Quantum Dynamics at Conical Intersections

Edited by

Stuart Althorpe
Graham Worth
Quantum Dynamics at Conical Intersections

Edited by

Stuart C. Althorpe
School of Chemistry
University of Nottingham
University Park
Nottingham
NG7 2RD
United Kingdom

and

Graham A. Worth
Department of Chemistry
King’s College London
The Strand
London
WC2R 2LS
United Kingdom
Suggested Dewey Classification: 541.2

ISBN 0-9545289-1-3

Published by

Collaborative Computational Project
on Molecular Quantum Dynamics (CCP6)
Daresbury Laboratory
Daresbury
Warrington
WA4 4AD
United Kingdom

©CCP6 2004
Preface

Conical Intersections and Photochemical Mechanisms: Characterizing the Conical Intersection Hyperline using Gradients, Second Derivatives, and Dynamics

Michael A. Robb, Michael J. Bearpark, Martial Boggio-Pasqua, Patricia Hunt, Martin Paterson, Massimo Olivucci, Lluis Blancafort and Gerrit Groenhof

Conical Intersections and Photostability of Aromatic Biomolecules

Wolfgang Domecke, Andrzej Sobolewski, Valérie Vallet, Zheng-gang Lan and Susanta Mahapatra

Control Strategies in the Presence of Conical Intersections

Regina de Vivie-Riedle and Dorothee Geppert

Topological Graph Theory and Conical Intersections

Arnout Ceulemans

Holding Computations of Conical Intersections to a Gold Standard

Terry A. Miller

H$_3^+$ in the Electronic Triplet State

António J.C. Varandas, Alexander Alijah, Mihail Cernai and Luís Pedro Viegas

A Continuous Representation of Seams of Conical Intersection - A Group Homomorphism Approach

Seungsuk Han and David R. Yarkony

Quantum Dynamics at Conical Intersections Treated Within the Multi-mode Vibronic Coupling Approach and its Generalizations

Horst Köppel

The Use of Elementary Reaction Coordinates in the Search of Conical Intersections

Yehuda Haas and Shmuel Zilberg

Extremely Narrow Photofragment Distributions Due to Conical Intersections

Marc C. van Hemert and Rob van Harrevelt
First Principles Ab Initio Multiple Spawning Dynamics of Electronically Excited trans-1,3-Butadiene with Wavefunction and Density Functional Theory
Benjamine Levine and Todd J. Martinez 65

Spectroscopy and Reactive Scattering Dynamics at Conical Intersections of Potential Energy Surfaces
Susanta Mahapatra 73

The Geometric Phase and the Hydrogen Exchange Reaction
Juan Carlos Juanes-Marcos and Stuart C. Althorpe 81

Treating Large Non-adiabatic Systems Using Quantum Dynamics: The MCTDH and Related Methods
Graham A. Worth 84

Reaction Dynamics on Conical Intersections for the OHF System
Octavio Roncero, Susana Gómez-Carrasco, Lola González-Sánchez, Miguel Paniagua and Alfredo Aguado 87

Rotation Operator Formalism For Open-Shell Complexes
Gerrit C. Groenenboom and Ad van der Avoird 98
Preface

This booklet was produced in connection with the CCP6 Workshop, “Quantum dynamics at conical intersections”, held at Nunspeet, The Netherlands, 2-5 September, 2004. The meeting brought together people from a diverse range of backgrounds working in this area, and was sponsored generously by CCP6 and by ChemReact. The workshop was also the official Satellite Meeting to the Molec XV International Conference on the Dynamics of Molecular Collisions.

CCP6 is the 6th Computational Chemistry Project (“Molecular Quantum Dynamics”) of the UK Engineering and Physical Sciences Research Council (EPSRC), and has funded a series of such workshops. Details of these and of the other activities of CCP6 may be found on the website (www.ccp.ac.uk). ChemReact is a consortium of researchers, who use the EPSRC HPC(X) High Performance Supercomputer, to pursue research in reaction dynamics and related areas (see www.chemreact.org).

