate (as for a chain in the Hückel model with parameters $\alpha_1 \neq \alpha_2$; $\beta_1 = \beta_2$) and the bond orders are equal, but with bond-order alternation waves (BOAW), bond orders alternate and charges are uniform (as for a chain in the Hückel model with parameters $\alpha_1 = \alpha_2$; $\beta_1 \neq \beta_2$). The application of the above Hückel analysis (Fig. 4) would thus predict distortion of the lattice for BAOW, but not necessarily for CDW.

Whether any of these has lower energy than the symmetrical one, cannot be answered in general (Čižek and Paldus, 1967), although criteria for the existence of the different kinds of instabilities have been given for

TABLE IV

DIFFERENT TYPES OF CHARGE-DENSITY WAVES IN A ONE-ELECTRON–ONE-ORBITAL CHAIN AND THE CORRESPONDING PHASES IN EQ. (37) AS WELL AS DENSITY-MATRIX ELEMENTS $D_{\alpha\beta}(j)$ IN EQ. (15)[a]

Diagonal charge-density wave (CDW)	$D_{11}(0) \neq D_{22}(0)$,	$D_{12}(0) = D_{21}(1)$;	$\omega_k = 0$,	$f_k \neq \pi/4$
Off-diagonal CDW, bond-order alternation wave (BOAW)	$D_{11}(0) = D_{22}(0)$,	$D_{12}(0) \neq D_{21}(1)$;	$\omega_k \neq 0$,	$f_k = \pi/4$
General CDW (GCDW)	$D_{11}(0) \neq D_{22}(0)$,	$D_{12}(0) \neq D_{21}(1)$;	$\omega_k \neq 0$,	$f_k \neq \pi/4$

[a] Numbering according to a double unit cell with two orbitals.

the PPP model of a cyclic polyene chain by Paldus and Čižek (1970). Accordingly, over a critical size of the chain, all instabilities occur within the studied parametrizations. Within the first-neighbor approximation for the infinite chain the total energy gain for a PPP model, due to the symmetry-breaking $E/N = E^{\mathrm{sym}}/N - E^{\mathrm{BS}}/N$, as function of the first-neighbor Coulomb repulsion γ_1, is depicted in Fig. 5 (Kertész, 1975). The CDW solution occurs above a critical value of γ_1 (Whangbo, 1980), while in the case of BOAW a BS solution always exists within the given model. We mention here that BS solutions have been found here as well as in all our calculations on metallic systems (Kertész *et al.*, 1976b,c; 1977a; 1978a; 1979b) by using an enlarged (doubled) cell and a starting density matrix with lower symmetry; then, uses of the standard SCF density iterations have converged, as usual. For all systems studied having partially filled energy bands, we have found at least one type of BS solution with a diagonal and/or off-diagonal CDW (Table V summarizes some selected results). We would like to emphasize that the energy-gain values have nothing to do with the electron correlation. On the contrary, they are manifestations of the limited validity of the HF model for metallic systems.

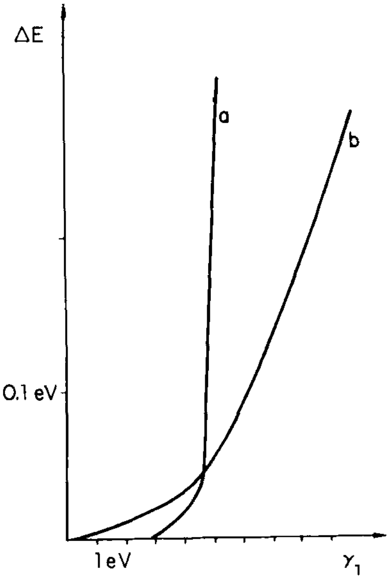


Fig. 5. Absolute value of total energy gain of broken-symmetry HF solutions in a PA chain within the PPP model as function of the first-neighbor repulsion integral γ_1. Both types of CDWs (diagonal and off-diagonal) are given: curve *a*, $E^{\mathrm{tot}}_{\mathrm{CDW}} - E^{\mathrm{tot}}_{\mathrm{SYM}}$; curve *b*, $E^{\mathrm{tot}}_{\mathrm{BAW}} - E^{\mathrm{tot}}_{\mathrm{SYM}}$. (After Kertész, 1975.)

TABLE V

(SPACE) BROKEN-SYMMETRY HARTREE–FOCK SOLUTIONS IN A FEW SELECTED POLYMERS

System	Method	Energy gain per cell with respect to the metallic solution (eV)	Energy gap (eV)	Type of wave	Ref.
PA[a]	PPP	0.24	5.58	Diagonal CDW	Kertész (1975)
PA	AI[b]	0.030	4.14	GCDW	Kertész *et al.* (1977a)
Carbon chain[c]	AI	0.16	5.79	Two perpendicular waves with shifted phases	Kertész *et al.* (1978a)
$(SN)_x$	AI	0.19	3.26	GCDW	Kertész *et al.* (1978f)
Hydrogen atomic chain[d], $(H_2)_\infty$	AI	0.034	6.23	BOAW	Kertész *et al.* (1976c)
$(H_2)_{17}$[e]	AI	0.036	—	BOAW	Bernard and Paldus (1980)

[a] For $\gamma_1 = 5.28$ eV.

[b] AI, *ab initio*.

[c] For $r_{cc} = 1.24$ Å.

[d] For $r_{HH} = 0.995$ Å.

[e] For $r_{HH} = 2.6$ a.u. $= 1.375$ Å.

Let us return to the problem of the coupling of the electronic instability with that of the lattice. Within the HF scheme the occurrence of the BS solution may signal the instability of the lattice. If the Hellmann–Feynman theorem holds for the chain, the forces acting on the nuclei are determined solely by the classical electrostatic forces due to the charge distribution of the electrons and nuclei. In order to see if the x component (along the chain) of the force acting on nucleus i, $F_{i,x}$ is zero or not, it is sufficient to check whether the charge distribution is invariant under the $x \to -x$ transformation or not. Since in the equidistant linear arrangement the field of the other nuclei is invariant, it is necessary to consider only the electrons. Solely from this consideration it follows that nonzero Hellmann–Feynman forces occur in the BOAW case but not in the (diagonal) CDW case. Further care is necessary at points of possible, degeneracy, i.e., at $\Delta r = 0$ in our case (Kertész and Mayer, 1979, unpublished). Suppose that the curves do cross at $\Delta r = 0$ as illustrated in Fig.

4c. We shall first demonstrate that mixing these two states does not change the total energy at all in the solid-state limit ($N \to \infty$). This is a special case of the properties of wave functions for extended many-particle systems. In our case the two wave functions correspond to Slater determinants with φ^{e} and φ^{o} interchanged. For an off-diagonal CDW this is equivalent to the two determinants one gets by $\Delta r \to -0$ and $\Delta r \to +0$ (reflection). If we denote the Bloch functions after the $\varphi^{\mathrm{e}} \leftrightarrow \varphi^{\mathrm{o}}$ interchange by a prime, we obtain the following results for the overlap of a primed and an unprimed such one-electron functions:

$$\langle \varphi_{k_1}^{\mathrm{BS}} | \varphi_{k_2}^{\mathrm{BS}'} \rangle = \delta_{k_1,k_2} \cos \omega_k \cos 2f_k = \delta_{k_1,k_2} s_k$$

The two states Φ_1 and Φ_2 in question are built up from unprimed and primed BFs, respectively. The configuration interaction equation of the problem is

$$\begin{pmatrix} H_{1,1} & H_{1,2} \\ H_{2,1} & H_{2,2} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \varepsilon \begin{pmatrix} 1 & S_{1,2} \\ S_{1,2} & 1 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

where $S_{i,j} = \langle \Phi_i | \Phi_j \rangle$, $H_{i,j} = \langle \Phi_i | \hat{H} | \Phi_j \rangle$. It is easy to show that for the chain with N electrons, $S_{1,2} = \prod_{i=1}^{N} s_i$, which is exponentially vanishing in the solid-state limit if $s_k \neq 1$. A similar result holds for the minors of the overlap determinant occurring in H_{12}, proving the nonmixing of the two BOAW (primed and unprimed) states for large N.

To calculate the Hellman–Feynman force in the $\Delta r = 0$ point for the BOAW it is only necessary to assign the one-determinant wave function (Φ_1 or Φ_2) to the curve in question due to the above-mentioned nonmixing. This assignment is, however, trivial because the bond-order elements of the density matrix indicate already to which of the two curves a given solution corresponds. We may therefore conclude that if BOAW is present in the CDW, the two curves do cross with a nonzero derivative (as on Fig. 4c).

The same conclusion can be obtained by applying the results of the Hückel analysis at the beginning of Section II,E. The correspondence can be established as follows (Kertész *et al.*, 1981): The diagonal CDW Fock matrix can be simulated by a Hückel model with alternating α_i, thus according to Eq. (34b) distortion may occur. In the BOAW the off-diagonal Fock matrix elements alternate already in the $\Delta r = |r_1 - r_2| = 0$ point ($\beta_1 = \beta_2$, $\gamma_1 = \gamma_2$), in the PPP model

$$F_{12}(0) = \beta_1 - \tfrac{1}{2}\gamma_1 D_{12}(0) \tag{38}$$

$$F_{21}(1) = \beta_2 - \tfrac{1}{2}\gamma_2 D_{21}(1) \tag{39}$$

because $D_{12}(0) \neq D_{21}(1)$. As a consequence, an infinitesimal change in Δr will lead necessarily to a decrease in the total energy as in Eq. (34c).

The energy gaps of the BS solutions are appreciable (see, e.g., Table V). In the PPP model for the BOAW case,

$$E_g = 2|F_{12}(0) - F_{21}(1)| \tag{40}$$

E_g is dominated by the exchange term. Thus, along the Δr path from a strongly alternating point to the nonalternating ($\Delta r = 0$) point the gaps are always appreciable in contrast to the Hückel gap $2|\beta_1 - \beta_2|$ which vanishes at $\Delta r = 0$. Thus the metallic point lies outside the $E_g(\Delta r)$ as well as the $E_{\text{tot}}(\Delta r)$ curves (see, e.g., Fig. 7).

2. *Nonsinglet Instabilities. Spin-Unrestricted HF (UHF) Solutions*

The various kinds of different orbitals for different spins (DODS) many-electron wave functions of the form (Slater, 1930, 1951) (where $\mathscr{A}$ is the antisymmetrizer)

$$\Phi_{\text{DODS}} = \mathscr{A}(\{\varphi_1^\alpha(1)\alpha(1)\varphi_1(2)\beta(2)\varphi_2^\alpha(3)\alpha(3) \cdots) \tag{41}$$

are able to account for a part of the electronic correlation energy without losing the simplicity of the one-electron picture with

$$\varphi_k^\alpha = \varphi_k^{\text{BS}} \qquad \text{and} \qquad \varphi_k^\beta = \varphi_k^{\text{BS}'} \tag{42}$$

Since this wave function is not a pure spin state, Löwdin (Löwdin, 1955; see also Pauncz, 1967) suggested the so-called "alternant molecular orbital" (AMO) version of the method where the one-determinantal DODS wave function is subjected to spin projection,

$$\Phi_{\text{AMO}} = \hat{\mathscr{D}}^S \Phi_{\text{DODS}} \tag{43}$$

The DODS method as applied to the study of the electronic structure of solids (Berggren and Johansson, 1968; Calais and Sperber, 1973; Laskowski *et al.*, 1973; Ovchinnikov *et al.*, 1972; Kertész *et al.*, 1978b) exhibits an interesting property (Mayer, 1980). The total energies per elementary cell of the spin-projected and unprojected wave functions tend to each other in the solid-state limit (N, the number of elementary cells, increases to infinity).

There is an important feature of all DODS methods most clearly apparent for 1D solids: Equation (41) describes an antiferromagnetic-type LR order if $\varphi_i^\alpha \neq \varphi_i^\beta$, as shown by Misurkin and Ovchinnikov (1974). Furthermore, with the restriction

$$\varphi_i^\alpha = \varphi_i^\beta \tag{44}$$

Φ_{DODS} approaches a doubly occupied determinant Φ_{R} (restricted). Therefore, it may be of interest to study under which circumstances the restricted Φ_{R} is unstable with respect to the relinquishing of the double-occupancy requirement (Čižek and Paldus, 1967). Three-dimensional studies (Laskowski *et al.*, 1973; Calais and Sperber, 1973) indicated that although the DODS wave function is appropriate for the description of the electron gas in the low-density limit, near the equilibrium densities of real materials the extra variational freedom introduced does not lead to improvement of the total energy; i.e., no correlation energy is obtained because the orbitals are spontaneously doubly occupied.

Nevertheless, the DODS method and its different variants seem to be interesting as applied to quasi-one-dimensional systems. As mentioned above, it is particularly well suited for the description of their antiferromagnetic states. It was also suggested (Calais, 1964) that if the lattice parameter is changed, the DODS methods may be able to describe a transition from a metallic state to an insulating one.

In this respect the fully variational form, the UHF formalism (Pople and Nesbet, 1954; Berthier, 1954; Biczó *et al.*, 1972, unpublished) seems to be most adequate to study this problem, because (1) without reference to the stability criteria (Paldus and Čižek, 1970) analogously to the above-discussed CDW case it is simple to obtain the UHF solutions by the usual SCF iterations (Kertész, 1976a) and (2) the fully variational form gives the lowest possible energy within the given Ansatz and so the (as it turns out) small correlation energies are not connected to the restrictions imposed in connection with a limited variation freedom as in the AMO method, although the difference of the "k-dependent λ" AMO and UHF total energies on a H atomic chain (André *et al.*, 1980) are very small for all interatomic distances as compared to the correlation energy involved. In the case of metallic systems a doubling of the unit cell is necessary in order to obtain a UHF solution different from that of the RHF similar to the above-considered CDW solutions. The largest energy gain has always been obtained for systems with geometry around an equidistant (metallic) model, while for strongly alternating models in several cases UHF solutions could not be found at all. Figure 6 shows RHF, UHF ferro-, and antiferromagnetic results of calculations on an equidistant H atomic chain. Neither in this case nor in the case of C atomic chains (Kertész *et al.*, 1978a) does a metal-to-insulator (antiferromagnetic) crossover point occur in the calculations; the antiferromagnetic state is more stable at all densities. Energy-gain values $(E_{\mathrm{UHF}} - E_{\mathrm{RHF}})/N$ and energy gaps for a few selected systems are given in Table VI. As previously mentioned, in 3D systems very small or no energy gain is obtained. In case of some poly-

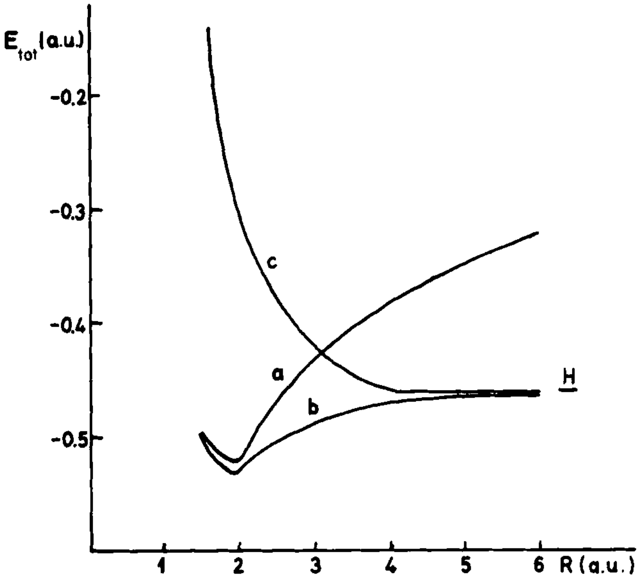


Fig. 6. Energy per hydrogen atom in an equidistant chain of hydrogen atoms; H indicates that the energy of the H atom is this basis set: (a) metallic, (b) antiferromagnetic, and (c) ferromagnetic states. (After Kertész *et al.*, 1979d.)

mers, the energy gains are more substantial, particularly, if we add that most of the correlation—as seen on the SCF wave function—comes from mutual avoidance of electrons of opposite spin near the FL [e.g., π electrons in $(CH)_x$]. If all correlations are assigned to those few electrons, an appreciable amount of correlation energy (0.1–0.5 eV/electron) results. Other (σ and core electrons) occupy practically the same orbitals twofold. The forbidden energy gaps E_g in the above polymer calculations are very large (9–15 eV). The large gaps are partly due to the BOAW coupled to the UHF wave function (André *et al.*, 1980) but mainly to the large difference of on-site densities of the same spin. These large gaps as well as the fact that only electrons around the FL are correlated are a consequence of the instability of the metallic HF ground state. In this sense one might say that the UHF stabilization energy is perhaps only partly due to the physical antiferromagnetic correlation in the ground state, but is certainly also a manifestation of the inadequacies of the RHF method for metallic systems as suggested by Overhauser (1960). Numerical large-scale configuration interaction (CI) calculations on H_6 and H_{14} rings (Cimiraglia and Resta, 1981) indicated that in the ground state of these systems there is antiferromagnetic-type correlation indicated by the LR oscillations of the spin-dependent pair correlation function. It should be remembered, that

TABLE VI

SOME (SPIN) UNRESTRICTED HF CRYSTAL CALCULATIONS

System	Method	Energy gain per electron (with respect to metallic solution) (eV)	E_g (eV)	Reference
Li crystal		—	0.08–0.16[a]	O'Keefe and Goddard (1969)
	AMO	0	0	Calais and Sperber (1973)[b]
Na crystal	APW	0.015	0.019	Boring (1970)
H atomic chain	AMO	Negative	—	Calais (1964)[b]
	Green's function	1[a]	15[a]	Berggren and Martino (1969)[b]
	Ab initio	0.11	9.96	Kertész *et al.* (1976c)[b]
$(CH)_x$	PPP	0.13	7.18	Kertész *et al.* (1974)
	Ab initio	0.083	13.52	Kertész *et al.* (1979b)
$(SN)_x$	*Ab initio*	0.287	14.56	Kertész *et al.* (1978f)

[a] Estimated value.

[b] At the most stable geometry.

for the UHF wave function this pair correlation is infinitely ranged (Misurkin and Ovchinnikov, 1974).

F. Remarks on Correlation

Simple models of electronic correlations in chains have been treated at various levels of sophistication (e.g., Lieb and Wu, 1968; Ukrainskii, 1977). Realistically correlated quantum chemical calculations that include a few degrees of freedom in the elementary cell for extended systems are virtually nonexistent, except for a few calculations based on the electronic polaron model (Kunz, 1972) or other models such as RPA (Monkhorst and Oddershede, 1973) or the Coulomb hole plus exchange model (Hedin, 1965). Extensive calculations have been done with the UHF method, as discussed in the previous section. Disagreement between theory and experiment is often attributed to absence of correlation in the calculations (e.g., Löwdin, 1955; Shustorovich, 1967; Ovchinnikov *et al.*, 1972; Ladik, 1973, 1980; Pantelides *et al.*, 1974; Brener, 1975; Čižek, 1978). Especially important is the artificial zero of the density of states at the FL in HF theory due to exchange, as discussed in Section II,D,4.

For insulators the most serious deficiency of the HF theory is the overestimation of the energy gap. This may be understood on the basis of perturbation arguments (Pickup and Goscinski, 1973; Pantelides *et al.*, 1974; Hubač and Urban, 1977) as sketched below. The correlated quasi-particle levels for the conduction band can be defined as (E^N is the total energy of the N-electron system)

$$\epsilon_{n\mathbf{k}} = E^{(N+1)} - E^{(N)} \tag{45}$$

and similarly for the valence bands. The HF bands $\epsilon^0_{n\mathbf{k}}$ are the first approximations for these

$$\epsilon_{n\mathbf{k}} = \epsilon^0_{n\mathbf{k}} + E_C^{(N+1)} - E_C^{(N)} \tag{46}$$

In perturbation theory of the second order, Pantelides *et al.* (1974) write $E_C^{(N)}$ in terms of pair correlation energies (b, c stands for occupied; r, s for virtual orbitals, respectively).

$$E_C^{(N)} = \tfrac{1}{2} \sum_{b,c} e_{bc}^{(N)} \tag{47}$$

with

$$e_{bc}^{(N)} = \sum_{r,s} |\langle \psi_b \psi_c | (1 - \hat{P}_{12})/r_{12} | \psi_r \psi_s \rangle|^2 / (\epsilon_b^0 + \epsilon_c^0 - \epsilon_r^0 - \epsilon_s^0) \tag{48}$$

Analysis of these expressions for nonmetals around the FL leads to the following general conclusions about the effects of correlation on the energy bands:

(1) Conduction bands move down
(2) Valence bands move up together with core bands, the latter to a larger extent
(3) As a consequence, the energy gap decreases substantially.

The following conclusion is dependent on the assumption that the matrix elements in the numerator of Eq. (48) do not change drastically.

(4) Valence bands undergo narrowing upon inclusion of the correlation
(5) The shift of that band is larger, which is flatter (usually the valence band)

Some model calculations have been done showing a drastic decrease of the gaps in different systems for which HF-based correlation calculations are available (e.g., Table VII). The too small gap of the HFS method is remarkable, a screened exchange alone is not sufficient, although the error is usually smaller in this case as compared to the exact exchange HF. On the other hand, the latter method can be used as basis of more systematic correlation work.

TABLE VII

CORRELATION CORRECTIONS TO *Ab Initio* HF ENERGY GAPS FOR A FEW SELECTED INSULATORS

System	Quality of HF	Correlation model	Energy gap (eV) HF	HFS[g]	Correlated	Expt.
Ar[a]	Local orbital method	Electronic polaron	16.2	7.08	<14.7[a]	14.3
NaCl[a]	Local orbital method	Electronic polaron	12.08	7.4	<10[a]	8.75
Diamond[b]	Extended basis	Coulomb hole plus screened exchange[d]	12.1[e]	—	5.6	5.5–5.6
			13.7[f]	—	7.6	7.3–7.4
Polycytosine[c]	Minimal basis	Local approximation to ΔSCF	10.65	—	6.95	4.3[h]
		Electronic polaron	10.65	—	9.79	

[a] Kunz (1972) (correction for conduction band only is given).
[b] Brener (1975).
[c] Ladik *et al.* (1977).
[d] Hedin (1965).
[e] Indirect gap.
[f] Direct gap.
[g] Hartree–Fock–Slater (local exchange).
[h] Value given corresponds to exciton excitation.

Systematic calculations that realistically evaluate the matrix elements and sums in expressions like Eq. (48) for any realistic polymer are not present in the literature. [Kapuy (1982) has performed PPP pertubations on cyclic finite polyenes based on localized orbitals.] The difficulty may be understood by writing down the matrix element in the numerator of Eq. (48) in terms of BFs. This can be transformed to integrals over WFs (with $\langle 12|12\rangle$ convention)

$$\left\langle {}^{b}_{k_1}{}^{c}_{k_2} \middle| {}^{r}_{k_3}{}^{s}_{k_4} \right\rangle = N^{-1}\,\delta(k_1 + k_2 - k_3 - k_4) \\ \times \sum_{\rho_1\rho_2\rho_3} \exp\{i(k_1\rho_1 + k_2\rho_2 - k_3\rho_3)\} \left\langle {}^{b}_{\rho_1}{}^{c}_{\rho_2} \middle| {}^{r}_{\rho_3}{}^{s}_{0} \right\rangle \tag{49}$$

This contains the Coulomb interaction of two charge distributions $w_c(\rho_2 - r)w_s(r)$ and $w_b(\rho_1 - r)w_r(\rho_3 - r)$. Both charge distributions have zero total charge due to the orthogonality of Wannier functions from different bands (b, c are occupied; r, s are empty bands). Thus the summand in Eq. (49) even in the least convergent case when the exponential factor does not oscillate decays at least as fast as $|\rho_1 - \rho_2|^{-3}$ asymptotically, which ensures the fast convergence of the sum in one dimension. If these integrals are evaluated through the use of WFs, then the transformation from an AO set to the WF set is followed by the transformation (49), and this for several representative k_1, k_2, k_3 point sets. Since the AO → MO integral transformation is known to be very time-consuming, it is easy to understand how much more difficult the evaluation of sums like Eq. (48) are. Alternatively, the integrals may be expressed directly in terms of the AO integrals using translation symmetry as

$$N^{-1}\ \delta(k_1 + k_2 - k_3 - k_4) \sum_{R_1R_2R_3} \sum_{\alpha\beta\gamma\delta} b_{\alpha k_1} c_{\beta k_2} r^*_{\gamma k_3} s^*_{\delta k_4} \times \exp\{i(k_1R_1 + k_2R_2 - k_3R_3)\} \langle {}^{\alpha\beta}_{R_1R_2} | {}^{\gamma\delta}_{R_30} \rangle \tag{50}$$

This is more similar to the traditional AO → MO integral transformation, although it is much more complicated and complex arithmetic cannot be avoided.