The workshop was a timely and focused sequel to the Faraday Discussion on Non-Adiabatic Chemical Dynamics, held earlier in the year at Oxford. The recent explosion of interest in conical intersections means that a variety of different fields in chemical dynamics are investigating the quantum dynamics that occurs near, around, and at conical intersections. Leading representatives from the fields of electronic structure theory, high-resolution spectroscopy, theoretical quantum dynamics, and direct dynamics gave talks at the meeting, and contributed the articles in this booklet. We should like to thank warmly these contributors, and more generally all those who attended the workshop, presented posters, and took part in the spirited discussions.

S.C. Althorpe, Nottingham
G.A. Worth, London
September 2004
Conical Intersections and Photochemical Mechanisms: Characterizing the Conical Intersection Hyperline using Gradients, Second Derivatives, and Dynamics.

Michael A. Robb, Michael J. Bearpark, Martial Boggio-Pasqua, Patricia Hunt, Martin Paterson
Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom

Massimo Olivucci
Dipartimento di Chimica, Università di Siena, Via Aldo Moro, I-53100 Siena, Italy

Lluís Blancafort
Departament de Química, Universitat de Girona, E-17071 Girona, Spain

Gerrit Groenhof
Dept. of biophysical chemistry, University of Groningen, 9747 AG Groningen, The Netherlands

Conical intersections (CIs) are essential for the description of radiationless decay processes involved in photochemistry. In two geometrical variables (i.e., the branching space spanned by the gradient difference vector and the inter-state coupling vector), a conical intersection appears as a funnel. However, we know that an intersection is in fact a hyperline, i.e., a (3N-8)-dimensional space, where (3N-6) is the number of vibrational degrees of freedom, and that the ‘conical intersections’ we optimize with gradient-driven algorithms are critical points in this (3N-8)-dimensional space. Now that on-the-fly dynamics is possible, computations are beginning to explore the nature of the intersection hyperline away from its minimum. Such competitions show that these higher-energy regions of a conical intersection hyperline can be chemically significant. In addition, algorithms have been developed to map out (minimum energy path) segments of the hyperline explicitly.

For a discussion of mechanistic photochemistry, one needs a minimum of three geometric variables to describe the non-adiabatic event: the reaction path, and the two vectors which span the branching space. When the reaction path is contained in the branching space, one has a “sand in the funnel model”. However, as we shall show, there are many chemical problems where it the reaction path lies almost “parallel” to the seam of the conical intersection. In this type of problem, dynamics is essential.
The quantum chemistry tools that we have available for the study of non-adiabatic processes include gradient driven methods that can be used to optimise a critical point on a conical intersection. Many questions on photochemical reactivity can be answered by optimising such conical intersections and by following minimum energy pathways on excited-state. In this approach, it becomes useful to determine whether or not an optimised conical intersection is a minimum on the conical intersection hyperline (or perhaps a transition state or higher order maximum). To this end, we will discuss a second order approach to the characterisation of conical intersections.

Our method uses the projected Hessians of the degenerate states, after elimination of the two branching space coordinates, and is equivalent to a frequency calculation on a single Born-Oppenheimer potential energy surface. Based on projected Hessians, we have developed an equation for the energy as a function of a set of curvilinear coordinates where the degeneracy is preserved to second-order (i.e., the conical intersection hyperline). The curvature of the potential energy surface in these coordinates is the curvature of the conical intersection hyperline itself, and thus determines whether one has a minimum or saddle-point on the hyperline. The equation used to classify optimized conical intersection points depends in a simple way on the first- and second-order degeneracy splittings calculated at these points. As an example, for fulvene we can show that the two optimized conical intersection points of $C_2v$ symmetry are saddle-points on the intersection hyperline. Accordingly, there are further intersection points of lower energy, including one of $C_2$ which is the global minimum in the intersection space.

When the sand in the funnel model is not appropriate because the reaction path does not lie in the branching space, then only dynamics can provide mechanistic information. Accordingly, the second thread in our development will be a review of the information on the topology of the conical intersection hyperline that has emerged from our dynamics computations. As an example we shall discuss the dynamics of the photoactivation of the photoactive yellow protein PYP. Our objective is to obtain an understanding of why photon absorption triggers a trans-to-cis isomerization of the chromophore in the protein.

In vacuo, there is a transition-state and minimum where the chromophore is partly twisted, and a minimum with a half twist. The coordinates that lift the degeneracy are the skeletal deformations. The main point is that the conical intersection in the protein and in the gas-phase are significantly different. Dynamics in the gas-phase involves substantial additional motion to reach the seam at the half twist geometry.
In the gas phase dynamics, using the same initial conditions as in the protein simulations, the system never makes it over the first partial twist torsion barrier. In contrast, in the protein, the excited state is specifically stabilized by the charge distribution of the protein. Thus in the protein one observes a decrease of the S₁-S₀ energy gap in the region of the twisted intermediate (from 80 kJ mol⁻¹ in vacuo to less than 1 kJ mol⁻¹ in the protein), accompanied by a displacement of the crossing seam closer to the global minimum. One also sees a decrease of the energy barrier separating the early planar S₁ minimum and the twisted S₁ minimum. In total 14 dynamics simulations are discussed in ref 16. In the protein, the lifetime of the excited state ranged from 129 to 2293 fs. The ratio of the number of successful isomerizations to the number of excited-state trajectories is ca. 0.3, close to the experimental quantum yield of 0.35. Statistically, the number of trajectories is small but nevertheless yields a consistent mechanistic picture.

The PYP example is a dramatic example of a situation the reactivity is changed when you add the electric field of the protein. Nature has been very careful to position one charged residue in exactly the right place.

Conical Intersections and Photostability of Aromatic Biomolecules

Wolfgang Domcke, Andrzej Sobolewski, Valérie Vallet, Zhenggang Lan and Susanta Mahapatra

a Department of Chemistry, Technical University of Munich, D-85747 Garching, Germany
b Institute of Physics, Polish Academy of Sciences, PL-02668 Warsaw, Poland
c Laboratoire PhLAM, Université des Sciences et Technologies de Lille, F-59655 Lille, France
d School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

I. INTRODUCTION

The aromatic amino acids tryptophan and tyrosine and the nucleic acid bases adenine, guanine, cytosine and thymine represent some of the most important building blocks of life. A characteristic feature of the photochemistry of these molecules in the condensed phase is the extremely low quantum yield of fluorescence of the strongly UV absorbing singlet $\pi\pi^*$ excited states, indicating the existence of very fast nonradiative processes which efficiently quench the fluorescence [1, 2]. It is conceivable that the evolution of life has selected molecular building blocks with particularly short excited-state lifetimes to minimize dangerous photoreactions in living cells. The nonradiative processes presumably are ultrafast internal conversion back to the electronic ground state and photoionization (formation of solvated electrons) in aqueous solution [3]. They quickly dissipate the photon energy before more profound chemical rearrangements take place. This so-called photostability obviously is particularly essential for the constituents of the DNA which encode the genetic information of all living matter.

Over the last few years, we have explored the excited-state potential-energy surfaces of chromophores of biological interest with multi-reference ab initio methods. Employing geometry optimization techniques, excited-state minimum-energy reaction paths have been determined (at the CASSCF, CIS or TDDFT level) which lead to conical intersections of the excited state(s) with the electronic ground state. The conical intersections provide the mechanism for ultrafast deactivation of the excited states [4].