As is apparent that an integral over BFs is of the order of $1/N$, in accordance with the normalization (5) and (6). Physically, Bloch electrons have repulsion of the order N^{-1} due to their spread over the whole crystal. This is the reason why in extended systems finite CI schemes cannot give any other correction than N^{-1} to the correlation energy. However, perturbation methods such as Eq. (48), as well as Green's function methods are size consistent (correct dependence on the number of particles). Among the few quantum chemical approaches of the application of Green's function methods (e.g., Cederbaum and Domcke, 1977) is the intermediate exciton theory (Kertész, 1979) and it is mentioned as an example here. Excited states of insulators can have bound electron–hole (e–h) pairs. Using a simplified spinless notation for the many-electron wave function $\Phi_{vc}(k \rightarrow k')$ for an electron excited from φ_{vk} to φ_{ck}, the following basis functions containing N determinants are used (Takeuti, 1957; Knox, 1963):

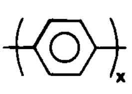
$$\phi_{vc}^{(K,\rho)} = N^{-1/2} \sum_k e^{ik\rho} \phi_{vc}(k - K \rightarrow k) \tag{51}$$

describing an e–h pair traveling with wave vector K at an average distance of ρ. The Schrödinger equation in this single CI space can be rewritten in a Green's function form (Takeuti, 1957), which deals with the problem of infinite number N of CI expansion functions in an appropriate way by transforming it to the finite direct-space problem in terms of the e–h separation. This method, together with its convergence properties on the summations similar to that in Eq. (50) and the e–h separation, is discussed in detail within the PPP model for the excitation energy of polyene by Kertész (1979). *Ab initio* level applications of this formalism (Kertész *et al.*, 1982b) predict large correlation corrections in chains of H_2 molecules.

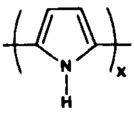
Less developed are methods for the treatment of the ground-state correlation. Here besides the application of the powerful coupled-cluster theory (e.g., Čižek, 1978; Čižek and Paldus, 1980), perturbation methods may be applied in the near future. It is promising in this respect that the former has been applied successfully to the electron gas problem (Freeman, 1977, 1978). Applications to infinite inhomogeneous systems are yet to be made.

III. Application of Theory to Conjugated Polymers

Much of the effort which led to the methods discussed in Section II has been motivated by the interest in the electronic structure of well-conducting polymers. Little suggested in 1964 an excitonic mechanism which might lead to high-temperature superconductivity in polymeric organic materials. Although such an effect has not been observed yet, the search for well-conducting polymers has indeed led to a new class of well-conducting polymeric composite materials. For instance, conductivities of polymer derivatives of up to $10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for polyacetylene (PA) (Figs. 1 and 8; Chiang *et al.*, 1977, 1979; Baeriswyl *et al.*, 1981); up to $100\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for poly(*p*-phenylene) [PPPh(I)], (Ivory *et al.*, 1979); up to $100\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for polypyrrol [PPy(II)] (Kanazawa *et al.*, 1979), have been observed. These high conductivities are reached by doping the polymers by acceptors such as I_2, Br_2, AsF_5, SbF_5, or by donors, NH_3, Na, Li, etc. Due to the polymerization process, the materials are available in partially crystalline to amorphous form only. Therefore, neither for the pure nor for the doped materials does detailed structural information exist, largely hampering the microscopic understanding of their electronic structure. On the other hand, quantum mechanical calculations can yield useful data on these otherwise unaccessible structural details.



(I)



(II)

In what follows we shall concentrate on the two most studied polymers (PA) and polydiacetylenes (PDA). We shall also discuss other conjugated polymers as analogs of PA, and a few others. For all of these conjugated polymers mobile π-electrons are fundamentally important. It is interesting to note in this respect that the bandgap/bandwidth ratio is a characteristic measure of the localizability of the electrons (Kertész *et al.*, 1982c). Accordingly, π electrons are more mobile than σ electrons, primarily due to the much smaller bandgap of the former.

A. The Electronic Structure of Polyacetylene

Long polyenes consisting of n (CH) units have been a favorite subject of theoretical studies. Early work, as summarized by Murrell (1963), has shown that the observed absorption peak around 2 eV can be explained on the basis of bond-length alternation. As much as these finite molecular conclusions could be extended to infinite chains ($n \rightarrow \infty$), the expectation has been that the long chains have a nonzero gap around 2 eV and their structure has nonuniform (alternating) bond lengths. Later it was argued (Misurkin and Ovchinnikov, 1966) that spin-density waves of an equidistant chain can also have nonzero gap. Here we discuss the energetics of the alternation, the gap related to the absorption peak around 2 eV, stability of other (cis) conformers, and some aspects of doping.

1. *Bond-Length Alternation in All-Trans-*$(CH)_x$

In this section *ab initio* results on all-*trans*-$(CH)_x$ are reviewed. Most calculations have been done on fixed-geometry models with small basis sets. The relative energies with respect to the metallic solution are summarized in Table VIII. The following conclusions emerge: Aside from the

TABLE VIII

Ab Initio RESULTS ON THE ALTERNATION OF ALL-*trans*-$(CH)_x$[a]

Reference	Basis set	$E_{alt.} - E_{met.}$	$E_{CDW} - E_{met.}$
André and Leroy (1971)		+242	—
Kertész *et al.* (1977a)	STO-3G[b]	−28.5	−5.9
Karpfen and Höller (1979)	STO-3G[b]	−30.6	−8.8
Karpfen and Petkov (1979b)	8s4p/4s[c]	−12.4	
Brédas (1979)		—	−1.7[d]
Suhai (1980a)	STO-3G[b]	−35.2	—

[a] The total energy per C_2H_2 units of alternating and equidistant models are compared to the metallic solution of the equidistant polymer (in KJ/ mol).

[b] Hehre *et al.* (1969).

[c] Huzinaga (1965, 1971).

[d] $E_{CDW} - E_{alt}$.

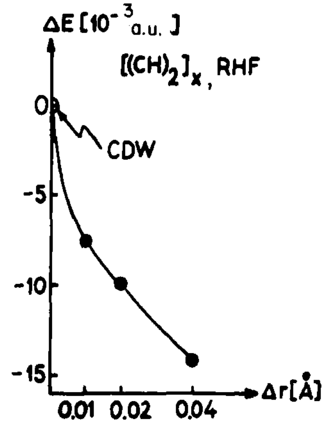


Fig. 7. Total RHF energy per unit cell (C_2H_2) in polyacetylene *trans*-$(CH)_x$ chain as function of the asymmetric lattice distortion $\Delta r = |r_1 - r_2|$, with $r_1 + r_2$ fixed at 2.784 Å (relative scale). The metallic state is above the CDW point by 0.0022 a.u. (After Kertész *et al.*, 1980a.)

metallic, a CDW solution can be found (Kertész *et al.*, 1977a) which is more stable by 5.9 kJ/mol than the metallic solution. This CDW contains bond-order alternations and, consequently, the lattice distorts, as discussed in Section II,E,1, and Eq. (14c). This situation is illustrated in Fig. 7 where the total energy is given as function of the distortion $\Delta r = |r_2 - r_1|$, while the sum $r_1 + r_2$ is fixed. The stabilization energy due to the distortion is of the order of 30 kJ/mol except for the calculations of André and Leroy (1971) which used symmetry-violating integral approximations. This 30 kJ/mol value is somewhat less than the energy stabilization calculated only on the basis of the gap opening [sum of energy levels in the total energy expressions of Eq. (19a)] due to the screening of the σ electrons (Kertész *et al.*, 1977a).

The finding of the *ab initio* results about the bond-length alternation has been directly verified by X-ray experiments only recently (Fincher *et al.*, 1982). All indirect experiences on the optical gap (Murrell, 1963; Fincher *et al.*, 1978; Chiang *et al.*, 1979; Tani *et al.*, 1980) on vibrational spectroscopy (Shirakawa and Ikeda, 1971; Tric, 1971; Rabolt *et al.*, 1979; Fincher *et al.*, 1979), and on X-ray data (see Baughman *et al.*, 1979) also indicate that the theoretical picture of the bond alternations is correct.

2. *Relative Stabilities of Polyacetylene Isomers*

Other isomers of $(CH)_x$ became important because the recent synthesis, which revolutionized the field (Shirakawa and Ikeda, 1971), produces films in the thermodynamically unstable cis form (Ito *et al.*, 1975). The

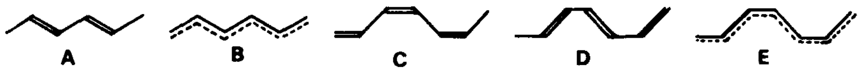


Fig. 8. Different polyacetylene conformers: A and B, trans; C, D, and E, cis.

desire to explain the relative stability of the conformers (Fig. 8) initiated investigations summarized in Table IX. Here most of the calculations agree with experiment on preferring the alternating trans over any cis form. Exceptions are the calculations of Kertész *et al.* (1978c) where the number of included neighbors was not sufficient to reach converged results as well as that of Suhai (1980a). A full geometry optimization may be required in order to be able to discriminate such small energy differences. According to Karpfen and Höller (1981) bond lengths and angles used in the idealized models of all other calculations in Table IX are far from the optimized ones. It is interesting that simple orbital arguments (Whangbo *et al.*, 1979; Whangbo, 1981) also led to a correct prediction of the cis-trans isomerization.

3. *Energy Gap in* $(CH)_x$

The intimate connection of the forbidden gap and the bond-length alternation in *trans*-$(CH)_x$ has been discussed in connection with the Peierls distortion in Section II,E. All experience on finite polyene mole-

TABLE IX

RELATIVE STABILITIES OF POLYACETYLENE ISOMERS: COMPARISON OF LITERATURE DATA[a]

			Ab initio			
Structure[b]	Extended Hückel (Whangbo *et al.*, 1979)	CNDO (Yamabe *et al.*, 1979a,b)	Kertész *et al.* (1977a, 1978c)	Brédas (1979)	Suhai (1980a)	Karpfen and Höller (1981)
All trans:						
alternating (A)	0.0	0.0	0.0	0.0	0.0	0.0
equidistant (B)	7.5	18.0	28.5	—	35.1	30.6
CDW	—	—	22.6	41.7	—	21.8
Cis-transoid (C)	45.6	8.0	−65.3	82.9	−10.9	8.0
Trans-cisoid (D)	40.2	18.0	−166	86.7	−0.4	8.8
Cis-trans (equidistant) (E)	—	27.6	−133	83.7	28.9	30.1

[a] Energies are given relative to the alternating all-trans structure per C_2H_2 unit in kJ/mol. [b] Letters in parentheses refer to Fig. 8.

cules, containing $(CH)_n$ (n = 2–20) fragments indicate that the distorted structure has a finite excitation energy, extrapolated to be 2.24 eV by Murrell (1963) for $n \rightarrow \infty$. This corresponds well to the first absorption peak in *trans*-$(CH)_x$ films observed at 1.4–1.9 eV (Fincher *et al.*, 1978; Shirakawa *et al.*, 1978b), offering the interpretation of this peak as being an excitonic transition below the gap, the gap being larger than 1.9 eV (Yarkony and Silbey, 1977; Kertész, 1979). Alternatively, the UHF wave function of an equidistant $(CH)_x$ has a nonzero gap too, which may be called correlation gap (Misurkin and Ovchinnikov, 1966; Ovchinnikov *et al.*, 1972). While the role of correlation has not been elucidated in much detail for these systems, this argument has the following drawbacks: (1) The UHF gap of an *ab initio* calculation for $(CH)_x$ is unrealistically large (13.5 eV, Kertész *et al.*, 1979b); (2) the PPP gap is also too large for $(CH)_x$ if UHF wave function is used. In order to reach agreement with experiment, Tyutyulkov *et al.* (1980) had to use electron-repulsion integrals in UHF *increased* by a factor of about 2. This nonphysical "screening" constant clearly demonstrates that the gap in $(CH)_x$ cannot be considered as essentially an antiferromagnetic gap (see also Barentzen *et al.*, 1980). Besides, there is no magnetic experimental evidence for strong Coulumb correlations (Fincher *et al.*, 1978; Weinberger *et al.*, 1979; Holczer *et al.*, 1981). Furthermore, the higher absorption energy peak of the cis isomers (Shirakawa *et al.*, 1978b) also fits into the RHF-based picture (see below).

Representative gaps and excitation energies calculated by different exciton models are given in Table X. As usual, CNDO and *ab initio* results are close and are too large. The PPP gap is ~50% less, due to the effect of implicit correlation in the parametrization. This value is further reduced by the consideration of the correlation of the electron and hole by the intermediate exciton formalism (Kertész, 1979), reaching a very close agreement with experiment. Similar agreement is observed in the use of the spectroscopically parametrized CNDO of Duke *et al.* (1978). It may be mentioned that the local exchange model underestimates the gap, as usual. The magnitude of the alternation cannot be traced back on the basis of the gaps due to the crude agreement with experiment, although the data are consistent with the alternation values of Section III,A,2. Calculated gaps of the most stable cis isomers vary with the method used, as given in Table XI. The predicted cis–trans shift of the gap is only indirectly related to the corresponding shift of the absorption peak, the value of which is about −0.3 eV (Shirakawa *et al.*, 1978b; Fincher *et al.*, 1979). We mention that the above excitonic assignment of the absorption peak is consistent with the finding of Tani *et al.* (1980) concerning the difference of this peak and the onset of photoconduction, the latter being at ~0.1 eV higher energy.

TABLE X

ENERGY GAPS AND EXCITATION ENERGIES (E_{ex}) OF ALL-*trans*-$(CH)_x$ IN DIFFERENT APPROXIMATIONS

Hamiltonian	Type of excitation	$\lvert r_2 - r_1 \rvert$[a] (Å)	E_{ex} (eV)	Reference
Hückel	Gap	0.0355[b]	1.45	Longuet-Higgins and Salem (1959) model
Hubbard	UHF gap	0	2.2	Misurkin and Ovchinnikov (1966)
PPP	UHF gap	0.066	7.2	Kertész *et al.* (1974)
	HF gap	0.066[b]	5.06	André and Leroy (1967)
	Frenkel (localized exciton)	0.066	3.50	Kertész (1976a, 1979)
	Intermediate exciton	0.066	1.4	Kertész (1979)
CNDO	Cluster (up to $C_{16}H_{18}$) exciton	0.09	2.3	Duke *et al.* (1978)
Nonempirical pseudopotential local exchange	Non-SCF gap	0.07	0.8	Grant and Batra (1979)
		0.20	2.3	
EHT	Gap	0.15[b]	2.41	Kertész and Vonderviszt (1982)
Ab initio	HF gap	0.066	6.12	André and Leroy (1971)
STO-3G	HF gap	0.066	7.24	Kertész *et al.* (1977a)
	HF gap	0.066	9.74	Suhai (1981a)
	HF gap	0.150[b]	8.05	Karpfen and Petkov (1979b)
8s4p–4s	HF gap	0.100[b]	5.74	Karpfen and Petkov (1979b)

[a] Experiment, 0.06 Å (Fincher *et al.*, 1982).

[b] Optimized value.

TABLE XI

ENERGY GAPS OF DIFFERENT $(CH)_x$ ISOMERS[a]

Method	Alternating trans	Trans–cisoid	Regular cis	Cis–transoid	Predicted cis–trans shift of gap (eV)	Reference
CNDO	7.5	—	3.2	*8.5*	−1	Yamabe *et al.* (1979)
Ab initio						
STO-3G	7.2	*10.4*	8.7	3.9	−3.2	Kertész *et al.* (1978c)
	9.74	7.8	5.2	*8.2*	+1.5	Suhai (1980a,b)
EHT	0.96	*0.71*	—	1.23	+0.25	Whangbo *et al.* (1979)

[a] Numbers in Italics are the most stable cis isomers within the given row.

4. *Electronic Structure of Doped PA*

Due to the lack of a detailed structure, all theoretical work is based on simple models of doped PA, the aim being a rationalization of the high conductivity. The idea that information from the undoped PA band structures can be used (rigid band model, for its limitation for the interchalation compounds of graphite, e.g., Fisher, 1978), is supported by the fact that the fundamental gap around 1.5–1.9 eV does not disappear upon doping (Fincher *et al.*, 1978, 1979; see, however, Shirakawa *et al.*, 1978a). On the other hand, this may be also due to inhomogenities of the samples (Tomkiewicz *et al.*, 1979; Jánossy *et al.*, 1981). According to the one-chain CNDO calculations of Yamabe *et al.* (1979a,b), the ionization potential is less in the trans chain than in the cis, thus the trans chain is preferred for interaction with acceptors. For donors, the calculated electron affinity is larger for the trans chain than for the cis, so, again, trans is more favorable for taking electrons from donors. This is in accordance with the observed cis–trans isomerization upon doping (Mihály *et al.*, 1980; Fincher *et al.*, 1979).

Calculations of the extended tight-binding type (a non-SCF local-exchange nonempirical model) have been done on 3D models of polyacetylene by Grant and Batra (1979) using the structural models of Baughman *et al.* (1978). The highly anisotropic band structure has the FL in the π–π^x gap. Then, using the rigid band model, Grant and Batra (1979) assume that extra electrons or holes may be generated upon doping with donors or acceptors, respectively. Either way large carrier concentration and thus large conductivity may be reached. Somewhat problematic is how the Peierls distorted structure can remain intact upon doping because the new partly filled band has a tendency to distort according to another periodicity. This problem has been studied by Brédas *et al.* (1981) using a PA chain with attached Li atoms as a model within the *ab initio* scheme. They obtained a bond-length equalization upon doping at the charge-transfer level of around 0.1 electrons per CH unit, however, their gap is not zero. In this sense even if they are weak, interchain interactions are necessary to stabilize the metallic state of doped $(CH)_x$. Nonetheless, the tendency of bond-length equalization is in accord with indirect experimental evidence based on IR data of Rabolt *et al.* (1979) who observed bond weakening in the carbon skeleton upon doping with acceptors; but they also noted that bond-length alternation must persist to some degree in doped $(CH)_x$.

Another interesting geometry change upon I_2 doping is the chain shortening observed by Druy *et al.* (1980) and Pekker and Jánossy (1981). EHT calculations based on the rigid-band model (Kertész *et al.*, 1982a) predict both a CCC bond-angle decrease and a bond-length decrease for acceptor doping and an increase for donors, being in accord with the above observation.

A 3D calculation using idealized models of doped $(CH)_x$ has led to metallic energy-band structure (Kasowski *et al.*, 1980). In their non-SCF calculation Kasowski *et al.* (1980) observed a large participation of dopant orbitals mixed with the π orbitals of the chain to form states around the FL. Similarities with band-structure effects of well-conducting intercalated graphite compounds is noteworthy (e.g., Fisher, 1978). This band structure, as well as that of the pure $(CH)_x$ of Grant and Batra (1979), is not more anisotropic than, say, 20–50, as estimated by the ratio of bandwidths along and perpendicular to the chain from the published figures. Of course, since the structure is not known, these anisotropies are merely reflections of somewhat arbitrary assumptions on the interchain contacts. These calculated anisotropies are far from the experimental spin-diffusion anisotropy of $\sim 10^6$ (Nechtschein *et al.*, 1980), which is consistent with a conductivity anisotropy of $\sim 10^5$. A way out of this problem may be that the dopants decrease the π–π overlaps between the chains, thus increasing the anisotropy (Yamabe *et al.*, 1979b). The soliton picture (Rice, 1979; Su *et al.*, 1979, 1980) should also be mentioned as a possible model for the high mobility of the charge carriers, although it has been criticized recently (Tomkiewitz *et al.*, 1979). Furthermore, as noted by Grüner (1981) disorder on a microscopic scale may be responsible for much of the observed magnetic properties and may stabilize the metallic state at nonzero temperatures. Further structural data are needed to describe the electronic structure of doped $(CH)_x$ more unequivocally.

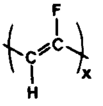
An X-ray analysis of oriented pristine all-*trans*-$(CH)_x$ by Fincher *et al.*, (1982) directly verified the existence of bond-length alternation. The observed degree of alternation (±0.03 Å) is close to previous theoretical predictions (see Table X).

B. Analogies of Polyacetylene

Replacement of some or all H atoms in $(CH)_x$, or replacement of some or all CH groups by isoelectronic atoms or groups, could lead in principle to materials with conductivities controllable over wide ranges. This is desirable, especially because in spite of the favorable properties of $(CH)_x$, it is susceptible to oxidation in air. In this section calculations on the electronic structure of a few polymers of this kind are summarized.

1. *Fluorinated Polyacetylenes*

Yamabe *et al.* (1980) reported CNDO/2 crystal orbital calculations on cis and trans models of polyfluoroacetylene [$(C_2FH)_x$, PFA(III)] and polydifluoroacetylene [$(C_2F_2)_x$, PDFA(IV)]. In both cases trans configurations are preferred as for $(CH)_x$. In PFA the charges on the carbon atoms



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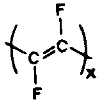
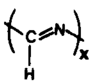


(IV)

alternate strongly. This fixation of the CDW is due to the large electronegativity of the fluorine atoms. The differences of the calculated bond orders in trans PA, PFA, and PDFA are 0.45, 0.25, and 0.39, respectively. The corresponding optimized bond-length differences are 0.085, 0.059, 0.083. Both quantities reflect a similar trend, namely, the alternation is damped in the PFA case. This is perhaps due to a switchover to a diagonal CDW state in favor of an off-diagonal CDW in the PA and PDFA cases, caused by the new periodicity of the F atoms which is present in the PFA case only. Thus while the potential energy surfaces of PA and PDFA can be described by a curve such as that in Fig. 4c around the equidistant configuration, for PFA a curve more similar to that in Fig. 4b holds in that region. The main change of the band structure upon fluorination is a downward shift of the conduction band due to the larger electronegativity of the fluorines. The lone-pair F π electrons push the highest (π) valence band downward, too, so that the decrease of the gap does not exceed 1 eV for the trans chains. Thus, on the basis of these calculations, Yamabe *et al.* (1980) expect these new polymers to be better acceptors than unsubstituted PA.

2. *Polymethineimine* [$(CHN)_x$]

Nitrogen is isoelectronic with CH, and replacement of every second CH by N in $(CH)_x$ leads to the simplest polynitril, polymethineimine



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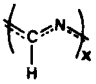

(VI)

(V, VI) possessing semiconducting properties (Wöhrle, 1974); EHT studies of Whangbo *et al.* (1979) indicated that the cis form is less stable than the alternating trans form by 23 kJ/mol. Since the preference of trans forms over cis in PA, PFA, and PDFA was indicated by both EHT and more sophisticated SCF theories, as discussed above, we can expect that the LR Coulomb forces induced by the C to N partial electron transfer do not affect this conclusion. The all-trans configuration has been subject of a double-zeta quality *ab initio* geometry optimization (Karpfen, 1979b). Accordingly, the alternating structure is preferred by 5.4 kJ/mol, which is close to the stabilization energy of polyene obtained in a somewhat smaller basis (6.7 kJ/mol, Karpfen and Petkov, 1979a,b). The total energy as a function of alternation changes as in Eq. (34c); UHF *ab initio* total energies on the equidistant and alternating structure indicated (Kertész *et al.*, 1980c) possible importance of correlation effects.

3. *Carbon Atomic Chain (Polyyne)*

Last in this section we discuss data available on the electronic structure of yet another hypothetical "polymer" with delocalized electrons, the carbon atomic chain $(C_2)_x$. There are indications that this third form of carbon can be synthetized (see Kasatochkin *et al.*, 1975, and references therein) or formed at temperatures above 2600 K under pressure from graphite (Whittaker, 1978) in different forms called carbynes. The structure of these chains has not been elucidated yet, although there are indications for the triple bonds in them (Whittaker, 1978). Longuet-Higgins and Burkitt (1952) using Hückel theory and Hoffmann (1966) using EHT predicted on theoretical grounds that the infinite carbon chain should have alternating short (triple) and long (single) bonds, like $\cdots{-}C{\equiv}C{-}C{\equiv}C{-}\cdots$ and not an equidistant $\cdots{=}C{=}C{=}C{=}C{=}\cdots$ arrangement. The analogy with the case of $(CH)_x$ has been emphasized by Shustorovich and Popov (see Shustorovich, 1967, for a review of these PPP-type calculations). This analogy is a consequence of the fact that due to the rotational symmetry along the chain (z axis) the $2p_x$ and $2p_y$ orbitals are equivalent. Therefore the two π systems (perpendicular to the x–z and y–z planes) become degenerate and the Peierls theorem is applicable, although the number of electrons is even in the elementary cell of the equidistant model.

Recent *ab initio* minimal basis set calculations (Kertész *et al.*, 1978a) indicated that the equidistant chain is unstable with respect to an alternation distortion of the bond lengths. Similarly, as in $(CH)_x$ this is a consequence of the occurrence of a CDW instability of the metallic HF solution, which is then driving the lattice to distort. A more complete geometry optimization with three larger basis sets (Karpfen, 1979c) also predicted an alternating geometry. This, as well as calculated force constant and phonon dispersion curves, waits for experimental confirmation. The role of polarization (d) functions is found to be small in contrast to studies on more polar chains (Karpfen, 1978). It is interesting to note that the ionization potential of $(C_2)_x$ was predicted to be smaller than that of $(CH)_x$ by the PPP method, which is the prediction of *ab initio* calculations, as well (Kertész *et al.*, 1978a).

Ab initio unrestricted HF calculations have been performed on equidistant and slightly alternating $(C_2)_x$ chains (Kertész *et al.*, 1979b). The HF metallic wave function is unstable with respect to UHF, but this instability disappears when moving toward the strongly alternating model.

The most stable geometry has also been found at an alternating geometry. It is interesting to note that RHF theory predicts that for long $(C_2)_x$ chains, there is a barrier to rotation of the terminal CH_2 group with respect to the CH_2 group at the other end of the chain (Shustorovich, 1967), even if the chain is infinitely long. Ukrainskii (1972) has shown that within the UHF scheme, this nonphysical effect is entirely due to the neglect of correlation of the two electrons in the biradical state of the twisted long chain.

C. Polydiacetylenes

The discovery (Wegner, 1969) that certain diacetylenes polymerize topochemically in the solid-state phase to yield conjugated chains of polydiacetylenes (PDA) provided us with an exceptional class of materials. These polymers, in contrast to the usual polymers, may be synthetized as nearly defect-free single crystals enabling studies of bulk electronic structure. The theory of these reactions has been reviewed by Baughman and Chance (1980). These crystals, which have been synthetized with a variety of side groups, exhibit many interesting physical properties (for a summary see Bloor, 1980) such as high optical anisotropy, large third-order susceptibilities, and resonantly enhanced Raman spectra, although highly conducting doped material has not been produced yet (S. Pekker, personal communication). Here we shall focus on properties which can be dealt with by quantum chemical calculations, i.e., conformations and the energy gap.

Most theoretical calculations rely on a one-chain approximation, and furthermore, side chains are usually neglected, or at most replaced by small groups[1] as —F, —OH, $—CH_2NH_2$, etc.

The basic structural problem in PDAs is related to the possibility of drawing the two alternative mesomeric structures illustrated on Fig. 9 which can be called the PDA and the polybutatriene (PBT) structures,

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[1] The effect of large side groups on the electronic structure in some PDAs may be significant; e.g., it has been found experimentally (Sebastian and Weiser, 1981; Sebastian, private communication) that the reduced effective mass of the charge carriers may differ by a factor of at least 2 when going from a PDA with the side group *p*-toluene sulfonate (TS) to another one with a carbazolyl side group (DCH). Our preliminary extended Hückel calculations (Kertész and Vonderviszt, 1982), including all valence electrons of these bulky side groups, indicate that such drastic changes in the energy band structure are related to the change of the delocalized character of the valence band which becomes a strongly localized orbital in the case of TS.

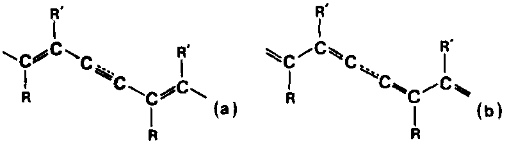


Fig. 9. Two forms of polydiacetylene backbone: (a) the polydiacetylene form (PDA) and (b) the polybutatriene (PBT) forms. Dots are localized π-electron bonds in the plane of the backbone and perpendicular to the delocalized π electrons.

respectively. It is noteworthy, however, that since both structures exhibit an energy gap, the structural preference cannot be told as simply as for PA by the Peierls argument. Actual structures represent intermediates of the two ideal structures, which are known because accurate X-ray diffraction measurements are possible. Most of the materials have chains closer to the PDA structure, but the actual bond distances vary from system to system depending on side groups (Enkelmann, 1977). These bond distances remain unchanged upon the phase transition of one of the polymers (Enkelmann, 1977).

Several semiempirical and *ab initio* studies have been reported on the electronic structure of the PDAs. Most of the semiempirical work has focused on the energy gap (onset of photoconduction, ~3 eV; Reimer and Bässler, 1975; Chance and Baughmann, 1976), which is found experimentally to be larger than the optical gap (~2 eV; Bloor *et al.*, 1974; Bloor, 1976). The latter has been therefore assigned to exciton excitations (Philpott, 1977; Yarkony, 1978), similar to $(CH)_x$. Table XII contains a collection of the gaps found by using a large variety of methods on models with fixed geometry, usually that found experimentally by Kobelt and Paulus (1974) for the PDA-like model. Close agreement of Hückel (Wilson, 1975) and extended Hückel (Parry, 1976; Whangbo *et al.*, 1979) result is natural. *Ab initio* gaps are too large, as usual. It is remarkable that the gaps as well as the effective masses are not sensitive to the change of the side group from hydrogen atom to fluorine to within 10% or less (Kertész *et al.*, 1978b).

It is interesting to comment on the shift of the gap as we go from the PDA structure to that of PBT. Unanimously, all band-structure models predict a shift to a smaller gap (i.e., a red shift). This may be understood by the simple argument that the π electrons see in the PBT case a more equidistant structure and thus they scatter to a smaller extent. In the language of orbitals (Karpfen, 1980a), for the PDA structure that orbital is favorable which has a bonding combination for the shorter (double and triple) bonds and an antibonding combination for the two single bonds (A_u in Fig. 10). For the PBT structure the B_g level is more stable. This

TABLE XII

CALCULATED ELECTRONIC PROPERTIES OF POLYDIACETYLENE MODELS

Method	Side groups	$E_g{}^a$ (eV)	Effective mass of electron	Effective mass of hole	$E_{PDA} - E_{PBT}{}^b$ (kJ/mol)	Reference
Hückel	No	1.36	0.24	0.24	—	Wilson (1975)
Extended Hückel	—H, —C≡CH	1.2	0.2[c]	0.3[c]	−46	Parry (1976), Whangbo *et al.* (1979)
SCF	—H, —F, —OH, —NH_2 —CH_2F, —CH_2OH, —CH_2NH_2	0.45	0.2[c]	0.4[c]	—	Parry (1977)
X_α	—H (closed-ring model)	2.21	—	—	—	Bodreaux (1976)
Ab initio	—H	—	—	—	−83 (STO-3G) −50[d] (7s3p–3s)	Karpfen (1980b)
STO-3G	—H, —F	11.0	0.17	0.19	−192	Kertész *et al.* (1978b)
	—H	5.7[c]	—	—	−86	Suhai (1980b)

[a] For —H side group; for the most stable structure, PDA. [b] For the ideal structures; the difference for the real structure is smaller. [c] Estimated from a figure. [d] Extrapolated (±8%).

leads to a crossover in the occupied orbital scheme of the two extreme conformations as indicated by the geometry optimization of Karpfen (1980a) at *ab initio* level. This has also been found at the EHT level (Whangbo *et al.*, 1979). In that non-SCF case due to this crossover, even a zero gap occurs for a specific intermediate configuration.

A different picture can also be used (Kertész *et al.*, 1981) to rationalize the above relationship between gap and stability in PDAs. Suppose that the system is frozen in and the π electrons are removed. The latter form a 1D electron gas having a BOAW-type ground state at HF level, as discussed for $(CH)_x$. Now if we bring these two systems together (frozen core plus CDW of π electrons), two entirely different situations arise for PDA and PBT. For PDA the BOAW may be in phase with all bond lengths

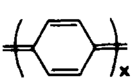
Fig. 10. Orbital pattern of the (a) A_u and (b) B_g orbitals at $k = 0$ for polydiacetylenes near the Fermi level.

(single–triple–single–double–, . . .), so its relaxation will be minor. For PBT such an all-in-phase relation is not possible, so it will tend to diminish the amplitude of the BOAW, leading to a decrease of the gap; however, this costs energy. In agreement with this reasoning, all one-electron theories predict the same order of stability.

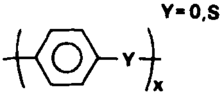
Experimentally, there is a controversy on the change of the gap which has been observed to be a PDA to PBT *blue* shift in connection with a thermochromic phase transition (Chance *et al.*, 1977; Iqbal *et al.*, 1977; Eckhardt *et al.*, 1979) in contrast to the general one-particle results. A small difference between the absorption energies of the two structures has been observed on systems with different side chains. Reimer *et al.* (1976) found the optical gap at 2.0 eV for a system closer to the PDA structure, while Chance and Sowa (1977) observed the absorption peak at 2.3 eV for another system with a main chain closer to the PBT structure. As noted above, no one-electron picture for the planar main chain, even involving excitons or twisting of the side groups (Whangbo *et al.*, 1979) has been able to predict the correct sign of the shift. However, the following alternative explanations have been suggested. Whangbo *et al.* (1979) have shown that the effective conjugation may be reduced by out-of-plane twisting of the backbone. Alternate planes of $C_4H_2R_2$ units have been rotated by $\pm\theta$ around the chain axis. The result is a slight destabilization and a tremendous increase of the energy gap. This finding may explain the thermochromism of some PDAs, for which Patel *et al.* (1979) also proposed a similar mechanism. An alternative mechanism is also based on the one-electron picture and involves the finiteness of the chains (Balasubramanian and Yarkony, 1980). As noted by Whangbo *et al.* (1979) collective effects may also play the role; e.g., the shifted CDWs suggested by Kertész *et al.* (1981) may be involved. More experimental and theoretical work is needed to clarify this phenomenon. According to the calculations, the PDA structure is more stable as discussed above (Table XII). Experimentally, Iqbal *et al.* (1977) found a phase transition in one of the polydiacetylenes. According to their results, the low-temperature form is closer to the PDA form, while the high-temperature form is closer to the PBT form. The absolute energy difference is not known experimentally. Most structures are closer to the PDA model, which also fits into the entire picture. In structures with H bonds or strain induced by cyclic ligands, the PBT backbone may be stabilized. This confirms the order of magnitude for the energy difference between PBT and PDA backbones found theoretically. In closing the section on PDAs we mention the overall agreement between the DOS of the *ab initio* calculation (Kertész *et al.*, 1978b) and the X-ray photoelectron spectrum (Knecht *et al.*, 1977), whereas the EHT band structure is less satisfactory. The typical bandwidth of the *ab initio* calculation (3–4 eV) is also in agreement with the estimated XPS half-width of 4 eV (Knecht *et al.*, 1977).

D. Other Conjugated Chains

Besides the polyacetylene already discussed, a number of highly conducting organic conjugated polymers have been produced. The conductivity of intrinsically insulating polymers can be changed by doping with acceptors and donors to yield an increase of the conductivity by more than ten orders of magnitude. Examples of such systems are poly(*p*-phenylene) [PPPh(I, VII); Ivory *et al.*, 1979], poly(*p*-phenylene sulfide) [PPPS(VIII); Rabolt *et al.*, 1980; Chance *et al.*, 1980a], polypyrrole [PPy(II); Kanazawa *et al.*, 1979]. Some other composite polymers with less or no conjugated bond structures are poly(*m*-phenylene) (Chance *et al.*, 1980a,b) and poly(*N*-vinylcarbazole) (Meier, 1974). In this section we shall briefly summarize the available calculational results on some selected idealized models, as the structure of these materials even in their pristine state is poorly characterized.



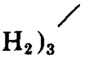
(VII)



(VIII)

1. *A Bridged Polyacetylene: Poly(1,6-Heptadyne)*

Gibson *et al.* (1980) reported results on an analog of PA with a bridging group. Conductivities rise from 10^{-12} up to 10^{-1} Ω^{-1} cm^{-1} upon doping. Although the chemical structure of the π system is very close to that of PA, the calculated DOS is quite different (Duke and Paton, 1981) as several new peaks appear, which may be due to the lower symmetry of the polymer (Brédas *et al.*, 1982). The small calculated red shift for the $\pi \rightarrow \pi^*$ gap with respect to PA awaits experimental verification. There is a predicted ionization potential shift with respect to PA of −0.3 eV in the calculation of Brédas *et al.* (1982), while this shift is too small in the calculation of Duke and Paton (1981) to be significant if compared with their 0.7 eV broadening of the lines. The calculations predict also an increased instability with respect to PA, in agreement with experience (Gibson *et al.*, 1980).


$(CH_2)_3$

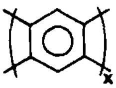
2. *Poly(p-Phenylene) and Related Polymers*

Extended-Hückel-based comparison of the benzonoid(I) geometry versus that of quinonoid(VII) (Whangbo *et al.*, 1979) showed that the former is more stable and exhibits a much larger gap than the latter. Consequently, the bond between the phenyles becomes weaker, in accordance with experiment (Bandour *et al.*, 1978) on five-membered polyphenylenes. The experimental gap of 3.4 eV (Shacklette *et al.*, 1980) could be well reproduced by the effective Hamiltonian method of Brédas *et al.* (to be published) only with the coplanar configuration. Although there is an appreciable delocalization along the bonds between the phenylene rings, some of the states become almost completely localized within the rings (Duke and Paton, 1981). However, the highest lying crystal orbitals turn out to be completely delocalized even for poly(*p*-phenylene oxide)(VIII) and poly(*p*-phenylene sulfide), as calculated by the fragment CNDO/S3 method of Duke and Paton (1981) in agreement with high conductivities found for these polymers.

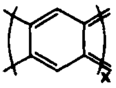
Definitely less delocalization is to be expected for polybenzyl, where the —CH$_2$— groups in the chain disrupt delocalization, and the corresponding calculated bandwidths are as small as 0.6 eV. The observed conductivities of doped polybenzyls are small (Brédas *et al.*, to be published). We think therefore that the electronic structure of these polymers becomes more similar to those of the pendant-group polymers (Duke, 1981).

3. *Polyacene*

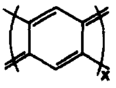
The crossing of the symmetric and antisymmetric π bands in polyacene(IX, X, XI) has been postulated by Boon (1971) and found in



(IX)



(X)



(XI)

actual EHT calculations by Whangbo *et al.* (1979), introducing distortions that hurt the mirror symmetry parallel to the chain axis of polyacene(IX), (e.g., as is illustrated in polyacene(XI). Perturbation arguments about the intrinsic instability of the polyacene chain (IX) preserving this symmetry cannot be proved (Salem and Longuet-Higgins, 1960). However, asymmetric distortions are always advantageous energetically (Boon, 1971). In the EHT calculations structures, (X) and (XI) have been found to be more stable (Whangbo *et al.*, 1979) and the corresponding gaps are very small (Whangbo *et al.*, 1979; Brédas *et al.*, 1982), in agreement with extrapolations from finite polyacenes (Berlin and Promyslow, 1970). As is well known, the 2D graphite layer has $E_g = 0$ (Coulson, 1947; Wallace, 1947a,b); thus polyacenes are natural intermediates between PA and graphite. There is a very large body of experimental and theoretical work on compounds of graphite with donors and acceptors (e.g., Fisher, 1978), and the analogy with doped conjugated polymers is apparent (Baughman *et al.*, 1978).

IV. Concluding Remarks

Recent experiments on highly conducting polymers of polyacetylene indicated the possibility of their practical uses as solar energy converters (Shirakawa *et al.*, 1981) and as electrodes in lightweight rechargable storage batteries (MacInnes *et al.*, 1981; polymers as electronic materials have been reviewed by Mort, 1980). There is no doubt that in the near future similar applicability of other members of the large class of conjugated polymers will be investigated. Nevertheless, there are many gaps in our understanding of the basic phenomena in these materials, due to a large extent to their low degree of crystallinity. Quantum chemistry contributed to the microscopic understanding of the basic structural and electronic properties via the study of periodic, mostly one-chain models, although it is obvious that structural and chemical disorder as well as interchain coupling affect the physical properties of this interesting class of materials.

The theoretical study of periodic models in the Hartree–Fock approximation is well founded both within the *ab initio* and semiempirical schemes. The *ab initio* method has been used with great success to predict absolute configurations of polymers, which is particularly important, as in many cases no direct information on structure is available. Most notable is the prediction of the higher stability of the alternating all-*trans* polyacetylene with respect to the equidistant model.

At present most serious difficulties of the *ab initio* theory lie in the following: (1) large basis set calculations are numerically hard to do because almost linear dependence (Löwdin, 1970; Karpfen, 1978) is reached faster than in molecules due to the overlapping neighbors. Therefore, more neighbors are needed in the explicitly treated lattice sums, the "long-range" region is pushed away. This leads to a need for farther-neighbor density-matrix elements, and thus to a need for including more **k** points in the integrations over **k**. Thus computer time rises more sharply with basis sets than usual in MO theory, and HF "limit" calculations are available for a few cases only (Karpfen, 1979a). (2) Correlation is very important in many cases although numerical correlation calculations are rare. While UHF can be applied routinely, it has only limited applicability. The HF gaps especially are too large, and its systematic correlation correction should be taken into account.

Semiempirical techniques are easy to apply and are free from the technical difficulties characteristic of the *ab initio* methods. They have proved to be extremely useful to correlate observables with calculated values especially for systems with larger elementary cells. The effects of disorder can yet only be treated within semiempirical frameworks (e.g., Kertész and Göndör, 1981).

Quantum chemical electronic structure calculations on polymers have contributed significantly to the microscopic understanding of the structure and electric properties of this class of materials. Hopefully, calculations of this type may aid in the design of further new well-conducting polymers.

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Elementary Unitary MO Transformations and SCF Theory

RAMON CARBÓ, LLORENÇ DOMINGO, and JOSEP-JORDI PERIS
Secció de Química Quántica
Departament de Química Orgánica
Institut Químic de Sarriá
Barcelona, Spain

I. Introduction

A. The Nature of the Unitary Transformations on MOs

Throughout the last 20 years there has been evidence in the literature of a trend to obtain molecular orbital (MO) wave functions in parallel to the classical iterative self-consistent field (SCF) process. The tech-

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nique that interests us, and the one that we shall study in this paper, is encompassed by the generic term MO unitary transformations. The main idea common to all such methods is based on the optimal construction of a unitary matrix $\mathbf{U} = \{u_{ij}\}$ acting on an initial MO set $\{|k, 0\rangle\}$, producing a transformed set $\{|i, u\rangle\}$ through the linear relationship

$$|i, u\rangle = \sum_k u_{ki}|k, 0\rangle, \qquad \forall\, i \tag{1}$$

The condition of unitarity of matrix $\mathbf{U}$ must hold the same as

$$\sum_k u^*_{ik}u_{jk} = \delta_{ij}, \qquad \forall\, ij \tag{2}$$

If the usual linear combination of atomic orbitals (LCAO) approach is taken into account, the initial MO set $\{|k, 0\rangle\}$ may be expressed as a linear combination of some atomic orbital (AO) basis set $\{\chi_\mu\}$, thus

$$|k, 0\rangle = \sum_\mu c^{(0)}_{\mu k}\chi_\mu \tag{3}$$

In this manner the transformed MOs $\{|i, u\rangle\}$ can be written

$$\begin{aligned} |i, u\rangle &= \sum_k u_{ki}\left(\sum_\mu c^{(0)}_{\mu k}\chi_\mu\right) \\ &= \sum_\mu \left(\sum_k c^{(0)}_{\mu k}u_{ki}\right)\chi_\mu = \sum_\mu c^{(u)}_{\mu i}\chi_\mu \end{aligned} \tag{4}$$

That is, if $\{c^{(u)}_{\mu i}\}$ are the unitary transformed MO coefficients, and if they are ordered in a column vector, we have the vector form isomorphic to Eq. (1):

$$\mathbf{C}^{(u)}_i = \sum_k u_{ki}\mathbf{C}^{(0)}_k \tag{5}$$

or, similarly, by constructing the matrices whose columns are composed of the previous vectors, one can write

$$\mathbf{C}^{(u)} = \mathbf{C}^{(0)}\mathbf{U} \tag{6}$$

where the matrix $\mathbf{C}^{(0)}$ must contain the complete initial coefficient set, including virtual unoccupied MO vector coefficients. Moreover, if the coefficient matrices in Eq. (6) are partitioned according to the MO electronic shell arrangement as in

$$\mathbf{C} = (\mathbf{C}_{g_1}, \mathbf{C}_{g_2}, \ldots, \mathbf{C}_{g_N}) \tag{7}$$

where $\{\mathbf{C}_{s_I}\}$ $(I = 1, N)$ are rectangular matrices containing as columns all MO vector coefficients belonging to the same shell s_I, then if an adequate partition is performed on the unitary matrix $\mathbf{U}$, the diagonal submatrices of the unitary transformation can be taken as unit matrices due to the invariant nature of the electronic energy when intrashell mixing of MOs is carried out (Roothaan, 1951; Huzinaga, 1969).

B. Historical Review

The family of techniques based on the previous ideas has evolved in the years since it first appeared. To understand such its evolution, we consider three different periods.

1. *Initial Developments*

As far as we know the first papers of this period can be attributed to Rossi (1965, 1966). Another complete work by Das (1967) was followed by one by Das and Wahl (1967), in which they initially described such a unitary transformation. Other papers followed: Levy and Berthier (1968) and Levy (1969, 1970), who employed Brillouin's theorem based on an old idea that (Lefebre and Moser, 1956; Lefebre, 1957, 1959) along unitary transformations achieve MO coefficient optimization.

2. *Transitional Phase*

A period of fruitful development, probably coincident with the emergence of new computing machines, began in the 1970s with the papers of Grein and Chang (1971) and Chang and Grein (1972), soon followed by other studies by Das (1973), Gianinetti (1973), Hinze (1973), Levy (1973), Kuprievich and Shramko (1975), Yaffe and Goddard (1976), Banerjee and Grein (1976), Kendrick and Hillier (1976), and Kuprievich and Klimenko (1976). The original ideas were analyzed with great care, and many new procedural possibilities and refinements were established in this period.