In all cases investigated so far, we have discovered optically dark, but pho-
FIG. 1: Potential-energy profiles of the lowest $^1\pi\pi^*$ states (squares and diamonds), the lowest $^1\pi\sigma^*$ state (triangles) and the electronic ground state (circles) as a function of the OH stretch (phenol) or NH stretch (indole, pyrrole) reaction coordinate. Geometries have been optimized in the excited electronic states at the CASSCF level; the PE profiles have been obtained with the CASPT2 method. The $S_0$ energy is calculated at the $^1\pi\sigma^*$ optimized geometries.

tochemically reactive excited states which play a decisive role for the excited-state decay dynamics of aromatic biomolecules. As an example, Fig. 1 shows reaction-path potential-energy profiles (see Ref. [5] for more details) of phenol (the chromophore of tyrosine), indole (the chromophore of tryptophan) and pyrrole. The latter is a building block of many biological chromophores, e.g., porphyrins or chlorophylls. The reaction coordinate is the OH stretching (phenol) or NH stretching (indole, pyrrole) coordinate. The novel aspect of Fig. 1 is the generic existence of a photochemically reactive dark $^1\pi\sigma^*$ state, which crosses both the optically allowed $^1\pi\pi^*$ state(s) (in indole and phenol) as well as the electronic ground state. The potential-energy crossings in the planar systems become conical intersections when out-of-plane modes are taken into account [5, 6]. Very similar photoreactive properties of $^1\pi\sigma^*$ states associated with NH or NH$_2$ groups have been found in the DNA base adenine [7]. To gain insight into the dynamics of conical intersections induced by hydrogen detachment, time-dependent quantum wave-packet calculations have been performed for pyrrole, the smallest system of interest in this context. These calculations will be discussed in more detail below.

Beyond the photostability of the individual DNA bases, the photostability of
the Watson-Crick base pairs GC and AT in DNA is of outstanding importance for the existence of life. To gain insight into the mechanisms which ensure the photostability of hydrogen-bonded base pairs at the molecular level, we have searched for conical intersections in a simplified biomimetic model of base pairs (2-aminopyridine dimer) [8] as well as in the real guanine-cytosine Watson-Crick base pair [9]. It has been found that in these systems an optically dark $^1\pi\pi^*$ state of charge-transfer character drives an inter-monomer proton transfer reaction (“the proton follows the electron”). The $^1\pi\pi^*$ (CT) state connects the optically accessible $^1\pi\pi^*$ state via two conical intersections with the electronic ground state [8, 9]. Recent experiments indeed have confirmed the existence of specific ultrafast excited-state deactivation processes in the 2-aminopyridine dimer as well as in the Watson-Crick structure of the guanine-cytosine dimer [10, 11].

In the following, we describe our first attempts towards an \textit{ab initio} based quantum wave-packet description of the photochemistry of pyrrole. The photophysics of pyrrole involves essentially the four lowest excited singlet states, which are $^1A_2(\pi\sigma^*)$, $^1B_2(\pi\pi^*)$, $^1B_1(\pi\sigma^*)$ and $^1A_1(\pi\pi^*)$ in order of increasing energy [12]. The second and the fourth excited singlet state, which correspond to valence excitations from $\pi$ to $\pi^*$ orbitals, are strongly UV absorbing states, which explains the presence of the intense band around 6 eV in the absorption spectrum. The first and the third excited singlet state correspond to excitations from the valence $\pi$ orbitals of pyrrole to the Rydberg-like $3s$ orbital. These electronic transitions possess very small oscillator strengths [13]. As discussed by Sobolewski and Domcke [5], the $3s$ Rydberg orbital of pyrrole has a significant anti-bonding character with respect to the NH bond ($\sigma^*$ character). Upon stretching of the NH bond, the $^1\pi\sigma^*$ potential-energy functions intersect the potential functions of the valence excited states, resulting in conical intersections along the reaction path for hydrogen abstraction. Due to the presence of these conical intersections between the bright valence states and the dark $^1\pi\pi^*$ states, the population of the bright states is transferred to the dark states on a very short time scale of $\approx 20$ fs. This has been confirmed recently by Köppel \textit{et al.} [14] for pyrrole and related five-membered heterocycles.

\section{THEORETICAL FRAMEWORK}

\subsection{Reduced-dimensionality model}

We treat the wave-packet dynamics of pyrrole in a two-dimensional space which is spanned by the NH-stretching coordinate (which tunes the energy gap between the ground and $^1\pi\sigma^*$ states) and the out-of-plane bending motion of the hydrogen atom of the azine group (which couples the two states). The other internal coordinates are kept frozen at their ground-state equilibrium values. Some of these modes may play a role as energy-accepting modes in the internal-
conversion process. It should be kept in mind that these effects are not included in the present dynamics simulations.