3. *Present Period*

Coincident with the birth of new, fast, and powerful computers, the more or less sophisticated glamor of the second period was reexamined in a paper by Dalgaard and Jørgensen (1978), which probably can be considered the starting point of the third, present period. This paper was followed by many others: Hinze and Yurtsever (1979), Yeager and Jørgensen (1979), Roothaan *et al.* (1979), Douady *et al.* (1980), Lengsfield (1980), Jørgensen *et al.* (1980), Polezzo and Fantucci (1980), Kosugi and Kuroda (1980), Werner and Meyer (1980), Polezzo (1980), Yeager *et al.* (1981), and finally, a recent and careful work by Siegbahn *et al.* (1981), wherein a very good review of the methodology is given and an elegant theoretical discussion developed.

Unitary transformation techniques and related problems seemed to be very fashionable at the end of the 1970s and at the beginning of the 1980s. While the present work was being written, some papers on the subject appeared, for example: Siegbahn *et al.* (1981), Das (1981), and Werner and Meyer (1981).

C. Other Considerations and Objectives

The main feature apparent through the literature reviewed above is that with few exceptions, every piece of research based on unitary transformations was directed toward multiconfigurational (MC) SCF problems. Certainly, MC problems are the most conspicuous, but although classical SCF procedures seem to be operative (see, for example, Carbó and Riera, 1978; Carbo *et al.*, 1975, 1977, 1980; Carbo and Gropen, 1980; Carbo and Hernandez, 1977), there are some problems inherent in the SCF computational structure not yet well understood. One of the main causes of this can be found in the structure of the classical SCF iterative process, which in some cases behaves unpredictably and escapes control, as many SCF users well know.

This situation has engendered some interesting attempts to understand, control, and accelerate SCF processes:

(1) *SCF intrinsic instability* has been studied by Paldus and Čižek (1967, 1970a,b,c, 1971; Paldus and Veillard (1977, 1978), Chambaud *et al.* (1978), Yoshioka *et al.* (1978), Mestechkin (1978, 1979), Dahl (1974), Huzinaga and Hart-Davis (1973), Toyota and Nakajima (1979), and Simkin *et al.* (1980), where a recent review of this topic can be found.

(2) *SCF convergence problems* have been studied, among others, by Saunders and Hillier (1973), Pongor (1974), Carbó *et al.* (1977), Firsht (1977), Rowe and Rosensteel (1976), Dementiev *et al.* (1974), Wood and Veillard (1973), Grabenstteter and Grein (1976), Guest and Saunders (1974), Firsht and Pickup (1977), Merhotra (1977), Röeggen (1973), Neilsen (1973), Bhattacharyya (1978), Barr and Basch (1975), Chong (1980), Pulay (1980), and more recently by Camp and King (1981).

These studies can be divided along two well-defined lines: the first sequence tries to develop an understanding of the energy surface, the second tries to obtain practical mathematical tools in order to achieve smooth, fast, or both, convergence. This kind of work usually appears to be quite general in the sense that it entails a classical SCF step.

From the theoretical and practical point of view it would be very interesting to develop some algorithm that would allow SCF users better insight and some means to control the behavior of the iterative process. However, if this can be achieved at each SCF step by finer divisions into elementary procedures, it seems that any SCF case might be fully mastered by the user.

In order to take a step toward the goal of SCF control, our aim in the present work is to study and test Jacobi-like unitary transformation techniques and to apply them to a simple energy expression. We shall analyze generally the structure of the energy variation under such a transformation.

Such analysis will not only provide a tool to work within a SCF framework, but will permit observation of the SCF variational energy surfaces. A general analysis of these surfaces can be made using the recently described catastrophe theory (Poston and Stewart, 1978) which leads us toward an understanding of SCF convergence behavior and energy surface topology relationships. At the same time, if one looks at the immediate practical side, new procedures to obtain energy minima and optimal MOs can be described: new algorithms based on energy variation upon unitary transformations. The advantages of such algorithms are the simple, albeit general, structure they bear. So, to a system to study SCF behavior one can attach a promising computational future. This new set of computational techniques shows another interesting characteristic: although they are iterative, they do not need any classical SCF concept whatsoever. In this sense, a whole new methodological structure can be built up completely independent of SCF.

In this article we present comprehensive viewpoints of the unitary Jacobi transformations applied to an energy formula containing simple MO integrals. This method was chosen in the beginning to eliminate complex situations as far as possible, thus leaving for the next step the extension of the methodology to, say, multiconfigurational problems. Paradoxically, this imposed limitation has with time given rise to a handful of exciting and complex patterns. We present here an in-depth analysis of these patterns.

This being understood, and the bibliographical introduction taken into account, we shall study the incidence of Jacobi transformations on the chosen energy formula following an introduction to classical SCF calculations. Other interesting results upon Jacobi rotations of MOs are also studied: Fock operators, density matrix, and molecular integrals. Some practical numerical techniques are also discussed in order to implement the possible algorithm which will achieve energy minimization. After this, simple computational examples and comparisons are studied. The next step in our work will be the study of the behavior of the energy variation structure after Jacobi rotations, from the point of view of catastrophe theory; very interesting situations arise when analyzing the shape of the surfaces encountered in energy variation, and these lead to a deeper comprehension of the SCF behavior.

II. Elementary Jacobi-Like Unitary Transformations

Following a short introduction to the classical SCF open-shell framework, we shall present in this section the structure and philosophy of elementary MO transformations. We show how this technique can be used in the electronic energy expression in order to obtain algorithms to achieve smooth minimization.

A. Electronic Energy and Classical SCF Equations

Many mono- and multiconfigurational cases are described by an energy expression which can be written as

$$\mathscr{E} = \sum_p \omega_p h_{pp} + \sum_p \sum_q (\alpha_{pq} J_{pq} - \beta_{pq} K_{pq}) \tag{8}$$

where $\{\omega_p\}$, $\{\alpha_{pq}\}$, and $\{\beta_{pq}\}$ are state parameters and $\{h_{pp}\}$, $\{J_{pq}\}$, and $\{K_{pq}\}$ are the well known monoelectronic, Coulomb, and exchange integrals. Variation of Eq. (8), subject to orthonormality constraints on the MO set, furnishes the Euler equations

$$F_p|p\rangle = \sum_q \varepsilon_{qp}|q\rangle, \qquad \forall\, p \tag{9}$$

$$\varepsilon_{qp} = \varepsilon^*_{pq}, \qquad \forall\, p,q \tag{10}$$

where $\{F_p\}$ are the Fock operators defined by

$$F_p = \tfrac{1}{2}\omega_p h + \sum_q (\alpha_{pq} J_q - \beta_{pq} K_q) \tag{11}$$

and h, $\{J_q\}$, and $\{K_q\}$ are the monoelectronic Hamiltonian, Coulomb, and exchange operators, respectively. The set of scalars $\{\epsilon_{qp}\}$ are the Lagrange multipliers used to restrict the MO set $\{|p\rangle\}$ so that it remains orthonormalized. Equation (10) is a Hermitian condition imposed upon the Lagrange multipliers matrix, and it can be easily shown to fulfill, at convergence, the equation

$$\langle p|F_q - F_p|q\rangle = 0, \qquad \forall\, p,q \tag{12}$$

which is obtained by taking Eq. (10) and applying the Hermitian property of Fock operators.

The most usual SCF procedures described to solve Eqs. (9) and (10) consist primarily in constructing a new operator $\mathcal{R}$ called the coupling operator, which reduces the Euler equations to a unique pseudosecular equation of the type

$$\mathcal{R}|p\rangle = \lambda_p|p\rangle, \qquad \forall\, p \tag{13}$$

which is then solved iteratively, due to the dependence of the coupling operator on the set of its eigenvectors. For more details, practical computations, and bibliography see Carbó *et al.* (1978).

B. Jacobi-Like Transformations

The search for an optimal set of MOs which gives minimal the energy expression (8) can be performed with a sequence of very simple steps related to Jacobi-like transformations. Such a unitary transformation can be defined for each pair of MOs $\{|i, 0\rangle, |j, 0\rangle\}$ belonging to different shells and to the same symmetry species. We shall call active MO pairs the orbital couples susceptible of being transformed in such a way. The Jacobi-like transformation is, in practice, a rotation employing two parameters $\{s, c\}$ bearing a sine and cosine structure; that is, they must fulfill $s^2 + c^2 = 1$. The rotation transforms the initial MO pair into a new one by means of the equations (see, for example, Hinze and Yurtsever, 1979),

$$|i, u\rangle = c|i, 0\rangle - s|j, 0\rangle \tag{14a}$$

$$|j, u\rangle = s|i, 0\rangle + c|j, 0\rangle \tag{14b}$$

The value of s and c is chosen so as to make minimal the electronic energy. A unitary transformation like Eq. (14) will preserve the orthonormality relationships between the whole MO set. This feature implies that there is no need to use Lagrange multipliers at all in the framework of unitary transformations.

The number of active MO pairs in a sequence of Jacobi transformations, a *sweep* in the language of Jacobi diagonalization processes (Wilkinson, 1965) can be computed in the following way: let us suppose that the total number of MOs n^σ of a given symmetry species σ is decomposed as a sum over the number of orbitals, $n^\sigma_{S_I}$ with the same symmetry structure belonging to each electronic shell, s_I. If the total number of shells, including the unoccupied orbital set, is N then

$$n^\sigma = \sum_{I=1}^{N} n^\sigma_{s_I} \tag{15}$$

Thus the total number of active orbital pairs belonging to the symmetry species n^σ_Λ chosen as mentioned earlier can be calculated by means of

$$n_{\mathrm{A}}^{\sigma} = \sum_{I=1}^{N} \sum_{J>I}^{N} N_{8_I}^{\sigma} N_{8_J}^{\sigma} \tag{16}$$

Equation (16) is valid for a symmetry species when the total number of rotations n_{R} are computed as a sum

$$n_{\mathrm{R}} = \sum_{\sigma} n_{\mathrm{A}}^{\sigma} \tag{17}$$

over all symmetry species bearing occupied MOs in a given problem.

The next step in order to use Jacobi rotations to obtain an optimal MO set is to find the electronic energy variation on a transformation of the type shown in Eq. (14).

C. Electronic Energy Variation

Electronic energy variation can be found by substituting the transformed orbitals in an energy expression like the one shown in Eq. (8) for the combination of the old orbital pair as given in Eq. (14). For purposes of simplicity we shall describe the variation of the monoelectronic and bielectronic energy terms separately.

1. *Monoelectronic Energy*

Starting from the monoelectronic energy term of Eq. (8), which we now write

$$\mathscr{E}_{\mathrm{M}}^{(0)} = \sum_{p} \omega_p h_{pp}^{(0)} \tag{18}$$

and carrying out a Jacobi transformation on a pair of active orbitals as in Eq. (14), one can obtain

$$\mathscr{E}_{\mathrm{M}}^{(u)} = \sum_{p \neq i,j} \omega_p h_{pp}^{(0)} + \omega_i h_{ii}^{(u)} + \omega_j h_{jj}^{(u)} \tag{19}$$

where

$$h_{pp}^{(0)} = \langle 0;\, p|h|p;\, 0\rangle \tag{20}$$

$$h_{ii}^{(u)} = \langle u;\, i|h|i;\, u\rangle \tag{21}$$

The sum in Eq. (19) can be arranged in a way that contains all the indexes, so that one can write

$$\mathscr{E}_{\mathrm{M}}^{(u)} = \mathscr{E}_{\mathrm{M}}^{(0)} - (\omega_i h_{ii}^{(0)} + \omega_j h_{jj}^{(0)}) + (\omega_i h_{ii}^{(u)} + \omega_j h_{jj}^{(u)}) \tag{22}$$

Then, calling $\Delta\mathscr{E} = \mathscr{E}_{\mathrm{M}}^{(u)} - \mathscr{E}_{\mathrm{M}}^{(0)}$ the monoelectronic increment due to the Jacobi transformation and taking into account that the integrals over the transformed orbitals (21) can be expressed by means of the integrals over the initial orbitals (20), we can use

$$h_{ii}^{(u)} = c^2 h_{ii}^{(0)} - 2cs h_{ij}^{(0)} + s^2 h_{jj}^{(0)} \tag{23a}$$

$$h_{jj}^{(u)} = s^2 h_{ii}^{(0)} + 2cs h_{ij}^{(0)} + c^2 h_{jj}^{(0)} \tag{23b}$$

Substituting Eqs. (23a) and (23b) in Eq. (22), after reordering terms, one can finally obtain

$$\Delta\mathscr{E}_{\mathrm{M}} = (\omega_i - \omega_j)(s^2(h_{jj} - h_{ii}) - 2cs h_{ij}) \tag{24}$$

Note that in Eq. (24) superscripts have been omitted because *all the integrals are computed with the set of initial orbitals.*

2. *Bielectronic Energy*

The two-electron term of the energy equation needs a little more effort, although the structure of the treatment follows pathways similar to the monoelectronic part discussed before. Let us now call $\mathscr{E}_{\mathrm{B}}$ the bielectronic part of the energy as found in Eq. (8) so that

$$\mathscr{E}_{\mathrm{B}}^{(0)} = \sum_p \sum_q (\alpha_{pq} J_{pq}^{(0,0)} - \beta_{pq} K_{pq}^{(0,0)}) \tag{25}$$

where the superscripts indicate initial orbital integrals. In order to be transformed, Eq. (25) can be written in three well-separated parts as follows:

$$\begin{aligned}\mathscr{E}_{\mathrm{B}}^{(u)} = {} & \sum_{p\neq i,j} \sum_{q\neq i,j} (\alpha_{pq} J_{pq}^{(0,0)} - \beta_{pq} K_{pq}^{(0,0)}) \\ & + 2 \sum_{p\neq i,j} [(\alpha_{pi} J_{pi}^{(0,u)} - \beta_{pi} K_{pi}^{(0,u)}) + (\alpha_{pj} J_{pj}^{(0,u)} - \beta_{pj} K_{pj}^{(0,u)})] \\ & + \{(\alpha_{ii} J_{ii}^{(u,u)} - \beta_{ii} K_{ii}^{(u,u)}) + (\alpha_{jj} J_{jj}^{(u,u)} - \beta_{jj} K_{jj}^{(u,u)}) + 2(\alpha_{ij} J_{ij}^{(u,u)} \\ & - \beta_{ij} K_{ij}^{(u,u)})\}\end{aligned} \tag{26}$$

Equation (26) can be rearranged as has been done before in the monoelectronic part. So, calling $\Delta\mathscr{E}_{\mathrm{B}} = \mathscr{E}_{\mathrm{B}}^{(u)} - \mathscr{E}_{\mathrm{B}}^{(0)}$ one can write, after some tedious but straightforward algebra, dropping the superscripts on the integrals, being all the orbitals in the expression that follows initial orbitals:

$$\begin{aligned}\Delta\mathscr{E}_{\mathrm{B}} = 2 & \sum_{p\neq i,j} \{(\alpha_{pi} - \alpha_{pj})[s^2(J_{pj} - J_{pi}) - 2sc(pp|ij)] \\ & + (\beta_{pi} - \beta_{pj})[s^2(K_{pj} - K_{pi}) - 2sc(pi|pj)]\} \\ & + 2(\alpha_{ij} - \beta_{ij})\{s^2c^2(J_{ii} - 4K_{ij} - 2J_{ij} + J_{jj}) \\ & + 2sc(c^2 - s^2)[(ii|ij) - (ij|jj)]\}\end{aligned}$$

$$
\begin{aligned}
&+ (\alpha_{ii} - \beta_{ii})\{s^4(J_{jj} - J_{ii}) + 2s^2c^2(J_{ij} - J_{ii} + 2K_{ij}) \\
&- 4cs[c^2(ii|ij) + s^2(ij|jj)]\} \\
&+ (\alpha_{jj} - \beta_{jj})\{s^4(J_{ii} - J_{jj}) + 2s^2c^2(J_{ij} - J_{jj} + 2K_{ij}) \\
&+ 4cs[c^2(ij|jj) + s^2(ii|ij)]\}
\end{aligned}
\tag{27}
$$

Although it looks cumbersome, Eq. (27) when simplified and added to the monoelectronic part furnishes the very simple form which we shall discuss next.

3. *Total Energy Increment*

Equations (24) and (27) can be summed up to obtain the total energy increment $\Delta\mathscr{E}$. One can also use Fock operators as defined in Eq. (11) in order to write a more compact expression, but this substitution is not at all necessary when using the energy variation in a Jacobi rotation context to obtain optimal MOs.

The final increment of the energy form appears to be a function of the rotation parameters and of the special kinds of molecular integrals depending on two or four indices, attached to the active molecular orbital pair. We can write

$$
\begin{aligned}
\Delta\mathscr{E} = {}& s^4[(A_{ij} - B_{ij})(J_{ii} + J_{jj} - 2(J_{ij} + 2K_{ij}))] \\
&+ 4s^3c[(A_{ij} - B_{ij})\{(ii|ij) - (ij|jj)\}] \\
&+ 2s^2[\langle i|F_j - F_i|i\rangle - \langle j|F_j - F_i|j\rangle + 2A_{ij}K_{ij} - B_{ij}(J_{ij} + K_{ij})] \\
&+ 4sc[\langle i|F_j - F_i|j\rangle]
\end{aligned}
\tag{28}
$$

where

$$
\begin{aligned}
A_{ij} &= \alpha_{ii} - 2\alpha_{ij} + \alpha_{jj} \\
B_{ij} &= \beta_{ii} - 2\beta_{ij} + \beta_{jj}
\end{aligned}
\tag{29}
$$

The energy increment in Eq. (28) can be expressed in a much simpler way as a polynomial such as:

$$
\Delta\mathscr{E} = s^4E_4 + s^3cE_3 + s^2E_2 + scE_1 \tag{30}
$$

with obvious definitions for the coefficients $\{E_k\}$ ($k = 1, 4$). As $c = (1 - s^2)^{1/2}$, $\Delta\mathscr{E}$ can be considered a function of the rotation sine and the active MO pair. Each coefficient E_k, in turn also depends on these two orbitals.

The fact must be noted that the coefficient E_1 is equivalent to the Hermitian condition on Lagrange multipliers, as shown in Eq. (12). Thus, as the MO active pair becomes optimal one will expect that $E_1 \rightarrow 0$. One can name this condition a Brillouin's, after the well-known theorem (Brillouin, 1934) which gives an equivalent situation when fulfilled.

Computation of the coefficients $\{E_k\}$ is very simple once MO integrals are known. In order to obtain the optimal rotation of the active pair, one must find a convenient way to compute the optimal sine from Eq. (30); this subject is discussed in the next section.

The four energy variation coefficients may be written more easily as follows:

$$E_4 = (A_{ij} - B_{ij})(\langle i|J_i - (J_j + 2K_j)|i\rangle + \langle j|J_j - (J_i + 2Ki)|j\rangle) \tag{31}$$

$$E_3 = 4(A_{ij} - B_{ij})\langle i|J_i - J_j|j\rangle \tag{32}$$

$$\begin{aligned} E_2 = 2(&\langle i|(F_j - F_i) + (A_{ij} - \tfrac{1}{2}B_{ij})K_j - \tfrac{1}{2}B_{ij}J_j|i\rangle \\ &+ \langle j|(F_i - F_j) + (A_{ij} - \tfrac{1}{2}B_{ij})K_i - \tfrac{1}{2}B_{ij}J_i|j\rangle) \end{aligned} \tag{33}$$

$$E_1 = 4\langle i|F_j - F_i|j\rangle \tag{34}$$

Thus, one can see that the even terms correspond to diagonal representations of some operators, but odd coefficients are related to off-diagonal terms.

To look at a very simple situation, let us suppose that we are dealing with a closed-shell situation. Then, only two shells will be taken into account; that is, the closed-shell orbitals, doubly occupied $\mathscr{C}$ and the unoccupied virtual orbitals $\mathscr{V}$. As is well known we have the state parameters defined as:

(1) $\omega_i = 2, \quad \alpha_{ij} = 2, \quad \beta_{ij} = 1, \quad \forall i,j \in \mathscr{C}$

(2) $\omega_i = \alpha_{ij} = \beta_{ij} = 0,$ in any other case.

Using these values and taking the active pairs $\{i, j\}$ as all the MO couples which fulfill $i \in \mathscr{C} \wedge j \in \mathscr{V}$ and since any unitary transformation within the sets $\mathscr{C}$ or $\mathscr{V}$ will leave the energy invariant, one will always obtain $A_{ij} = 2$ and $B_{ij} = 1$ if $i \in \mathscr{C} \wedge j \in \mathscr{V}$ holds. Moreover, the values $A_{ij} = B_{ij} = 0$ will be obtained in any other case. So, Eqs. (31)–(34) may be written in this situation as:

$$E_4 = J_{cc} + J_{vv} - 2(J_{cv} + 2K_{cv}), \qquad E_2 = 2(F_{vv} - F_{cc}) + 3K_{cv} - J_{cv}$$

$$E_3 = 4\{(cc|cv) - (cv|vv)\}, \qquad E_1 = -4F_{cv}$$

where $\{c, v\}$ stands for any occupied virtual pair of MOs and $\{F_{cv}\}$ is an element of the closed-shell Fock operator expressed over the MO basis.

As already discussed, the first-order coefficient E_1 represents the Brillouin condition. In the monoconfigurational closed-shell virtual terms of the Fock operator as the optimal energy expression is reached and $E_1 \rightarrow$

0, this means $F_{cv} \to 0$; or, in other words, one can chose the sine of each active pair as the Jacobi sine nullifying the elements $\{F_{cv}\}$. This is a possibility already pointed out by Hinze and Yurtsever (1979).

The general energy structure of the multiplet electronic spin distribution recently discussed in a classical coupling operator SCF treatment (Carbó *et al.*, 1980) may be used as another example. In this case, the open-shell $\mathcal{O}$, where all the single occupied orbitals are placed, must be added to the shells $\mathcal{C}$ and $\mathcal{V}$. Two Fock operators are needed: $F_{\mathcal{C}}$ and $F_{\mathcal{O}}$ belonging to the corresponding shells. Three cases must be considered, giving the following parameters:

(1) $A_{\mathcal{C}\mathcal{O}} = 1, \quad A_{\mathcal{C}\mathcal{V}} = 2, \quad A_{\mathcal{O}\mathcal{V}} = 1/2$

(2) $B_{\mathcal{C}\mathcal{O}} = 1/2, \quad B_{\mathcal{C}\mathcal{V}} = 1, \quad B_{\mathcal{O}\mathcal{V}} = 1/2$

The coefficients for each pair of shells are as follows:

(1) *Closed-shell–open-shell interaction*

$$E_4^{\mathcal{C}\mathcal{O}} = \tfrac{1}{2}(J_{\mathcal{C}\mathcal{C}} + J_{oo}) - (J_{\mathcal{C}o} + 2K_{\mathcal{C}o})$$

$$E_3^{\mathcal{C}\mathcal{O}} = 2[(cc|co) - (co|oo)]$$

$$E_2^{\mathcal{C}\mathcal{O}} = 2[(F_{\mathcal{O},cc} + F_{\mathcal{C},oo}) - (F_{\mathcal{C},cc} + F_{\mathcal{O},oo})] + 3K_{\mathcal{C}o} - J_{\mathcal{C}o}$$

$$E_1^{\mathcal{C}\mathcal{O}} = 4(F_{\mathcal{O},co} - F_{\mathcal{C},co})$$

(2) *Closed-shell–virtual space interaction.* It has the same form as in closed-shell case (1), but uses its corresponding Fock operator $F_{\mathcal{C}}$.

(3) *Open-shell–virtual space interaction*

$$E_4^{\mathcal{O}\mathcal{V}} = E_3^{\mathcal{O}\mathcal{V}} = 0, \qquad E_2^{\mathcal{O}\mathcal{V}} = 2(F_{\mathcal{O},vv} - F_{\mathcal{O},oo}) + 3K_{\mathcal{O}\mathcal{V}} - J_{\mathcal{O}\mathcal{V}}$$

$$E_1^{\mathcal{O}\mathcal{V}} = -4F_{\mathcal{O},ov}$$

We have used here the same convention as in the closed-shell case, adding the o index when we want to refer to any MO belonging to the open-shell $\mathcal{O}$. Note the formal similarity between $E_4^{\mathcal{C}\mathcal{O}} - E_4^{\mathcal{C}\mathcal{V}}$, $E_3^{\mathcal{C}\mathcal{O}} - E_3^{\mathcal{C}\mathcal{V}}$, and $E_2^{\mathcal{C}\mathcal{V}} - E_2^{\mathcal{O}\mathcal{V}}$.

Finally, it must be noted that a formula related to Eq. (30) was developed by Chang and Grein (1972), within a paired excitation multiconfigurational (PEMC) context. This should not be surprising because it is well known that the PEMC energy expression has the same form as Eq. (8) (see, for example, Carbó and Hernández, 1977, and Carbó and Riera, 1978). Thus, the present formalism can be easily extended to the PEMC cases without any modification.

D. Computation of Optimal Sine

The cornerstone of the present methodoloy is the evaluation of the optimal sine from Eq. (30). As the energy increment is a quartic polynomial in the sine, but also contains first-order cosine terms, an iterative procedure shall necessarily be constructed for this purpose. Due to the variation range of the sine function, the optimal solution will lie in the closed interval (−1, +1).

The algorithm adopted here can be described as follows:

Algorithm A1. Optimal sine computation

(1) An intial value for the sine must be guessed. A possible method consists of supposing that as $s \rightarrow 0$ then $c \rightarrow 1$, so Eq. (30) may be approximated as:

$$\Delta\mathscr{E} \simeq sE_1 + s^2E_2 + \theta(s^3) \tag{35}$$

Then, the first derivative is computed, giving

$$\partial\,\Delta E/\partial s \simeq E_1 + 2sE_2 \tag{36}$$

and for the extremum condition one obtains

$$s \simeq -E_1/2E_2 \tag{37}$$

Computational experience indicates that the approximation (37) is a very accurate one, even at earlier stages of the optimization process. The coefficient E_2 must be positive in order to fulfill the minimum condition, through the approximate Hessian:

$$\partial^2\,\Delta\mathscr{E}/\partial s^2 \simeq 2E_2 > 0 \tag{38}$$

This condition is also reflected in Eq. (35) by substituting for the values of s those given in Eq. (37). This yields

$$\Delta\mathscr{E} = -E_1^2/4E_2 \tag{39}$$

Thus, only $E_2 > 0$ can give $\Delta\mathscr{E} < 0$, which is the desired feature here. Computational experience also shows that Eq. (39) is very useful for obtaining an order of magnitude of the expected energy variation in a given active orbital pair. In Section VI,C, all these questions shall be discussed in depth.

(2) The exact gradient and Hessian are computed from Eq. (30):

$$\partial\,\Delta\mathscr{E}/\partial s = -c\{(E_3s^2 + E_1)t^2 - 2(2E_4s^2 + E_2)t - (3E_3 + E_1)\} \tag{40}$$

$$\begin{aligned}\partial^2\,\Delta\mathscr{E}/\partial s^2 = {} & -2(E_1 + 3E_3s^2)t + 2(E_2 + 6E_4s^2)\\ & - (s/c^3)(E_1 + s^3E_3) + 6E_3sc\end{aligned} \tag{41}$$

where $t = s/c$ is a tangent.

With the values of the coefficients $\{E_k\}$ and the pair $\{s, c\}$, using the extremum condition in Eq. (40), one can obtain a new value of t. If this value gives a positive Hessian, one can accept t as the current value.

(3) A new sine is computed by means of

$$s = t(1 + t^2)^{-1/2} \tag{42}$$

(4) This value is used to update the sine in step 2 until convergence is reached. That is, when for some tolerance ϵ: $|s^{(n)} - s^{(n+1)}| \leq \epsilon$. More details concerning the problems of minima localization in the energy variation polynomial are given in Section VI,C.

III. Variation of Other Interesting Quantities

Besides the electronic energy variation, when a unitary rotation is applied to a pair of active orbitals it would be worthwhile to consider the variation of other SCF-related quantities. We shall study in this section the behavior of the density matrix, Fock operators, and molecular integrals.

All these elements are related to the procedures we shall describe later on. In fact, transformation of molecular integrals is essential to obtain optimized algorithms in the present framework. Variation of Fock operators and the density matrix will give some insight into the structure and convergence properties of SCF procedures.

A. Variation of the Density Matrix

Usually, given the set of MOs $\{|p\rangle\}$ with occupation numbers $\{\omega_p\}$, one can write the density matrix **D** of the system as:

$$\mathbf{D} = \sum_p \omega_p |p\rangle\langle p| \tag{43}$$

Variation of an active pair $\{i, j\}$ through an elementary transformation as in Eq. (14) needs the structure of the MOs $|i\rangle$ and $|j\rangle$ projector variation, which with some straightforward algebra can be written

$$|i\rangle\langle i| \rightarrow |i\rangle\langle i| + s^2\{|j\rangle\langle j| - |i\rangle\langle i|\} - sc\{|i\rangle\langle j| + |j\rangle\langle i|\} \tag{44}$$

$$|j\rangle\langle j| \rightarrow |j\rangle\langle j| + s^2\{|i\rangle\langle i| - |j\rangle\langle j|\} + sc\{|i\rangle\langle j| + |j\rangle\langle i|\} \tag{45}$$

Substituting Eqs. (44) and (45) in Eq. (43), the density matrix variation upon a rotation of the MO pair $\{i, j\}$, $\mathbf{\Delta}_{ij}$, has the form

$$\Delta_{ij} = (\omega_j - \omega_i)\{s^2 \mathbf{A}_{ij} + 2sc\, \mathbf{B}_{ij}\} \tag{46}$$

where the following definitions for the matrices $\mathbf{A}_{ij}$ and $\mathbf{B}_{ij}$ have been used

$$\mathbf{A}_{ij} = |i\rangle\langle i| - |j\rangle\langle j| \tag{47}$$

$$\mathbf{B}_{ij} = \tfrac{1}{2}\{|i\rangle\langle j| + |j\rangle\langle i|\} \tag{48}$$

Some interesting conclusions can be obtained from Eq. (46). Obviously, only orbital pairs with different occupation numbers can contribute to the density variation. This fact speeds up elementary rotation algorithms when the active orbital pairs whose density matrix variation is significant are taken. As can be deduced from the projector structure of the density matrix, the variation must follow a second-order dependence on rotation sine, as shown in the final structure (46).

When convergence is approached, that is when $s \rightarrow 0$ and $c \rightarrow 1$, the asymptotic formula can be written as:

$$\mathbf{\Delta}_{ij} \simeq 2(\omega_j - \omega_i)s\mathbf{B}_{ij} \tag{49}$$

B. Variation of Fock Operators

Taking the definition given by Eq. (11), the structure of Fock operators can be expressed by means of the sum

$$F_p = M_p + B_p \tag{50}$$

where M_p is the rotationally invariant monoelectronic part of the operator and B_p is the active part of the Fock operator variation which we define as:

$$B_p = \sum_q (\alpha_{pq}J_q - \beta_{pq}K_q) \tag{51}$$

Thus, the variation of B_p upon the rotation of a MO active pair will depend on the Coulomb operator $\{J_i, J_j\}$ and exchange operator $\{K_i, K_j\}$ variation. The structures of the increments are easily computed taking into account the well-known structure of these operators (Roothaan, 1951).

Using the unitary transformation (14), one obtains after some manipulations:

$$\begin{aligned} J_i &\rightarrow J_i + s^2(J_j - J_i) - 2csX_{ij}, \quad & K_i &\rightarrow K_i + s^2(K_j - K_i) - 2csZ_{ij} \\ J_j &\rightarrow J_j + s^2(J_i - J_j) + 2csX_{ij}, \quad & K_j &\rightarrow K_j + s^2(K_i - K_j) + 2csZ_{ij} \end{aligned} \tag{52}$$

Two types of operators have been used in Eqs. (52) apart from the involved Coulomb and exchange operators:

(1) *The generalized Coulomb operator* $\{X_{ij}\}$, which can be easily defined through the equality

$$(ij|kl) = \langle k|X_{ij}|l\rangle \tag{53}$$

(2) *The generalized exchange operator* $\{Z_{ij}\}$, constructed by means of another set $\{Y_{ij}\}$ and defined with the symmetrization expression

$$Z_{ij} = \tfrac{1}{2}\{Y_{ij} + Y_{ji}\} \tag{54}$$

and with the aid of the matrix form

$$\langle k|Z_{ij}|l\rangle = \tfrac{1}{2}\{(ik|jl) + (jk|il)\} \tag{55}$$

In this sense, contrary to the operators $\{Y_{ij}\}$ which fulfill the property

$$Y_{ij} = Y_{ji}^{\dagger} \tag{56}$$

the set of $\{Z_{ij}\}$ operators are symmetric if their subscript pairs are interchanged as in

$$Z_{ij} = Z_{ji} \tag{57}$$

a characteristic equivalent to the generalized Coulomb operators $\{X_{ij}\}$.

Taking into account the variation structure (52) of the involved operators into the bielectronic part of the Fock operator (51), one can write

$$\begin{aligned} \Delta F_p &= \Delta B_p \\ &= (\alpha_{pj} - \alpha_{pi})\{s^2(J_i - J_j) + 2scX_{ij}\} \\ &\quad -(\beta_{pj} - \beta_{pi})\{s^2(K_i - K_j) + 2scZ_{ij}\} \end{aligned} \tag{58}$$

It must be noted that there exists a relationship between the formal structure of ΔF_p with the previously considered density matrix variation as shown in Eq. (46). As a consequence of this, variation of Fock operators is second order only. Thus, it is possible that the slow convergent patterns which appear in many classical SCF cases may be ascribed to this feature. When convergence is approached, the asymptotic variation formula for ΔF_p can be written as follows:

$$\Delta F_p \sim 2s\{(\alpha_{pj} - \alpha_{pi})X_{ij} - (\beta_{pj} - \beta_{pi})Z_{ij}\} \tag{59}$$

which takes an equivalent structure as a density matrix variation.

C. Variation of Molecular Integrals

1. *General Transformation Structure*

Within the framework of MO theory, when using Jacobi-like elementary rotation techniques, the operator matrix form and other similar or related quantities behave as we have seen in an easily generalized manner.

Trying to construct the most general formalism possible, we shall assume that a rotation between the MO pair $\{i, j\}$ has been optimally searched with rotation sine and cosine s and c respectively.

Rotation of any quantum mechanical integral, operator, or matrix, can be obtained by considering abstract elements, which hereafter we shall call *objects*, depending on one active index, $\theta_1 = \{[i], [j]\}$; two active indices, $\theta_2 = \{[ii], [jj], [ij]\}$, etc. We shall also use the terms first order or one-index objects, second order or two-index objects, and so on, in order to identify the elements of the sets θ_1, θ_2, . . . , respectively.

In the present description, molecular repulsion integrals can behave as fourth-order objects; a projection operator has second-order behavior; a two-electron operator raises it to fourth order, . . . , an nth electron operator gives maximal terms up to $2n$th order. The behavior of nth-order objects can be expressed as a direct product of lower order objects; for example:

$$\begin{aligned}[x_1, x_2, \ldots, x_n] &\equiv [x_1] \otimes [x_2, x_3, \ldots, x_n] \\ &\equiv [x_1, x_2] \otimes [x_3, \ldots, x_n] \\ &\vdots \\ &\equiv [x_1] \otimes [x_2] \otimes \cdots \otimes [x_n] \end{aligned} \tag{60}$$

where $\{x_p\}$ represents an arbitrary nth-order sequence of the active index pair $\{i, j\}$. Thus, given any quantum mechanical object, depending on MO indices, the set of all the elements associated to this quantity can be divided into subsets behaving as zero-, first-, second-, . . . , order objects.

Variation of quantities of interest such as the density matrix, Fock operators, and MO integrals can be easily deduced from the transformation of the essential one-index objects $\{[i], [j]\}$, which, using Eq. (14), may be written as:

$$[i] \rightarrow c[i] - s[j], \qquad [j] \rightarrow s[i] + c[j] \tag{61}$$

All other transformation formulas can be derived from Eqs. (61). For example, the transformation of two-index objects: $\{[ii], [jj], [ij], [ji]\}$ may be written as direct products of the elements of Eqs. (61):

$$[ii] \rightarrow [i] \otimes [i] \rightarrow [ii] + s^2\{[jj] - [ii]\} - sc\{[ij] + [ji]\} \tag{62}$$

$$[jj] \rightarrow [j] \otimes [j] \rightarrow [jj] + s^2\{[ii] - [jj]\} + sc\{[ij] + [ji]\} \tag{63}$$

$$[ij] \rightarrow [i] \otimes [j] \rightarrow [ij] - s^2\{[ij] + [ji]\} + sc\{[ii] - [jj]\} \tag{64}$$

$$[ji] \rightarrow [j] \otimes [i] \rightarrow [ji] - s^2\{[ij] + [ji]\} + sc\{[ii] - [jj]\} \tag{65}$$

so $[ij]$ is equivalent to $[ji]$, but it must be taken into account that the order of the rotation changes the sign of the sine, giving $s_{ij} = -s_{ji}$. Hence, one can easily write the variation of more than two-index objects, for example, $[iji]$, . . . , through the appropriate direct product, which is to say, in this case particularly:

$$\begin{aligned}[iji] \rightarrow [ij] \otimes [i] \rightarrow [i] \otimes [ji] \rightarrow c[iji] &+ s\{[iji] \\ &+ [jii] - [ijj]\} \\ &- s^2c\{[ijj] + [jij] + [jji] \\ &- [iii]\} - s^3\{[iij] + [iji] + [jii] - [jjj]\} \end{aligned} \tag{66}$$

The two-index-object transformation can be constructed through two basic structures, namely,

$$\Delta[ij] = [ii] - [jj] \tag{67}$$

$$\Sigma[ij] = \tfrac{1}{2}([ij] + [ji]) \tag{68}$$

With Δ and Σ, one can rewrite Eqs. (62)–(65) as follows:

$$[ii] \rightarrow [ii] - (s^2\,\Delta[ij] + 2sc\,\Sigma\,[ij]) \tag{69}$$

$$[jj] \rightarrow [jj] + (s^2\,\Delta[ij] + 2sc\,\Sigma\,[ij]) \tag{70}$$

$$[ij] \rightarrow [ij] - 2s^2\,\Sigma\,[ij] + sc\,\Delta[ij] \tag{71}$$

So, one-electron molecular integrals are transformed according to Eqs. (69)–(71). Also, any many-index object can be formally studied without effort by performing some tiresome algebraic manipulation. Let us take as an example the molecular integral $(ij|ij)$, which transforms as a fourth-order object according to the following rule:

$$\begin{aligned}(ij|ij) &\rightarrow [ij] \otimes [ij] \\ &\rightarrow (ij|ij) + s^2(1 - s^2)\{(ii|ii) + (jj|jj) - 2[(ii|jj) + 2(ij|ij)]\} \\ &\qquad + 2cs(1 - 2s^2)\{(ii|ij) - (ij|jj)\} \\ &= (ij|ij) + \Delta(ij|ij) \end{aligned} \tag{72}$$

With this convenient tool we are ready for systematic study of the two-electron integral variation.

2. *Variation of Two-Electron Molecular Integrals*

The variation of two-electron molecular integrals $\{(pq|rs)\}$ under a rotation attached to an active MO pair $\{i,j\}$ can be classified to represent five different cases, depending on the number and position of the index pair $\{i,j\}$ in the integral. Accordingly, the five classes correspond to first-order objects, second-order with Coulomb or exchange-structure objects, and so on. Each case will be discussed separately and the final formulas will be given without details.

After the admittedly tiresome deduction of the following formulas, a set of easily programmable structure appears as a final result.

3. *One Active Index*

There are two integral types in this case, $(iq|rs)$ and $(jq|rs)$ being any other position of the active indices equivalent. The use of the transformation structure (61) furnishes

$$(iq|rs) \rightarrow c(iq|rs) - s(jq|rs) \tag{73}$$

$$(jq|rs) \rightarrow s(iq|rs) + c(jq|rs) \tag{74}$$

4. *Two Active Indexes*

Two possible integral classes must be studied separately, because the index position will give Coulomb and exchange structures as follows.

a. Coulomb-like integrals. There are three possible integral types, namely, $(ii|rs)$, $(jj|rs)$, and $(ij|rs)$, which transform according to two-index-object rules. In this sense, using Eqs. (62)–(65), one arrives at the simple expressions:

$$(ii|rs) \rightarrow (ii|rs) + s^2\{(jj|rs) - (ii|rs)\} - 2sc(ij|rs) \tag{75}$$

$$(jj|rs) \rightarrow (jj|rs) + s^2\{(ii|rs) - (jj|rs)\} + 2sc(ij|rs) \tag{76}$$

$$(ij|rs) \rightarrow (ij|rs) - 2s^2(ij|rs) + sc\{(ii|rs) - (jj|rs)\} \tag{77}$$

b. Exchange-type integrals. Again, three integral types are possible: $(iq|is)$, $(jq|js)$, and $(iq|js)$, which transform in the same way as the Coulomb integrals, being exchange-type integrals with two-index objects; but one must take into account that if $q \neq s$, then $(iq|js) \neq (jq|is)$, although their transformation is formally the same. Then we shall have

$$(iq|is) \rightarrow (iq|is) + s^2\{(jq|js) - (iq|is)\} - sc\{(iq|js) + (jq|is)\} \tag{78}$$

$$(jq|js) \rightarrow (jq|js) + s^2\{(iq|is) - (jq|js)\} + sc\{(iq|js) + (jq|js)\} \tag{79}$$

$$(iq|js) \rightarrow (iq|js) - s^2\{(iq|js) + (jq|is)\} + sc\{(iq|is) - (jq|js)\} \tag{80}$$

Transformation of integral $(jq|is)$ is exactly the same as $(iq|js)$.

5. *Three Active Index Integrals*

There are six possible integrals, transforming as three-index objects as in the transformation discussed in Eq. (66). The final variation structure of the six possible integrals $(ii|is)$, $(ii|js)$, $(jj|is)$, $(jj|js)$, $(ij|is)$, and $(ij|js)$ is found to be

$$\begin{aligned}(ii|is) \rightarrow{}& c(ii|is) - s[(ii|js) + 2(ij|is)] + s^2c[2(ij|js) + (jj|is) - (ii|is)] \\ &+ s^3[2(ij|is) + (ii|js) - (jj|js)]\end{aligned} \tag{81}$$

$$\begin{aligned}(ii|js) \rightarrow\ & c(ii|js) + s[(ii|is) - 2(ij|js)] + s^2c[(jj|js) - (ii|js) - 2(ij|is)] \\ & + s^3[(jj|is) - (ii|is) + 2(ij|js)] \end{aligned} \tag{82}$$

$$\begin{aligned}(jj|is) \rightarrow\ & c(jj|is) + s[2(ij|is) - (jj|js)] - s^2c[2(ij|js) + (jj|is) - (ii|is)] \\ & - s^3[2(ij|is) + (ii|js) - (jj|js)] \end{aligned} \tag{83}$$

$$\begin{aligned}(jj|js) \rightarrow\ & c(jj|js) + s[2(ij|js) + (jj|is)] + s^2c[2(ij|is) + (ii|js) - (jj|js)] \\ & - s^3[2(ij|js) + (jj|is) - (ii|is)] \end{aligned} \tag{84}$$

$$\begin{aligned}(ij|is) \rightarrow\ & c(ij|is) + s[(ii|is) - (jj|is) - (ij|js)] - s^2c[(ii|js) + 2(ij|is) \\ & - (jj|js)] + s^3[(jj|is) + 2(ij|js) - (ii|is)] \end{aligned} \tag{85}$$

$$\begin{aligned}(ij|js) \rightarrow\ & c(ij|js) + s[(ij|is) + (ii|js) - (jj|js)] - s^2c[(jj|is) + 2(ij|js) \\ & - (ii|is)] - s^3[(ii|js) + 2(ij|is) - (jj|js)] \end{aligned} \tag{86}$$

Note that $(ii|is)$, $(jj|js)$; $(ij|is)$, $(ij|js)$; and $(ii|js)$, $(jj|is)$ are related pairs of integrals. Their formulas are interchangeable if index i is changed by index j and s by $-s$.

6. *Four Active Indices*

Four-index integrals can only be of six different types: $(ii|ii)$, $(ii|ij)$, $(ii|jj)$, $(ij|ij)$, $(ij|jj)$, and finally, $(jj|jj)$. As the structure of the variation of the exchange integral $(ij|ij)$ has been discussed previously, we shall give here the remaining five:

$$\begin{aligned}(ii|ii) \rightarrow\ & (ii|ii) - 4sc(ii|ij) + 2s^2[2(ij|ij) + (ii|jj) - (ii|ii)] \\ & - 4s^3c[(ij|jj) - (ii|ij)] \\ & + s^4[(jj|jj) + (ii|ii) - 2(ii|jj) - 4(ij|ij)] \end{aligned} \tag{87}$$

$$\begin{aligned}(ii|ij) \rightarrow\ & (ii|ij) - sc[2(ij|ij) + (ii|jj) - (ii|ii)] + s^2[3(ij|jj) - 5(ii|ij)] \\ & + s^3c[4(ij|ij) + 2(ii|jj) - \{(ii|ii) + (jj|jj)\}] \\ & - 4s^4[(ii|jj) - (ii|ij)] \end{aligned} \tag{88}$$

Note that $(ii|jj)$ transforms in the same manner as $(ij|ij)$, both belonging to equivalent objects

$$\begin{aligned}[iijj] &\equiv [i] \otimes [i] \otimes [j] \otimes [j] \equiv [ii] \otimes [jj] \\ &\equiv [ij] \otimes [ij] \equiv [i] \otimes [j] \otimes [i] \otimes [j] \equiv [ijij] \end{aligned}$$

thus,

$$(ii|jj) \rightarrow (ii|jj) + \Delta(ij|ij) \tag{89}$$

where $\Delta(ij|ij)$ was defined in Eq. (72).

Because $[ii]$ is practically equivalent to $[jj]$, one must change only $\{i\}$ into $\{j\}$ and s into $-s$ to obtain without effort the remaining few integrals:

$$\begin{aligned}(ij|jj) \rightarrow (ij|jj) &+ sc[2(ij|ij) + (ii|jj) - (jj|jj)] + s^2[3(ii|ij) - 5(ij|jj)] \\ &- s^3c[4(ij|ij) + 2(ii|jj) - \{(ii|ii) + (jj|jj)\}] \\ &- 4s^4[(ii|ij) - (ij|jj)] \end{aligned} \tag{90}$$

and finally,

$$\begin{aligned}(jj|jj) \rightarrow (jj|jj) &+ 4sc(ij|jj) + 2s^2[2(ij|ij) + (ii|jj) - (jj|jj)] \\ &+ 4s^3c[(ii|ij) - (ij|jj)] \\ &+ s^4[(ii|ii) + (jj|jj) - 2(ii|jj) - 4(ij|ij)] \end{aligned} \tag{91}$$

IV. Computational Procedures

The theoretical framework developed so far permits the implementation of various algorithms, all of which point to energy minimization and optimal MO calculation. We have implemented four basic kinds of algorithms in a context that we call a single-rotation (SR) framework. By this we mean that even if we use one Jacobi rotation after another, we shall not take into account the coupling between two succesive rotations.