The Hamiltonian of the system is written in a diabatic electronic basis as [15]

\[ \mathcal{H} = \mathcal{H}^N + \mathcal{H}^{el} = T^N \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}, \]

(2.1)

where \( \mathcal{H}^N \) and \( \mathcal{H}^{el} \) represent the nuclear and the electronic part of the Hamiltonian operator, respectively. \( T^N \) is the nuclear kinetic-energy operator. \( V_{11} \) and \( V_{22} \) are the potential energies of the diabatic \( S_0 \) and \( ^1\pi\sigma^* \) states, respectively. The diabatic coupling element \( V_{12} = V_{21} \) describes the coupling between the two states. It vanishes for planar geometries (\( C_{2v} \)) by symmetry.

The system is considered as an effective three-body system, composed of hydrogen, nitrogen and \( M \), the center of mass of the rest of the rigid pyrrole ring. The nuclear geometry is described in terms of Jacobi coordinates. \( r_{MN} \) is the distance between the ring center \( M \) and the nitrogen atom. This distance is kept fixed in the dynamics calculation. \( r \) is the distance between the active hydrogen and the center of mass of the M-N unit, and \( \gamma \) is the angle between \( \tilde{r}_{MN} \) and \( \tilde{r} \).

In this set of coordinates, the kinetic operator takes the following form

\[ T^N = \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2I} \frac{\partial^2}{\partial \gamma^2}, \]

(2.2)

with

\[ \mu = \frac{m_H(m_M + m_N)}{(m_H + m_M + m_N)}, \]

(2.3)

\[ \mu_{MN} = \frac{m_Mm_N}{(m_M + m_N)}, \quad m_M = 4(m_C + m_H), \]

\[ \frac{1}{I} = \frac{1}{\mu r^2} + \frac{1}{\mu_{MN} r_{MN}^2}. \]

B. \textit{Ab initio} calculation of the adiabatic potential-energy surfaces

The \( ^1B_1(\pi\sigma^*) \) state has a 3s Rydberg character at the equilibrium geometry, but rapidly acquires H(1s) character when hydrogen atom dissociates [5]. This change of character is reflected by a small barrier (\( \approx 0.26 \) eV) in the \( ^1\pi\sigma^* \) potential-energy function close to the equilibrium geometry (\( r_{NH} \approx 1.25 \) Å). In order to account for the diffuseness of the \( \sigma^* \) orbital, it is necessary to use rather extended basis sets on each atom, and in particular on the N-H end. All atoms are described by the augmented correlation-consistent polarized valence quadruple zeta (aug-cc-pVDZ) [16] basis. One diffuse s function and one set
of diffuse $p$ functions were added to the nitrogen, and two diffuse $s$ functions and two sets of diffuse $p$ functions were added to the active hydrogen. Their exponents were derived in an even-tempered manner from the most diffuse $s$ and $p$ functions present in the aug-cc-pVDZ basis by dividing the exponents successively by a factor of 3.0.

As a reference for the definition of internal coordinate displacements, the ground-state equilibrium geometry has been determined at the Møller-Plesset (MP2) level of theory using the Gaussian 98 ab initio package [17]. The $ab$ initio calculations of the ground and excited state potential-energy surfaces have been performed at the CASSCF level using the MOLPRO package [18]. The active space involves three $\pi$ orbitals ($1b_1 - 2b_1, 1a_2$), two $\pi^*$ orbitals ($3b_1, 2a_2$), and one $\sigma^*$ ($10a_1$) orbital. It turned out to be necessary to include three occupied orbitals of $\sigma$ character ($8a_1 - 9a_1, 6b_2$), and three additional virtual orbitals of $\sigma^*$ character ($11a_1 - 12a_1, 7b_2$) to obtain smooth potential-energy surfaces in the region of the barrier of the $^1\pi\sigma^*$ surface. This active space corresponds to a distribution of 12 electrons in 12 orbitals.