We followed this philosophy first to test a sequence of rotations, taking each active orbital pair in turn. This was followed by the same sequence, but elementary rotations were accumulated and applied all at the same time; we called this accumulated rotations (AR). The same structures were used, but energy variation coefficients were taken only up to second order (SO). Finally, we used a sequence of couples of active orbital pairs which we called a double-rotation (DR) framework. We shall describe each algorithm and furnish commentaries on the observed computational behavior.

A. Single Rotations

This procedure is based on the following: given a pair of active orbitals for which the orbital sine has been computed, the pair of orbitals is modified according to Eq. (14). This process is repeated for each active orbital pair, as in the Jacobi diagonalization sweeps. A new sweep is performed unless all active orbital pairs contribute less than a given threshold to the energy. The general scheme of this procedure will be given briefly in Algorithm A2 as follows:

Algorithm A2. Single Rotations

```
(1) Compute trial vectors
    One can use the one-electron Hamiltonian vectors, or in some cases, vectors from other calculations. If one wishes to start with well-adapted vectors, a set of vectors coming out of a classical SCF procedure can be used after a small number of iterations (three or four will be enough for this purpose).
(2) Compute molecular integrals
        Loop over the active orbital pairs $\{i, j\}$
(3)     Compute the electronic energy $\mathscr{E}_0$ and energy variation coefficients $E_1, E_2, E_3, E_4$
(4)     Use algorithm A1 to obtain the optimal sine $s$ and the energy increment $\Delta\mathscr{E}$
(5)     Rotate molecular integrals according formulas shown in Section III,C
(6)     Compute new energy $\mathscr{E} = \mathscr{E}_0 + \Delta\mathscr{E}$.
    End of loop $\{i, j\}$
    If for some $\{i, j\} : |\Delta\mathscr{E}| > \epsilon$ go to loop, else: stop.
```

In order to find out whether the ordering of the Jacobi rotations influences convergence patterns or not, we have performed the same computations as in Algorithm A2 above. Instead of using a sequential ordering of active pairs, however, we carried out the rotation scheme in a disordered fashion. The results have shown that as far as we know, the order in which the rotations are performed is of no consequence. We have adopted the sequential ordering of Algorithm A2 taking this into account.

A possible variant of Algorithm A2 may consist of using, instead of molecular integrals directly, a scheme based on SCF concepts as projectors and Fock operators with the atomic orbital integrals, but this has appeared much less efficient than the procedure described above.

B. Accumulated Rotations

We call accumulated rotations (AR) a procedure which can simplify the *single rotation* method. We construct a unitary matrix $\mathbf{U}$ to be used in the general transformation as discussed in Eq. (6). The matrix $\mathbf{U}$ is constructed as a product of the Jacobi rotation pairs, that is,

$$\mathbf{U} = \prod_{\{i,j\}} \mathbf{U}[i,j] \tag{92}$$

The structure of $\mathbf{U}[i, j]$ is well known in Jacobi diagonalization procedures:

$$\forall\, p \neq i,j \;\wedge\; \forall\, q \neq i,j\colon \quad \mathbf{U}[i,j]_{pq} = \delta_{pq}$$

$$\mathbf{U}[i,j]_{ii} = \mathbf{U}[i,j]_{jj} = c, \quad \mathbf{U}[i,j]_{ij} = -\mathbf{U}[i,j]_{ji} = -s, \quad c^2 + s^2 = 1 \qquad (93)$$

The differences with respect to the previous procedure may be summarized as follows:

(1) The AR algorithm does not transform the MO coefficient matrix at each rotation but rather at the end of each sweep. Thus MO integrals, if used, can be transformed in the classical way from the AO integral matrix with the updated MO coefficients.

(2) The method can be considered a SCF variant where each sweep may be related with a classical SCF iteration. There is, however, an advantage in the present formulation: one can analyze, at each sweep, each rotation in turn and exclude those which are unsuitable or useless for the energy lowering. This possibility may be very helpful for controlling convergence.

(3) This procedure is well structured for a simultaneous computation. A paper by Seeger (1981) on the subject of hardware philosophy may be useful to illustrate this point.

The following algorithm will synthesize steps which serve to implement this method:

Algorithm A3: Accumulated Rotations

```
(1) Computation of trial vectors $\mathbf{C}$
    The same considerations apply as in step 1 of Algorithm A2
(2) Computation of Fock operators and energy $\mathcal{E}$. Also $\mathbf{U} = \mathbf{I}$.
    Loop over all active orbital pairs $\{i, j\}$
(3) Compute energy coefficients $E_1$, $E_2$, $E_3$, $E_4$
(4) Use Algorithm A1 to obtain $s$ and
(5) Construct matrix $\mathbf{U}$: $\mathbf{U} \leftarrow \mathbf{U} * \mathbf{U}[i, j]$
    End of loop $\{i, j\}$
(6) Test convergence: if $\mathbf{U} = \mathbf{I}$, stop;
    or else:
    Modify MO vectors $\mathbf{C} \leftarrow \mathbf{C} \cdot \mathbf{U}$
    (go to 2)
```

C. Second-Order Rotations

As a simple inspection of Eq. (28) or (30) shows, the terms bearing the coefficients E_3 and E_4 in the energy variation were not so important, and less so when the iterative system was approaching convergence, so we tried to design a simplified approach taking only rotation sine terms up to second order. In this scheme, Eq. (30) becomes

$$\Delta\mathscr{E} \simeq scE_1 + s^2E_2 + \theta(s^3) \tag{94}$$

Thus, Algorithms A2 and A3 will be fully reproduced, but in step 3 only the coefficients E_1 and E_2 need to be computed, omitting E_3 and E_4. Also, from E_2 only the Fock operator terms were conserved. This feature has no practical meaning in Algorithm A2 because very few operations are spared. It is, however, more meaningful in Algorithm A3 (which approaches the structure of SCF classical procedures) because of the second-order nature of Fock-operator variation, as shown in Section III,B.

The difference here is the advantage of cutting each SCF-like iteration at will and in small steps that can be controlled as the sweep proceeds. It is therefore possible to make sure, for example, that each rotation step really gives an energy increment $\Delta\mathscr{E} < 0$. We shall refer to second-order accumulated rotations (SOAR) when speaking of this simplified procedure.

D. Double Rotations

We shall analyze one last possible way to use the theoretical framework of Jacobi-like unitary transformations by describing an intermediate strategy between those shown in Sections IV,A and IV,B: the possible framework of double rotations. By this term we understand the application of two different active rotation pairs, namely $\{i, j\}$ and $\{k, l\}$, simultaneously and without considering the coupling between them, which is discussed later.

The structure of this algorithm has conserved the main form of Algorithm A2, but instead of a unique loop, two have been used. This requires a little more computational effort, but a shorter number of full iterative steps. Computational experience indicates that convergence precision will depend on the number of elementary rotations performed.

The following algorithm resumes the procedure discussed above:

Algorithm A4: Double Rotations

```
(1) Computation of starting MO coefficient matrix
    See the comments in step 1 of Algorithm A2
(2) Compute molecular integrals
    Loop over active orbital pairs $\{i, j\}$
    Loop over active orbital pairs $\{k, l\} \neq \{i, j\}$
(3) Compute electronic energy $\mathscr{E}_0$
(4) Compute electronic energy variation coefficients
    $E_1[ij]$, $E_2[ij]$, $E_3[ij]$, $E_4[ij]$ and $E_1[kl]$, $E_2[kl]$, $E_3[kl]$, $E_4[kl]$
(5) Compute the optimal sines $s[i, j]$ and $s[k, l]$
```

```
    Twice using Algorithm A1, obtain the total energy increment
    $\Delta\mathscr{E} = \Delta\mathscr{E}[i, j] + \Delta\mathscr{E}[k, l]$
(6) Rotate MO Integrals
    According to formulas shown in Section III,C
(7) Rotate MO Coefficients
    According to $s[i, j]$ and $s[k, l]$
(8) Compute new energy $\mathscr{E} = \mathscr{E} + \Delta\mathscr{E}$
    End of loop $\{k, l\}$
    End of loop $\{i, j\}$
    If for some $\{i, j\}$, $\{k, l\}$, $|\Delta\mathscr{E}| > \epsilon$ go to loop $\{i, j\}$; else: stop.
```

We have developed so far four possible kinds of iterative sequences and some small variants, which are analyzed in the next section by using some simple systems and are then compared with standard SCF results.

It is easy now to see that one can use Jacobi-like rotations in a wide variety of ways, but we feel that we are far from the optimal procedure. Computer technology development, especially computational experience with trial-and-error programming, will give rise to improved algorithms more efficient than those discussed previously. Here an important point must be stressed. Efficient algorithms to compute the full set of MO integrals are needed. Fortunately, a good review on the subject by Shavitt (1977) is to be found in the literature.

E. Coupling between Two Successive Rotations

The high effectiveness of the double-rotation method, as described in the previous section, has raised the question: Why does the effect of simultaneous rotations act as a powerful aid to convergence? We tried to see the structure of the coupling between two simultaneous rotations. Two cases must be considered: when the first rotation takes the active pair $\{i, j\}$, and when the second rotation uses type (1) $\{i, k\}$ or type (2) $\{k, l\}$ with $k, l \neq i, j$ in both cases.

When we perform the rotation of the $\{i, j\}$ pair, it is seen that the energy variation takes the form of Eq. (30), with the coefficients $\{E_k\}$ ($k = 1, 4$) defined by means of Eqs. (31)–(34). When we perform the second rotation of type (1) or (2), it will act on $\Delta\mathscr{E}$, varying the coefficients in an amount $\{\Delta\mathscr{E}_k\}$ ($k = 1, 4$). We should like to study this further variation.

1. *Case $\{i, j\}$, Followed by $\{i, k\}$*

After the transformation of the active pair $\{i, j\}$, performed as shown in Eq. (14), we suppose that one also rotates the pair $\{i, k\}$. A new set of equations

$$|i\rangle \rightarrow c_{ik}|i\rangle - s_{ik}|k\rangle, \qquad |k\rangle \rightarrow s_{ik}|i\rangle + c_{ik}|k\rangle \tag{95}$$

is therefore needed in addition to Eq. (14). The parameters $\{s_{ik}, c_{ik}\}$ are the new sine and cosine for the pair $\{i, k\}$. The following expressions have resulted where we have also used the definitions:

$$A_{ijkl} = \alpha_{ik} - \alpha_{il} - \alpha_{jk} + \alpha_{jl}, \qquad B_{ijkl} = \beta_{ik} - \beta_{il} - \beta_{jk} + \beta_{jl} \tag{96}$$

In this way one can write

$$\begin{aligned}
\Delta E_1 = {} & (c_{ij} - 1)\langle i|F_k - F_i|k\rangle + 8s_{ij}\{A_{ijik}(ij|ik) \\
& - \tfrac{1}{2}B_{ijik}[(ii|jk) + (ij|ik)]\} \\
& + 2c_{ij}s_{ij}^2\{A_{ijik}[2(ik|ii) - 2(ik|jj) - (ij|jk)] \\
& - B_{ijik}[2(ik|ii) - 2(ij|ik) - \tfrac{1}{2}((ik|jj) + (ij|jk))]\} \\
& - s_{ij}^3\{A_{ijik}[(ij|jk) - (jj|jk) + 8(ij|ik)] \\
& - B_{ijik}[5(ij|ik) - (jj|jk) + 4(ii|jk)]\}
\end{aligned} \tag{97}$$

for the increment of the first-order coefficient, now:

$$\begin{aligned}
\Delta E_2 = {} & 2s_{ij}c_{ij}\{A_{ijik}[(ii|ij) + (ij|kk)] - B_{ijik}[(ii|ij) + (ik|jk)] \\
& - A_{ik}(ik|jk) - B_{ik}[(ij|kk) + (ik|jk)]\} \\
& + s_{ij}^2\{A_{ijik}[(ii|ii) - (ii|jj) + (ii|kk) - (jj|kk) - 2(ij|ij)] \\
& -B_{ijik}[(ii|ii) - (ij|ij) + (ik|ik) \\
& -(jk|jk) - 2(ij|kk) - 2(ik|jk)] \\
& + A_{ij}[(jk|jk) - (ik|ik)] \\
& + B_{ij}[(jj|kk) - (ii|kk) + (jk|jk) - (ik|ik)]\} \\
& + 2s_{ij}^3c_{ij}(A_{ijik} - B_{ijik})[(ij|jj) - (ii|ij)] \\
& + s_{ij}^4\{(A_{ijik} - B_{ijik})[(jj|jj) - (ii|ii) + (ij|ij)] \\
& + A_{ikij}(ij|ij) - B_{ikij}(ii|jj)\}
\end{aligned} \tag{98}$$

where once again definitions (29) were used for $\{A_{ik}, B_{ik}\}$. One notes the presence of terms up to third order in ΔE_1 and up to fourth order in ΔE_2. The other coefficient increments bear a somewhat less complex structure:

$$\begin{aligned}
\Delta E_3 = {} & 4(A_{ik} - B_{ik})\{(c_{ij} - 1)[(ii|ik) - (ik|kk)] \\
& - s_{ij}[(ii|jk) + 2(ij|ik) - (jk|kk)] \\
& + s_{ij}^2c_{ij}[(ik|jj) + 2(ij|jk) - (ii|ik)] \\
& - s_{ij}^3[(jj|jk) - (ii|jk) - 2(ij|ik)]\}
\end{aligned} \tag{99}$$

$$\begin{aligned}\Delta E_4 = (A_{ik} - B_{ik})\{&-4s_{ij}c_{ij}[(ii|ij) + (ij|kk) + 2(ik|jk)]\\ &+ 2s_{ij}^2[(ii|jj) + (jj|kk) - (ii|kk) - (ii|ii)\\ &+ 2((ij|ij) + (jk|jk) - (ik|ik))]\\ &+ 4s_{ij}^3c_{ij}[(ii|ij) - (ij|jj)]\\ &+ s_{ij}^4[(jj|jj) + (ii|ii) - 2(ii|jj) - 4(ij|ij)]\}\end{aligned} \tag{100}$$

In this case it is also possible to write the energy increment as:

$$\Delta\mathscr{E}[i, j, k] = \mathscr{E}_1[i, j] + \mathscr{E}_4[i, j, k] \tag{101}$$

where $\mathscr{E}_1[i, j]$ has the same form as Eq. (30) and can be written as:

$$\mathscr{E}_1[i, j] = s_{ij}c_{ij}E_1[i, j] + s_{ij}^2E_2[i, j] + s_{ij}^3c_{ij}E_3[i, j] + s_{ij}^4E_4[i, j] \tag{102}$$

In addition, $\mathscr{E}_4(i, j, k)$ is a fourth-order coupling term in $\{s_{ij}, s_{ik}\}$. It can be expressed as:

$$\begin{aligned}\mathscr{E}_4[i, j, k] = s_{ik}c_{ik}&(E_1[i, k] + \Delta E_1[i, j, k])\\ &+ s_{ik}^2(E_2[i, k] + \Delta E_2[i, j, k])\\ &+ s_{ik}^3c_{ik}(E_3[i, k] + \Delta E_3[i, j, k])\\ &+ s_{ik}^4(E_4[i, k] + \Delta E_4[i, j, k])\end{aligned} \tag{103}$$

where the coefficients $\{\Delta E_p\}$ $(p = 1, 4)$ are defined in Eqs. (97)–(100). Thus, $\mathscr{E}_4$ adopts in this case a form like Eq. (30) with coefficients $E_p \rightarrow E_p + \Delta E_p$; then Algorithm A1 may be used to obtain s_{ij} over the polynomial with modified coefficients.

The variation of $\{i, k\}$ followed by $\{i, j\}$,

$$\Delta\mathscr{E}[i, k, j] = \mathscr{E}_1[i, k] + \mathscr{E}_4[i, k, j] \tag{104}$$

can be used to obtain s_{ik} in the same way.

2. *Case $\{i, j\}$, Followed by $\{k, l\}$*

Suppose now that we want to look at the energy variation upon the simultaneous application of two rotations affecting two distinct active orbital pairs, $\{i, j\}$ and $\{k, l\}$. The form of the energy variation can be written then as:

$$\Delta\mathscr{E}[i, j] = \mathscr{E}_1[i, j] + \mathscr{E}_1[k, l] + \mathscr{E}_2[i, j, k, l] \tag{105}$$

where the terms of type $\mathscr{E}_1[i, j]$ have the same form as Eq. (30), and the same holds for $\mathscr{E}_1[k, l]$. The term $\mathscr{E}_2[i, j, k, l]$ contains the coupling between both rotations. After the cumbersome, albeit simple, algebra of all of the previous formulas, it can be shown that the coupling between both rotations can be expressed by the following equation:

$$\begin{aligned}\mathscr{E}_2[i,j,k,l] = {} & 2s_{ij}^2 s_{kl}^2 \{A_{ijkl}(J_{ik} + J_{jl} - J_{il} - J_{jk}) \\ & - B_{ijkl}(K_{ik} + K_{jl} - K_{il} - K_{jk})\} \\ & + 4s_{ij}^2 s_{kl} c_{kl} \{A_{ijkl}[(ii|kl) - (jj|kl)] \\ & - B_{ijkl}[(ik|il) - (jk|jl)]\} \\ & + 4s_{ij} c_{ij} s_{kl}^2 \{A_{ijkl}[(ij|kk) - (ij|ll)] \\ & - B_{ijkl}[(ik|jk) - (il|jl)]\} \\ & + 2s_{ij} c_{ij} s_{kl} c_{kl} \{4A_{ijkl}(ij|kl) \\ & - 2B_{ijkl}[(ik|jl) + (il|jk)]\}\end{aligned} \tag{106}$$

Now there is no variation in the third- and fourth-order coefficients when the active pairs are different. In Eq. (106) we have used the previous definitions (96). As in the former case this result can be stated by writing the following for the ΔE_1 and ΔE_2 increments:

$$\begin{aligned}\Delta E_1 = {} & 4s_{ij}^2 \{A_{ijkl}[(ii|kl) - (jj|kl)] \\ & - B_{ijkl}[(ik|il) - (jk|jl)]\} \\ & + 8s_{ij} c_{ij} \{A_{ijkl}(ij|kl) - \tfrac{1}{2}B_{ijkl}[(ik|jl) + (il|jk)]\}\end{aligned} \tag{107}$$

$$\begin{aligned}\Delta E_2 = {} & 2s_{ij}^2 \{A_{ijkl}[J_{ik} - J_{il} - J_{jk} + J_{jl}] \\ & - B_{ijkl}[K_{ik} - K_{il} - K_{jk} + K_{jl}]\} \\ & + 4s_{ij} c_{ij} \{A_{ijkl}[(ij|kk) - (ij|ll)] \\ & - B_{ijkl}[(ik|jk) - (il|jl)]\}\end{aligned} \tag{108}$$

being $\Delta E_3 = \Delta E_4 = 0$.

Once all the integrals are known, note that the introduction of couplings gives a role to other integrals not needed to compute the terms of $\mathscr{E}_1[i,j]$ type, and one can easily obtain the $\mathscr{E}_2[i,j,k,l]$ terms and add them to both uncoupled variations. In this case, the computation of optimal sines may follow a procedure similar to Algorithm A1. This is so because one can rewrite $\mathscr{E}_2$ as:

$$\begin{aligned}\mathscr{E}_2[i,j,k,l] = {} & 2s_{ij}^2 s_{kl}^2 E_{22} + 4s_{ij}^2 s_{kl} c_{kl} E_{21} \\ & + 4s_{ij} c_{ij} s_{kl}^2 E_{12} + 2s_{ij} c_{ij} s_{kl} c_{kl} E_{11}\end{aligned} \tag{109}$$

with obvious definitions for the coefficients $\{E_{pq}\}$ $(p, q = 1, 2)$, and then, for example,

$$\partial\mathscr{E}_2/\partial s_{ij} = 2s_{ij}Z_2[i, j, k, l] + (c_{ij} - s_{ij}t_{ij})Z_1[i, j, k, l] \tag{110}$$

with

$$Z_1 = 2s_{kl}^2E_{22} + 4s_{kl}c_{kl}E_{21}$$

$$Z_2 = 4s_{kl}^2E_{12} + 2s_{kl}c_{kl}E_{11}$$

Thus, the optimal sine s_{ij} can be obtained (although depending on s_{kl}), with Algorithm A1 applied to Eq. (30), and with coefficients $\{Z_1, Z_2\}$ instead of $\{E_1, E_2\}$.

The same structure may be applied to the optimal sine s_{kl}; so one can propose the following:

Algorithm A5. Optimal Coupled Sines

(1) $s_{ij}^0, s_{kl}^0 = 0$
(2) Use of Algorithm A1 on polynomials $\mathscr{E}_1[i, j]$ and $\mathscr{E}_1[k, l]$ to obtain values of sines $\{s_{ij}, s_{kl}\}$
(3) Compare $\{s_{ij}^0 : s_{ij}\}$ and $\{s_{kl}^0 : s_{kl}\}$.
if equal, stop. If not, update the $\{s_{ij}^0, s_{kl}^0\}$ values and go to step 2.
(4) Use s_{kl} to obtain Z_1, Z_2, and a modified polynomial $\mathscr{E}_1[i, j]$. Use s_{ij} to do the same in $\mathscr{E}_1[k, l]$.

V. Results. Comparison with Classical SCF

We have performed various calculations using the ideas of Section IV. We have chosen simple systems because trial calculations are inexpensive and results are not obscured by a great number of AO and electrons. The atoms with occupied s orbitals only (He, Li, Be) and some ions (Li^+, Li^-, Be^+, and B^+) are well-known systems with a sufficient number of optimized basis sets (i.e., Clementi and Roetti, 1974) to be ideal for this purpose.

Table I shows the various calculations performed with versions of the already-described algorithms, but using a SCF structure when computing the needed MO integrals. That is, Fock operators are employed and the integrals needed computed with the transformed vectors at each rotation step in the SR and DR cases, and at the end of each sweep in the AR and SOAR cases. When comparing with SCF classical results, one can immediately see that except in few cases where the difference is unfavorable or equal, the number of iterative steps is much shorter in the rotation domain than in SCF. This is remarkable in SR and much more spectacular in DR. Timing, however, is not comparable and it seems that any Jacobi rotation procedure will be slower if one follows this computational philosophy.

TABLE I

EXECUTION TIMES,[a] NUMBER OF ITERATIONS, AND RELEVANT INFORMATION FOR GROUND-STATE SINGLETS AND DOUBLETS USING VARIOUS APPROACHES: COMPUTATIONS WITHIN A SCF SCHEME[b]

Atom	Number of AOs	Spin multiplet	Number of shells	Energy (a.u.)	SCF		SR			DR			AR		SOAR	
					Time	I[c]	Time	I[c]	R/I[d]	Time	I[c]	R/I[d]	Time	I[c]	Time	I[c]
He	2	1	2	−2.8616726	3.6	5	3.2	2	1	—	—	—	3.6	2	3.8	5
He	5	1	2	−2.8616799	19.7	7	38.2	5	4	50.2	3	6	32.1	8	18.2	9
Li	4	2	3	−7.4327214	63.9	32	44.9	5	5	66.2	3	10	27.9	9	24.0	11
Li	6	2	3	−7.4327257	249.7	34	700.6	11	9	911.4	3	36	558.1	53	594.8	90
Be	4	1	2	−14.572369	34.0	17	50.3	7	4	53.1	4	6	29.5	11	26.9	14
Be	6	1	2	−14.573021	156.1	19	562.8	10	8	713.6	3	28	1076.8	104	196.0	30
Li^+	4	1	2	−7.236414	10.3	6	16.7	5	3	19.3	4	3	14.3	7	9.9	7
Be^+	4	2	3	−14.277391	54.3	27	37.1	4	5	69.4	3	10	23.7	7	19.9	9
B^+	5	1	2	−24.237566	75.0	17	205.8	9	6	200.0	3	15	97.7	18	66.9	18
Li^-	6	1	2	−7.428229	182.1	24	930.4	17	8	1193.5	5	28	305.9	28	198.8	30

[a] Times are in seconds of CPU utilization in a Univac System 80.

[b] Slater *n*s AOs from Clementi and Roetti (1974) have been used.

[c] I, iteration.

[d] R/I, rotation/iteration.

Note that all computations, in order to keep starting structures similar insofar as possible, have been performed using one-electron vectors initially. These differences are related to the intrinsic methodology and are not due to starting-point vectors.

One can conclude that although these are highly convergent procedures, methodology should not rely on SCF classical concepts if it is to become ameliorated from a computational point of view. However, as we have pointed out, the SOAR calculations are most like the SCF when analyzing second-order approximations.

In Table II we show the time gain when one uses molecular integrals, transformed according to the ideas of Section III,C and without using Fock operators, although this last detail does not contribute much to the time gain if one constructs the scalar products of the operators with MOs through known molecular integrals. The important thing is that not only a better convergence rate is obtained, but when using the suitable framework, the CPU time gain is very impressive.

Depending on the number of AO and iteration number, the time expended in SR or DR is considerably lower than in classical SCF calculations. This can be interpreted so as to encourage competitiveness between rotation methodology and SCF. In any case, one can say that DR are slightly slower than SR and that owing to the extra number of rotations performed, accuracy is usually better in DR if we measure accuracy by the closeness of E_1 and $\Delta\mathscr{E}$ to zero.

In order to have more information on other cases, we studied some excited states using the same systems and basis sets. That is to say, for singlets we used triplets, and for ground-state doublets we used quadruplets. The results of these computations are shown in Table III. We used the optimized algorithms for SR and DR, but for accumulated rotations due to the SCF resemblance, we used classical computational forms. Again, in all the frameworks, one can reiterate what was said about ground-state calculations. Only a slightly better performance by AR methods over SCF must be noted in some cases. The meaning of this last finding has to do with the nature of each sweep, which may not be fully comparable to a classical SCF iteration.

Inspection of timing and convergence rates in Tables I–III gives the procedure of SR, as described in Algorithm A2, as the fastest Jacobi routine described here. That is not to suggest abandonment of the remaining three methods. Implementation on minicomputers of 16-bit words may counsel SOAR methodology because only very few MO integrals are needed; or perhaps a very refined result is desired and DR algorithms would be suitable. More experience will be needed before an optimal computational strategy can be adopted.

TABLE II

Execution times,[a] Number of Iterations, and Relevant Information for Ground-State Singlets and Doublets Using Various Approaches: Computations within a MO Integral Scheme[b]

Atom	AO number	Spin multiplet	Number of shells	SCF		SR		DR	
				Time	Iterations	Time	Iterations	Time	Iterations
He	2	1	2	3.6	5	3.2	2	—	—
He	5	1	2	19.7	7	13.8	5	17.2	3
Li	4	2	3	63.3	32	10.8	5	16.7	3
Li	6	2	3	249.7	34	56.3	11	64.1	4
Be	4	1	2	34.0	17	12.5	7	23.8	3
Be	6	1	2	156.1	19	47.4	10	67.9	3
Li^+	4	1	2	10.3	6	8.3	5	9.5	4
Be^+	4	2	3	54.3	27	10.2	4	15.7	3
B^+	5	1	2	75.0	17	26.1	9	30.4	3
Li^-	6	1	2	182.1	24	69.4	17	99.5	5

[a] Times are in seconds of CPU utilization in a Univac System 80.

[b] Slater *n*s AOs from Clementi and Roetti (1974).

TABLE III

EXECUTION TIMES,[a] NUMBER OF ITERATIONS, AND RELEVANT INFORMATION FOR TRIPLETS AND QUADRUPLETS USING VARIOUS APPROACHES: COMPUTATIONS WITHIN A MO INTEGRAL SCHEME[b]

Atom	Spin multiplet	Number of AOs	Number of shells	Energy	SCF		SR		DR		AR		SOAR	
					Time	I[c]	Time	I[c]	Time	I[c]	Time	I[c]	Time	I[c]
He	3	5	2	−1.8003607	70.3	17	12.9	3	21.1	2	28.0	6	28.3	4
Li	4	4	2	−4.7887354	86.7	25	8.3	4	8.7	3	23.6	5	21.4	4
Li	4	6	2	−5.2020001	580.6	41	46.4	12	74.6	3	453.5	33	588.2	34
Be	3	4	3	−14.344774	118.9	36	8.9	4	15.0	3	26.4	6	25.0	5
Be	3	6	3	−14.355024	729.8	51	51.6	11	105.9	3	342.7	25	453.0	25
Li^+	3	4	2	−5.0082900	31.1	16	7.7	3	9.0	2	15.6	6	14.4	4
Be^+	4	4	2	−8.7298308	81.7	24	7.8	4	8.8	3	20.5	5	21.9	4
B^+	3	5	3	−23.558625	316.7	41	16.0	4	42.7	3	63.9	8	69.5	7
Li^-	3	6	3	−7.4146353	911.8	64	78.2	19	157.9	5	631.5	47	612.3	35

[a] Times are in seconds of CPU utilization in a Univac System 80.

[b] Slater *n*s AOs from Clementi and Roetti (1974).

[c] I, iteration.

VI. Analysis of the Energy Surface: Catastrophe Theory

The structure of Eq. (30) furnishes more than a possible alternative SCF iterative algorithm: the simple form it has permits us to think in terms of the general behavior of the energy variation surface when elementary rotations, as given by Eq. (14) are performed on active MO pairs. Catastrophe theory may be applied for this purpose.

A. Catastrophe Theory

Elementary catastrophe theory was introduced by Thom (1969, 1972, 1975) in an attempt to provide a new kind of approach to the study of complex phenomena such as those found in biological systems. Thom's philosophical schemes were adopted for use in other areas (see, for example, the work of Wasserman, 1974, 1975; Godwin, 1971; Guckenheimer, 1971; Bröcker, 1975; Jänich, 1974; Berry, 1975; Berry and Nye, 1977; Thompson and Hunt, 1975; Woodcock, 1978; Woodcock and Poston, 1974; Zeeman, 1973). In the field of quantum chemistry some work connecting catastrophe theory with density functions has been already done by Collard and Hall (1977), Bader *et al.* (1979a,b), and Tal *et al.* (1981).

Catastrophe theory provides a qualitative description of the behavior of the system when its constraints or control parameters change. This theory is particularly applicable to scientific situations characterized by everywhere differentiable potential energy-like functions. It predicts the existence of *catastrophe manifolds,* which are hypersurfaces generated by the stationary values of these energy-like functions. A catastrophe manifold structure is determined by *control factors* values and represents stationary energy states available to the described system.

Changing control factors produce two different types of system behavior:

(1) A *smooth evolutionary movement* over the manifold of a point representing the nature of the system.

(2) A *sudden jump* of the point from one layer of the manifold to another.

The point (2) represents a catastrophic annihilation of a starting energy state as it becomes unstable through changes in the constraints of the system (a catastrophe can be associated to a singularity on a map). The general description of the theory can be obtained considering a set of potential functions $V(\mathbf{c}, \mathbf{x})$ parametrized by a set of elements $\mathbf{c}$ belonging to the *control space* $\mathscr{C}$ on a manifold $\mathbf{x}$ belonging to the *behavior space* $\mathscr{X}$. Furthermore, one considers the functions V to be derivable in all orders.

The catastrophe manifold is defined by means of the set of all vectors $(\mathbf{c}, \mathbf{x}) \in \mathscr{C} \times \mathscr{X}$ which fulfill

$$\partial V/\partial \mathbf{x} = 0$$

and which can be associated with the condition

$$\partial^2 V/\partial \mathbf{x}^2 = 0,$$

eliminating $\mathbf{x}$ to generate the *bifurcation set* of the catastrophe manifold. Thus, values of the control factors are represented where two stationary states of the potential energy function, one maximum the other minimum, merge and disappear. Thom (1969) in his original study, described those catastrophes in which the dimension of the control space was less than 4, that is, $\dim(\mathscr{C}) \leq 4$. Within this restriction, and requiring the existence of an associated, everywhere differentiable potential energy function, only seven catastrophes are present: *the elementary catastrophes*. A further classification is obtained when considering the dimension of the behavior space:

(1) When $\dim(\mathscr{X}) = 1$, one obtains the *cuspoid catastrophes*
(2) $\dim(\mathscr{X}) = 2$ gives rise to the *umbilic catastrophes*.

In both cases a suitable polynomial function can be attached to each elementary catastrophe. The structure of these functions is shown in Table IV and consists of two parts:

TABLE IV

THE SEVEN ELEMENTARY CATASTROPHES

Class and name	Unfolding	Catastrophe manifold
Cuspoid:		
Fold	$x^3/3 + ax + b$	$x^2 + a = 0$
Simple cusp	$x^4/4 + ax^2/2 + bx + c$	$x^3 + ax + b = 0$
Swallowtail	$x^5/5 + ax^3/3 + bx^2/2 + cx + d$	$x^4 + ax^2 + bx + c = 0$
Butterfly	$x^6/6 + ax^4/4 + bx^3/3 + cx^2/2 + dx + e$	$x^5 + ax^3 + bx^2 + cx + d = 0$
Umbilic:		
Hyperbolic	$x^3 + y^3 + wxy + ux + vy$	$3x^2 + wy + u = 0$ $3y^2 + wx + v = 0$
Elliptic	$x^3 - 3xy^2 + w(x^2 + y^2) + ux + vy$	$3x^2 - 3y^2 + 2wx + u = 0$ $2y(w - 3x) + v = 0$
Parabolic	$x^2y + y^4 + ty^2 + wx^2 + ux + vy$	$2x(y + w) + u = 0$ $x^2 + 4y^3 + 2xy + v = 0$

(1) *The germ of the singularity,* which is associated with the terms without control parameters.
(2) *The unfolding terms,* where both control factors and behavior variables are mixed.

The complete equation for the function V is referred to as the *unfolding of the catastrophe.*

B. Elementary Catastrophes and Energy-Variation Surfaces

The final form of the energy variation after performing a single rotation involving the active pair $\{i, j\}$, as shown in Eq. (30), has the required structure for study using the catastrophe theory. The electronic energy variation upon a Jacobi-like transformation can be expressed as a quartic polynomial in s, with the first- and third-order terms multiplied by a cosine function c. This last feature complicates the analysis slightly and needs further study before catastrophe theory can be used. When searching for the structure of the energy variation surfaces, both analytical and graphical points of view were considered. We describe them as follows.

1. *Analytical Approach*

In order to use catastrophe theory in a numerical framework, one must attach to the energy variation polynomial an elementary catastrophe of cuspoid type. The best way is to transform the polynomial in s and c into a unique function of the sine; that is, considering that one can write

$$c = (1 - s^2)^{1/2} \tag{111}$$

and using the Taylor expansion

$$c = 1 - (\tfrac{1}{2}s^2 + \tfrac{1}{8}s^4 + \tfrac{1}{16}s^6 + \cdots) \tag{112}$$

one can obtain the so called K jets of $\Delta\mathscr{E}$, $\Delta\mathscr{E}^{(k)}$, truncating the Taylor expansion up to the Kth order. Here we have studied the jets up to sixth order, because of the structure of the elementary catastrophes of cuspoid type. The form of the four K jets obtained in this way is

Order	K jet
$K = 0$	$\Delta\mathscr{E}^{(0)} = s^4E_4 + s^3E_3 + s^2E_2 + sE_1$
$K = 2$	$\Delta\mathscr{E}^{(2)} = s^5Z_5 + s^4E_4 + s^3Z_3 + s^2E_2 + sE_1$
$K = 4$	$\Delta\mathscr{E}^{(4)} = s^7Z_7 + s^5A_5 + s^4E_4$ $+ s^3Z_3 + s^2E_2 + sE_1$
$K = 6$	$\Delta\mathscr{E}^{(6)} = s^9Z_9 + s^7A_7 + s^5A_5 + s^4E_4$ $+ s^3Z_3 + s^2E_2 + sE_1$

(113)

where we have used the following definitions:

$$\begin{aligned} &Z_3 = E_3 - E_1/2, \quad Z_5 = -E_3/2, \quad && A_5 = -(E_3 + E_1/4)/2 \\ &Z_7 = -E_3/8, \quad A_7 = -(E_3 + E_1/2)/8, \quad && Z_9 = -E_3/16 \end{aligned} \tag{114}$$

On Eqs. (113) one can perform the following changes of variable in order to obtain the final catastrophe structure:

$$k = 0, \quad \theta = s + E_3/(4E_4), \qquad k = 2, \quad \theta = s + E_4/(5Z_5) \tag{115}$$

Then one obtains for:

$$\begin{aligned} &k = 0, \qquad \Delta\mathscr{E}^{(0)} = \theta^4 E_4 + \theta^2 E_2 + \theta E_1 \\ &k = 2 \qquad \Delta\mathscr{E}^{(2)} = \theta^5 Z_5 + \theta^3 Z_3 + \theta^2 E_2 + \theta E_1 \end{aligned} \tag{116}$$

The four equations obtained in this way can be compared with those of Table IV, and one can see that

(1) $\Delta\mathscr{E}^{(0)}$ has the same structure as a simple cusp
(2) $\Delta\mathscr{E}^{(2)}$ has a swallowtail structure
(3) $\Delta\mathscr{E}^{(4)}$ may be considered the product of a fold and a simple cusp
(4) $\Delta\mathscr{E}^{(6)}$ is the product of a butterfly and a fold after eliminating the sixth-order term and performing the following change of variable:

$$\sigma = s + E_5/(7E_7)$$

The relationship between Eq. (30) and catastrophe theory functional forms having been established, it is important to find out which one of the elementary catastrophes of Table IV best fits the energy variation. In the next section we will try to evaluate the error committed when considering the Taylor expansion of Eq. (30) up to sixth order.

2. *Error Analysis*

It is interesting to establish where the Taylor series (112) can be truncated in order to yield an adequate approximation of the energy variation by means of the described K jets (113).

In order to measure the error one can define a quadratic error integral $e_K^{(2)}$ between the exact polynomial $\Delta\mathscr{E}$ in any K-jet approach $\Delta\mathscr{E}^{(k)}$, in the range of interest for a sine function $s \in [-1, +1]$. That is,

$$e_k^{(2)} = \int_{-1}^{+1} |\Delta\mathscr{E} - \Delta\mathscr{E}^{(K)}|^2 \, ds \tag{117}$$

After more tiresome algebra, one can find out the general form for the error:

$$e_k^{(2)} = a_k E_3^2 + b_k E_1^2 + c_k E_3 E_1 \tag{118}$$

TABLE V

COEFFICIENTS OF THE QUADRATIC ERROR FUNCTION AS SHOWN IN EQ. (118)

K jet	a_k	b_k	c_k
0	0.10377	0.14794	0.24317
2	0.012905	0.015713	0.028293
4	0.0048710	0.0055830	0.010395
6	0.0025507	0.0028314	0.0053641

where $\{a_k, b_k, c_k\}$ are constants, depending on the K jets used, and $\{E_1, E_3\}$ are the energy-variation coefficients of Eq. (30). The quadratic error function behaves like a generalized quadratic without linear terms, which must be definite positive. Table V gives the parameters computed for each K-jet level studied. As the quadratic error in the energy variation is a second-order polynomial in the energy-variation coefficients $\{E_1, E_3\}$, the expected error behavior will be seen to increase as both parameters are further from zero.

As discussed, E_1, explicitly contains the Brillouin condition; error will therefore increase as this condition does not hold. In many cases E_3 has been found to be null; looking at Eq. (32), this happens when one or both of the following conditions hold: (a) $A_{ij} = B_{ij}$, (b) $(ii|ij) = (ij|jj)$.

Condition (a) seems more readily fulfilled than condition (b), and, by the way, also causes the nullity of E_4. Usually in the computations we have found $E_3 = E_4 = 0$ simultaneously, so one can safely say that the main cause of the vanishing E_3 coefficient is condition (a).

Both $\{E_1, E_3\}$ coefficients have been traced, rotation after rotation, in all the performed computations. From this data collection we can say that the values of those parameters always may be supposed to fulfill $\{|E_1|, |E_3|\} \leq 1$. Inspecting Table V, one can see how from the 0-jet to the 2-jet approximation the quadratic error varies in an order of magnitude, just as it does when one goes from the 2 jet to the 4 jet, but this become stable, except for the variation of the constant, when one goes a step further into the 6 jet.

The swallowtail structure of the 2-jet approach and the sufficient smallness of the error coefficients in this case may indicate that this approach is adequate for qualitative analysis of the behavior of the energy-variation surface. The adequacy of this surface becomes greater as MOs are optimized. In order to obtain a visual confirmation of this hypothesis, we tried to compute the surface for some special values of the coefficients.

TABLE VI

VALUES OF THE COEFFICIENTS CHOSEN TO REPRESENT ENERGY-VARIATION SURFACES

Figure	Coefficient			
	E_1	E_2	E_3	E_4
1	*	-2	-5	1
2	1	-2	*	1
3	1	*	-5	1

3. *Graphical Approach*

Given a certain set of coefficients $\{E_k\}$ $(k = 1, 4)$, one can represent the energy variation polynomial $\Delta\mathscr{E}$ as expressed in Eq. (30) as a function of the sine s.

We studied the two-dimensional surface arising from a calculation of $\Delta\mathscr{E}$-varying s and one of the four coefficients $\{E_k\}$. We used the ranges $(-1, +1)$ for s and $(-5, +5)$ for the coefficients involved. We present here three different examples which, after a scanning of all the points in the above-mentioned ranges, had shown conspicuous behavior. Table VI shows the coefficients made constant in each example, the starred sites indicating which coefficient varies between the mentioned range. The plotted examples correspond to Figs. 1–3. For each figure, three different orientations have been chosen in order to present a better view of the surface features.

Looking at the whole set of figures, Fig. 1a and particularly Fig. 3b might be adopted as typical illustrations of a partial model of swallowtail-catastrophe behavior.

The complex structure of the energy-variation surfaces with many kinds of extrema gives an approximate idea of the problems that one encounters in the implementation of energy-optimization procedures.

In Section V we have seen how slicing the SCF iterations into small, controllable modules ameliorates by around 50% the SCF convergence pattern. A whole step procedure, such as the usual implementation of the Hartree–Fock method, cannot discern unoptimized direction movements in the energy-variation space. The choice of Jacobi-like unitary transformations as energy-increment reducing devices would be preferable.

Following this, a less general discussion is possible based on the themes already studied in the previous sections. Accordingly, we present next the details of an analytical study on the energy-variation surfaces when some logical simplifications are made.

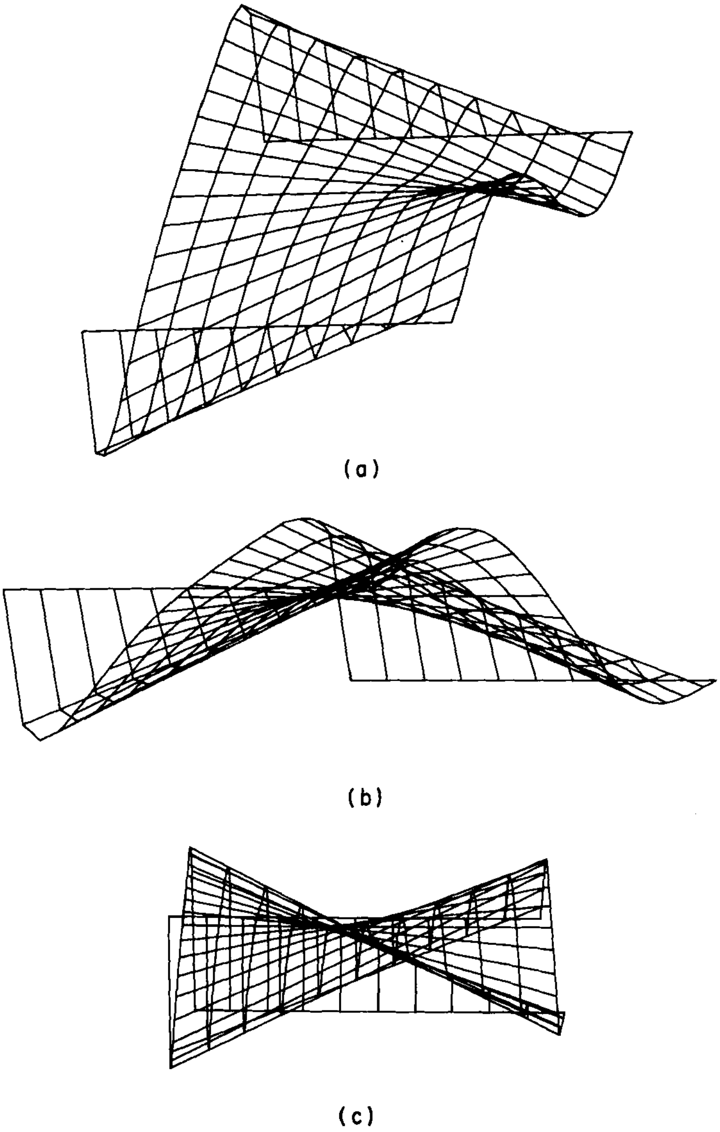
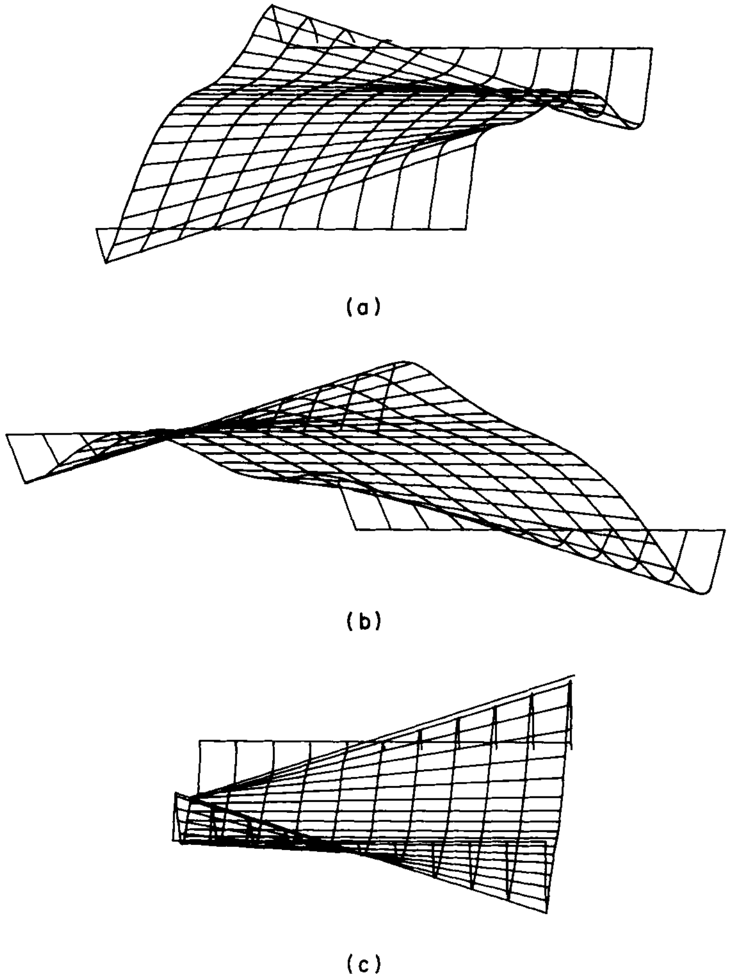


Fig. 1. Energy-variation surface for E_1 = free, $E_2 = -2$, $E_3 = -5$, and $E_4 = 1$ under three different surface orientations.



(a)

(b)

(c)

Fig. 2. Energy-variation surface for $E_1 = 1$, $E_2 = -2$, $E_3 =$ free, and $E_4 = 1$ under three different surface orientations.