![FIG. 2: Diabatic ($V_{11}$ and $V_{22}$) (a) and adiabatic (b) potential-energy surfaces of the $S_0$ and $^1\pi\sigma^*$ states as a function of the NH-stretching coordinate $r_{NH}$ and the H-out-of-plane angle $\theta$.](image)

**C. Analytical representation of the diabatic potential functions**

We wish to construct an analytical diabatic potential model which should be as simple as possible and at the same time should reproduce the $ab$ initio potential-energy data within an accuracy of 0.1 eV or better. For the description of the potential-energy surfaces, the intermolecular distance $r_{NH}$ between nitrogen
and hydrogen and the out-of-plane bond angle $\theta$ of the hydrogen atom are the most natural coordinates. We have constructed the potential-energy surfaces in these coordinates, while the wave-packet propagation is performed in the Jacobi coordinates.

The diabatic $S_0$ and $^1\pi\sigma^*$ potential functions are approximated by Morse-type functions in NH-stretch direction and parabolic functions in the angular coordinate $\theta$, whereby the diabatic angular vibrational frequencies are functions of $r_{NH}$. The diabatic inter-state coupling term is taken to be linear in $\theta$ and is allowed to vary with $r_{NH}$. The diabatic potential-energy functions thus are nonseparable in $r_{NH}$ and $\theta$. The adiabatic potential-energy functions acquire an additional pronounced nonseparability through the conical intersection. The maximum deviation between the adiabatic model potential-energy and the ab initio data is 0.05 eV. The resulting diabatic and adiabatic potentials as functions of the internal coordinates $r_{NH}$ and $\theta$ are displayed in Figs. 2(a) and 2(b), respectively.

### D. Wave-packet propagation method

The photoinduced dynamics of pyrrole is treated in the time-dependent picture by solving the time-dependent Schrödinger equation with a wave-packet propagation method on a two-dimensional grid. The initial wave function $\Psi(t = 0)$ is given, in the Condon approximation, by the initial vibrational state in the electronic ground state. The excited-state wave function is propagated using the split-operator (SO) method [20]. We have used the fast Fourier transform (FFT) method [21] to evaluate the kinetic-energy part of the time propagator. The grid consists of 1024 $\times$ 128 points, ranging from 3 au to 27 au in $r$ and from -2.0 rad to 2.0 rad in $\theta$. To avoid problems with the finite range of the grid, we apply a damping function as defined in Ref. [22]. The time-dependence of the adiabatic electronic populations are calculated from the expectation values of the projection operators in the respective electronic states.

We have generated the eigenfunctions of the diabatic $S_0$ state by using the spectral-quantisation method detailed in Ref. [23]. The dissociation probabilities have been calculated using as the time-cumulated flux through a dividing surface $r = r_{flux}$, which is placed beyond the conical intersection:

$$P_R(t) = \frac{\hbar}{\mu} \int_{t=0}^{t} \text{Im} \left[ \langle \Psi(r_{flux}, \gamma, t) | \frac{\partial \Psi(r_{flux}, \gamma, t)}{\partial r} \rangle \right] dt. \quad (2.4)$$

The energy-resolved dissociation probability is defined in a similar way

$$P_R(E) = \frac{\hbar}{\mu} \text{Im} \left[ \langle \Psi(r_{flux}, \gamma, E) | \frac{\partial \Psi(r_{flux}, \gamma, E)}{\partial r} \rangle \right], \quad (2.5)$$
using the energy-normalized wave function $\Psi(r, \gamma, E)$, which is obtained by
Fourier-transforming the time-dependent wave packet on the dividing surface:

$$\Psi(r, \gamma, E) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(r, \gamma, t)e^{iEt/\hbar} dt.$$  \hfill (2.6)

III. RESULTS AND DISCUSSION

The main focus of the present work is on the investigation of the effect of mode-
specific vibrational excitation on the dynamics near the conical intersection. The
wave function is propagated for 300 fs with a time step $\Delta t = 0.05$ fs. The total
propagation time is long enough to ensure that the probabilities of the different
channels are converged. The probabilities are monitored by the calculation of the
time-cumulated flux and energy-resolved flux on the $S_0$ and $1\pi\sigma^*$ states before
the conical intersection ($r = 5$ au) and at the dissociation limits ($r = 9$ au).