C. Discussion of the Energy-Variation Behavior: A Second-Order Approach

To better understand the behavior of the four-term energy variation polynomial (30) and in order to look at the location of its minima, we may take each part and study its corresponding forms when plotted against the sinus values. The adequate combination of these elementary patterns will

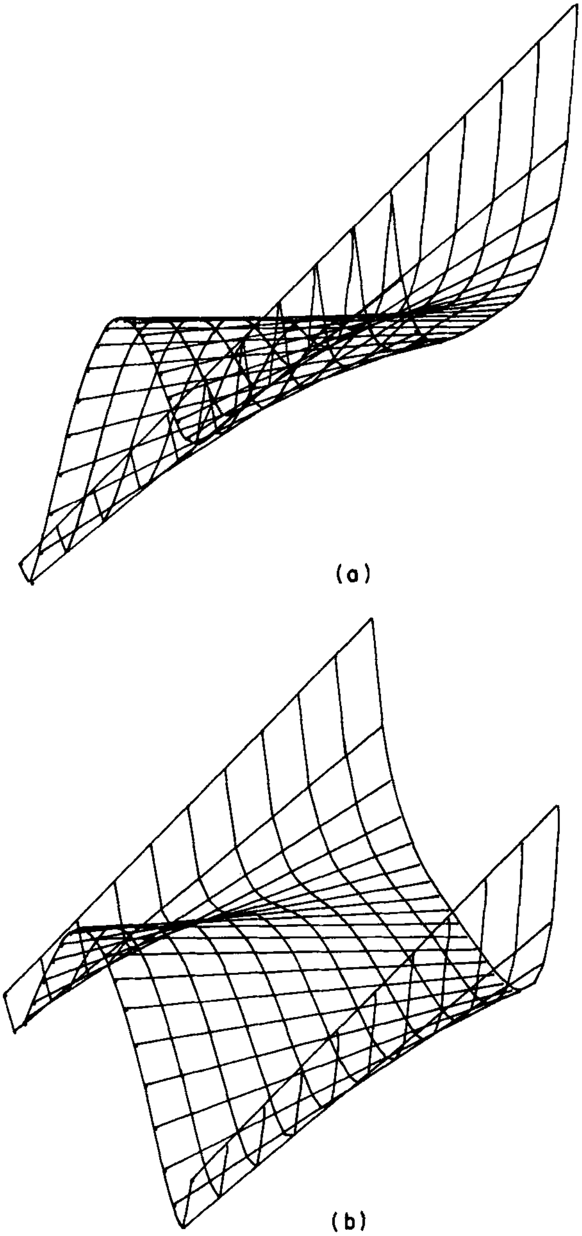


Fig. 3. Energy-variation surface for $E_1 = 1$, E_2 = free, $E_3 = -5$, and $E_4 = 1$ under three different orientations.

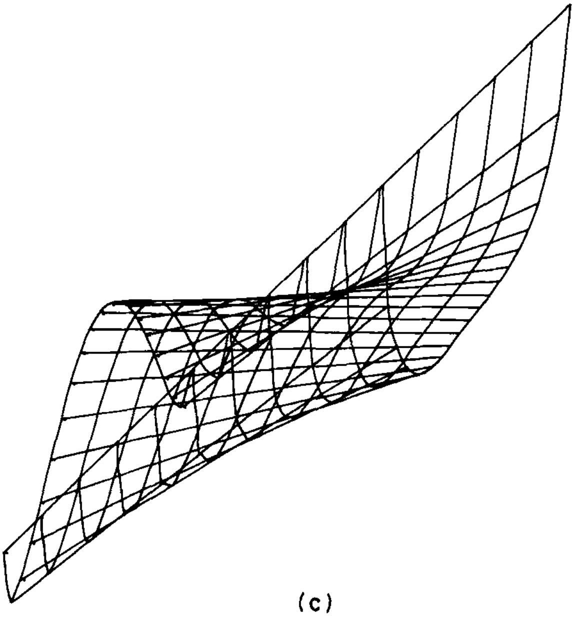


Fig. 3. (*Continued*)

give us the form of the global variation. Yet it is necessary to remark that the forms of the s^3c and s^4 terms, which in practice will have a very small contribution to the energy variation (see Fig. 4d), will not add any new insight to the principal forms sc and s^2. Also, it is interesting to consider the combination of these terms in the neighborhood of zero, where one would expect to find the optimal rotations, and to consider the higher order terms perfectly negligible. Thus, the energy-variation function patterns will be studied within a second-order simplified expression, in which only two terms will remain:

$$\Delta\mathscr{E} = E_1sc + E_2s^2 \tag{119}$$

An interesting parametrization, which will allow us to work with one-dimensional control spaces, is obtained making $a = E_1/E_2$, and writing the energy expression now as:

$$\Delta\mathscr{E} = E_2(asc + s^2) \tag{120}$$

Leaving aside the parameter E_2, which acts as a scaling factor, one can see that the variation of the energy depends only on the control parameter a.

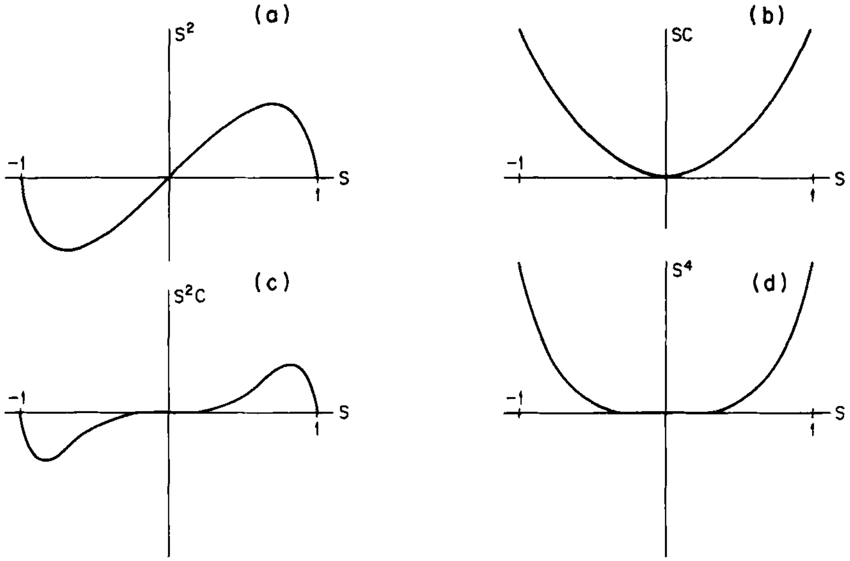


Fig. 4. Form adopted by the four terms present in the energy-variation formula (30): (a) s^2, (b) sc, (c) s^3c, (d) s^4.

This structure gives a form which possesses a minimum and a maximum (see Fig. 5). In order to obtain the minimum, which is the interesting feature here, the usual first and second derivatives can be computed. One finds

$$\partial E/\partial s = -cE_2(at^2 - 2t - a) \tag{121}$$

$$\partial^2 E/\partial s^2 = E_2[2 - at(3 + t^2)] \tag{122}$$

with $t = s/c$ and $dc/ds = -t$.

Taking the extremum condition in Eq. (121), the form of t can be expressed as:

$$t_0 = a^{-1}[1 \pm (1 + a^2)^{1/2}] \tag{123}$$

with the sign ambiguity corresponding to the existence of two possible extrema. Substituting Eq. (123) into the energy variation and second derivative, one has,

$$\Delta \mathscr{E}_0 = a^{-2}E_2[2(1 + a^2) \pm (2 + a^2)(1 + a^2)^{1/2}](1 + t_0)^{-1} \tag{124}$$

$$\left.\frac{\partial^2 \Delta \mathscr{E}}{\partial s^2}\right|_0 = -4a^{-2}E_2(1 + a^2)[1 \pm (1 + a^2)^{1/2}] \tag{125}$$

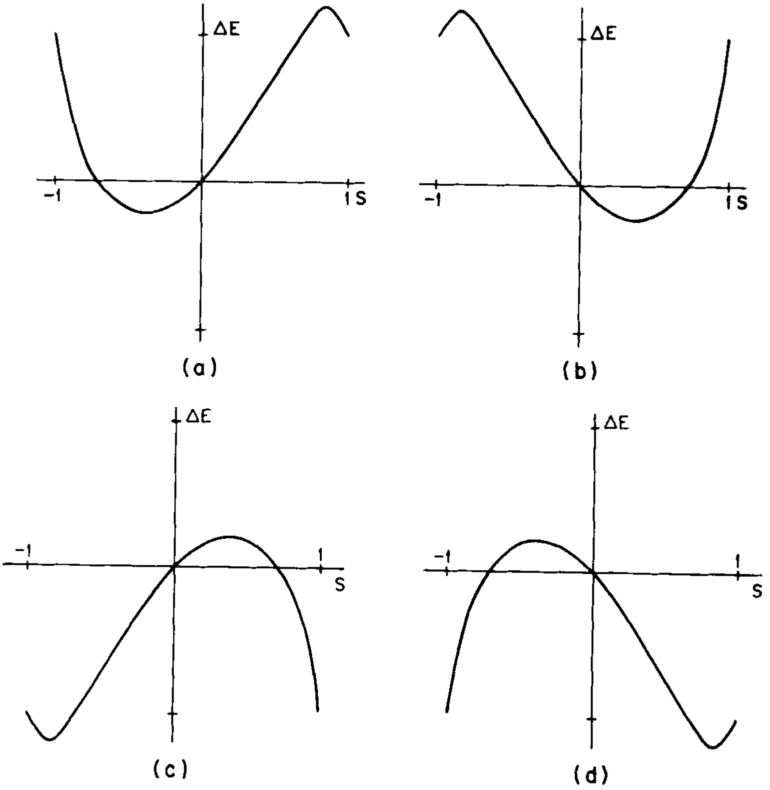


Fig. 5. Form adopted by the energy curve under several conditions: (a) $E_1 > 0$, $E_2 > 0$, $a = 1$; (b) $E_1 < 0$, $E_2 > 0$, $a = -1$; (c) $E_1 > 0$, $E_2 < 0$, $a = -1$; (d) $E_1 < 0$, $E_2 < 0$, $a = 1$.

because $2(1 + a^2) \leq (2 + a^2)(1 + a^2)^{1/2}$ and $(1 + a^2)^{1/2} \geq 1$.

It is evident that the signs of $\Delta\mathscr{E}$ and the second derivative depend only on the sign of E_2 and the one we take in front of the square root in Eq. (123). Thus, to always obtain $\Delta\mathscr{E}_0 < 0$ and $\partial^2\Delta\mathscr{E}/\partial s^2|_0 > 0$, we shall take the following:

$$\text{if} \quad E_2 > 0 \quad \rightarrow \quad t_0 = [1 - (1 + a^2)^{1/2}]a^{-1} = -a[1 + (1 + a^2)^{1/2}]^{-1} \tag{126}$$

$$\text{if} \quad E_2 < 0 \quad \rightarrow \quad t_0 = [1 + (1 + a^2)^{1/2}]a^{-1} \tag{127}$$

In Eq. (126) we use the well-known alternative form in order to increase the computation precision and avoid the difference between very similar quantities. In terms of the energy-variation coefficients, the optimal tangent expression can be written as:

$$E_2 > 0 \rightarrow t_0 = -E_1[E_2 + (E_1^2 + E_2^2)^{1/2}]^{-1} \tag{128}$$

$$E_2 < 0 \rightarrow t_0 = -[(E_1^2 + E_2^2)^{1/2} - E_2]E_1^{-1} \tag{129}$$

As can be seen, the parameter a measures the degree of mixing of the two active orbitals, this being the ratio of E_1, which represents the fulfillment of Brillouin's theorem, and E_2 which contains a difference between similar quantities measured on each orbital. There appears to be a reasonable equivalence to the perturbation theory in a first-order correction to the MO coefficients $a \simeq \{\langle i|F_j - F_i|j\rangle/[\langle i|F_j - F_i|i\rangle - \langle j|F_j - F_i|j\rangle]\}$.

In this manner the Brillouin term can be attached, according to the degree of orbital mixing, and one can understand why at convergence when MO are stable, this term becomes null.

The sign of E_1 influences only the sign of the rotation, but the sign of E_2 has a deeper significance. If negative it indicates the tendency to invert the ordering of MO in the spectrum; when positive, it indicates that the optimal rotation is located near zero in a smooth minimum. In comparison, when it is negative the sine falls near ±1 in a narrow minimum with $s > 2^{-1/2}$.

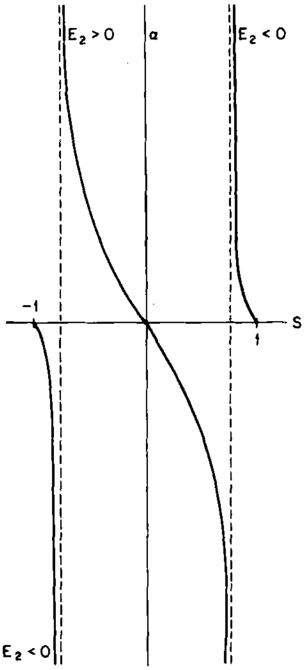


Fig. 6. Form adopted by the optimal tangent expressions (128) and (129).

The location of the minimum in front of the values of the control factor a clearly gives the frontier created by the E_2 sign, as well as the asymptotic behavior near values of $s = \pm 2^{-1/2}$. When a tends toward infinite, a situation occurs in which the highest degree of mixing takes place. The initial MO order is either maintained ($E_2 > 0$) or is inverted ($E_2 < 0$) (see Fig. 6).

It is also interesting to consider the behavior of optimal solutions near the point $a = 0$ where the system approaches convergence and orbital mixing is null. We have two cases:

(a) Where $E_2 > 0$, then $s_0 \simeq t_0 \simeq -a/2 = -E_1/(2E_2)$; thus $\Delta\mathscr{E}_0 \simeq -E_1^2/(4E_2)$ and $\partial^2\Delta\mathscr{E}/\partial s^2|_0 \simeq 2E_2(1 + 3a^2/4)$

(b) Where $E_2 < 0$, then $t_0 \simeq 2/a = -2E_2/E_1$ and $s_0 \simeq 1 - a^2/8$; thus $\Delta\mathscr{E}_0 \simeq E_2(1 + a^2/4)$ and $\partial^2\Delta\mathscr{E}/\partial s^2|_0 \simeq -8a^{-2}E_2$

These expressions give the limits of no interaction with (situation a) or without (situation b) full exchange of the orbitals. All these considerations have been proved equally valid in practice, especially in sign considerations for optimal solutions when Eq. (119) is used instead of Eq. (30), and the quadratic form is that of Eq. (120) instead of Eq. (119).

VII. Conclusions

The simple rules which can be deduced from the previous discussion enable us to obtain the mathematical form of the variation upon the rotation of an active pair $\{i, j\}$ of any quantum mechanical object in the framework of MO theory. As a consequence, a simple energy-variation expression might be obtained, leading to various computational mechanisms with a high degree of control possibilities and producing energy extrema with much less difficulty than the classical SCF procedures.

From our experience, the procedure which has been called here single rotation seems to be the most efficient of the computational techniques tested. If a high degree of precision is required, one might choose the double-rotation technique at the risk of needing (in fewer double sweeps) more CPU time than in SR techniques. The other possibilities tested are less interesting from a computational point of view, and in many cases the performances obtained are very similar to SCF procedures.

It must be stressed that Jacobi-like rotation techniques need not resemble the formalism of SCF. In fact, the best computational performances are obtained when Jacobi's rotations are implemented with his own computational philosophy.

In order to obtain the maximum yield from an algorithm of this kind, based on elementary transformations, one must avoid the tendency to mimic the basic structure of classical SCF calculations. For example, although used to shorten the expression of Eqs. (29) and (31), Fock operators are not necessary at all if one is working on a MO basis instead of the AO basis. In our experience, it is best to construct molecular integrals with approximate starting vectors at the beginning of the process (we use the one-electron Hamiltonian vectors in all computations, but other starting sequences will surely work as well). Then one should use the variation formulas above for each pair $\{i, j\}$, transforming only the variant integrals and leaving the remaining ones undisturbed. This is a very fast process if the appropriate set of variant integrals can be reached without time-consuming short steps.

Thus, for the first time in the literature, as far as we know, one is able to look at the surface structure of the energy variation during the optimization process. This is consequence of cutting the energy minimum search into a set of elementary steps, whereby one can know *a priori* if a given step will be worthwhile.

In the future, however, this will not be the unique advantage of these procedures. Given a structured computational hardware in which the elementary steps can be performed in parallel fashion and not sequentially, the search for optimal MO coefficients may be reduced to times which will be very like some classical extended Hückel performances. It is not difficult to predict for the near future a rising interest in the Jacobi rotation techniques.

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Index

CONTENTS OF PREVIOUS VOLUMES

Volume 1

The Schrödinger Two-Electron Atomic Problem
Egil A. Hylleraas

Energy Band Calculations by the Augmented Plane Wave Method
J. C. Slater

Spin-Free Quantum Chemistry
F. A. Matsen

On the Basis of the Main Methods of Calculating Molecular Electronic Wave Functions
R. Daudel

Theory of Solvent Effects on Molecular Electronic Spectra
Sadhan Basu

The Pi-Electron Approximation
Peter G. Lykos

Recent Developments in the Generalized Hückel Method
Y. I. Haya

Accuracy of Calculated Atomic and Molecular Properties
G. G. Hall

Recent Developments in Perturbation Theory
Joseph O. Hirschfelder, W. Byers Brown, and Saul T. Epstein

AUTHOR INDEX—SUBJECT INDEX

Volume 2

Quantum Calculations Which Are Accumulative in Accuracy, Unrestricted in Expansion Functions, and Economical in Computation
S. F. Boys and P. Rajagopal

Zero Differential Overlap in π-Electron Theories
Inga Fischer-Hjalmars

Theory of Atomic Hyperfine Structure
S. M. Blinder

The Theory of Pair-Correlated Wave Functions
R. McWeeny and E. Steiner

Quantum Chemistry and Crystal Physics, Stability of Crystals of Rare Gas Atoms and Alkali Halides in Terms of Three-Atom and Three-Ion Exchange Interactions
Laurens Jansen

Charge Fluctuation Interactions in Molecular Biophysics
Herbert Jehle

Quantum Genetics and the Aperiodic Solid. Some Aspects on the Biological Problems of Heredity, Mutations, Aging, and Tumors in View of the Quantum Theory of the DNA Molecule
Per-Olov Löwdin

AUTHOR INDEX—SUBJECT INDEX

Volume 3

Approximate Hartree–Fock Calculations on Small Molecules
R. K. Nesbet

Single-Center Molecular Wave Functions
David M. Bishop

Molecular Orbital Theory
Frank D. Harris

Nonadditivity of Intermolecular Forces
H. Margenau and J. Stapmer

Quantum Theory of Chemical Reactivity
R. Daudel

Electronic Theories of Hydrogen Bonding
S. Bratož

Molecular Orbital Calculations of π-Electron Systems
Kimio Ohno

Quantum Theory of Time-Dependent Phenomena Treated by the Evolution Operator Technique
Per-Olov Löwdin

AUTHOR INDEX—SUBJECT INDEX

Volume 4

Functional Analysis for Quantum Theorists
Bela A. Lengyel

The Symmetric Group Made Easy
A. J. Coleman

Field Theoretic Approach to Atomic Helium
Donald H. Kobe

Atomic Intensities: A Comparison of Theoretical and Experimental *f*-Values for Zn I, Cd I, and Hg I
T. M. Bieniewski, T. K. Krueger, and S. J. Czyak

Probability of Singlet–Triplet Transitions
Lionel Goodman and Bernard J. Laurenzi

Molecular Orbital Theories of Inorganic Complexes
J. P. Dahl and C. J. Balhausen

Paramagnetic Properties and Electronic Structure of Iron in Heme Proteins
Masao Kotani

Aspects of the Electronic Structure of the Purine and Pyrimidine Bases of the Nucleic Acids and of Their Interactions
Alberte Pullman and Bernard Pullman

AUTHOR INDEX—SUBJECT INDEX

Volume 5

Some Aspects of the Quantum Theory of Photochemical Reactivity of Organic Molecules
R. Daudel

The Origin of Binding and Antibinding in the Hydrogen Molecule-Ion
M. J. Feinberg, Klaus Ruedenberg, and Ernest L. Mehler

Adiabatic Approximation and Its Accuracy
Wodzimierz Kolos

The Theory of Nonadiabatic Transitions: Recent Development with Exponential Models
E. E. Nikitin

On the Nonorthogonality Problem
Per-Olov Löwdin

Symmetry Properties of Reduced Density Matrices and Natural *p*-States
W. A. Bingel and W. Kutzelnigg

Symmetry Adaptation to Sequences of Finite Groups
D. J. Klein, C. H. Carlisle, and F. A. Matsen

The Method of Optimized Valence Configurations: A Reasonable Application of the Multiconfiguration Self-Consistent-Field Technique to the Quantitative Description of Chemical Bonding
Arnold C. Wahl and G. Das

AUTHOR INDEX—SUBJECT INDEX

Volume 6

Statistical Exchange-Correlation in the Self-Consistent Field
John C. Slater

Aspects of the Localizability of Electrons in Atoms and Molecules: Loge Theory and Related Methods
Claude Aslangul, Raymond Constanciel, Raymond Daudel, and Philemon Kottis

Volume 7

Volume 8

Current Problems and Perspectives in the MO–LCAO Theory of Molecules
Giuseppi Del Re

Photoelectron Spectra Showing Relaxation Effects in the Continuum and Electrostatic and Chemical Influences of the Surrounding Atoms
Christian Klixbüll Jøorgensen

Some Recent Developments in the Theory of Coordination Compounds of Metals
G. Berthier

Effective Hamiltonian Methods for Molecular Collsions
David A. Micha

SUBJECT INDEX

Volume 9

Utilization of Transferability in Molecular Orbital Theory
Brian O'Leary, Brian J. Duke, and James E. Eilers

A Series of Electronic Spectral Calculations Using Nonempirical CI Techniques
Sigrid D. Peyerimhoff and Robert J. Buenker

Time-Independent Diagrammatic Approach to Perturbation Theory of Fermion Systems
J. Paldus and J. Cižěk

Coupled-Channel Studies of Rotational and Vibrational Energy Transfer by Collision
William A. Lester, Jr.

Theory of Low-Energy Electron Scattering by Complex Atoms
R. K. Nesbet

SUBJECT INDEX

Volume 10

Accurate X-Ray Diffraction and Quantum Chemistry: The Study of Charge Density Distributions
Philip Coppens and Edwin D. Stevens

Evaluation of Momentum Distributions and Compton Profiles for Atomic and Molecular Systems
Per Kaijser and Vedene H. Smith, Jr.

Analysis of Electron–Atom Collisions
Hans Kleinpoppen

Theoretical Interpretation of Hund's Rule
Jacob Katriel and Ruben Pauncz

Linked-Cluster Perturbation Theory for Closed- and Open-Shell Systems
B. H. Brandow

Quantum-Mechanical Approach to the Conformational Basis of Molecular Pharmacology
Bernard Pullman

SUBJECT INDEX

Volume 11

Experimental Measurements of Charge and Momentum Densities, Generalized Oscillator Strengths, and Excitation Frequencies
R. A. Bonham, J. S. Lee, R. Kennerly, and W. St. John

Convergence Limit in the Electronic Spectra of Linear Polyenes
Sadhan Basu

Localized Orbitals in Spectroscopy
Dennis Caldwell and Henry Eyring

Electronic Molecular Structure, Reactivity, and Intermolecular Forces: An Heuristic Interpretation by Means of Electrostatic Molecular Potentials
Eolo Scrocco and Jacopo Tomasi

Complex Eigenvalue Problems in Atoms and Molecules
Tokio Yamabe, Akitomo Tachibana, and Kenichi Fukui

The Unitary Group and the Many-Body Problem
F. A. Matsen

The Zero-Range Potential Model and Its Application in Atomic and Molecular Physics
G. Drukarev

Volume 12

Volume 13

Volume 14