We use the 15 lowest eigenfunctions of the $S_0$ state as initial wave functions,
placing them vertically in the $1\pi\sigma^*$ diabatic excited state. For all initial con-
ditions, we observe similar features in the evolution of the excited-state wave
function. In all cases, we note very fast, but weak oscillations (Rabi-type oscil-
lations) in the diabatic population of the $1\pi\sigma^*$ and $S_0$ states, see Fig. 3, which
result from the non-zero coupling of these two states in the Franck-Condon re-
gion. Due to the existence of a barrier in the $1\pi\sigma^*$ potential-energy surface,
there are two ways for the wave packet to escape the potential well in which it is
placed by vertical excitation. The high-energy part of the wave packet overcomes
the barrier and reaches the conical intersection directly within about 10 fs. The
low-energy part escapes the potential well by tunneling, which happens on a
longer time scale. These two processes can be distinguished via the profile of the
population dynamics and the time-cumulated flux, see Figs. 3 and 4. The
time constant of about 150 fs for the $S_1(\pi\sigma^*)$ decay and thus the appearance
of hydrogen atoms has recently been confirmed in time-resolved pump-probe
experiments \[24\].

When the wave packet reaches the region of the conical intersection, it splits
into two parts. One part follows a diabatic path and moves towards the lower
adiabatic dissociation limit, as illustrated by the flux calculated on the lower
dissociation channel, see Fig. 4. The other part is transferred to upper adiabatic
surface, see Fig. 3. It dissociates directly to the higher adiabatic limit without
being trapped in the upper adiabatic cone (see Fig. 4). The reason is that the
initial mean energy of the wave packet is higher than both dissociation limits.
Therefore, the wave packet passes the conical intersection region only once, as
revealed by the monotonous population dynamics in the adiabatic picture. The
probability of internal conversion, that is, return of the system to the electronic
ground state without dissociation, is close to zero in the present model. This
FIG. 3: Population probabilities of the diabatic $^1\pi\sigma^*$ state and ground state of pyrrole (full lines). The population probabilities of the upper adiabatic ($S_1$) and lower adiabatic ($S_0$) states are shown by the lines with crosses and circles, respectively, for the initial conditions (0,0) (a), (0,1) (b) and (1,0) (c). The insets display the diabatic population of the $^1\pi\sigma^*$ state for the first 20 fs.

finding may not reflect the real situation for two reasons. First, we have neglected the coupling of the highly excited $^1B_1(\pi\pi^*)$ state with the lower-lying $^1A_2(\pi\sigma^*)$ and $^1B_2(\pi\pi^*)$ excited states. Second, we have neglected intramolecular vibrational relaxation (IVR) effects, arising from the anharmonic coupling of the photochemically active with the many inactive vibrational degrees of freedom. Extensions of the model are required to account for these effects.

In order to shed light on the influence of mode-selective vibrational excitation on the branching ratio of two dissociation channels, we discuss the flux at the dissociation limits for different initial states. If we put one quantum of energy into the tuning mode, initial vibrational state (1,0), the wave packet reaches the conical intersection earlier than in the (0,0) case and the population transfer occurs on a short time scale, see Fig. 3(c). It is noteworthy that the branching ratio does not depend on excitations along the tuning mode (see Fig. 5(a)).

The branching of the reactive flux at the conical intersection depends, on the
other hand, strongly on the excitation level of the coupling mode, as shown by Fig. 5(b) and 5(c). For the (0,0) initial wave function, most of the wave packet (75%) dissociates to the lower adiabatic limit, while 25% of the flux arrives at the upper adiabatic limit. When exciting the coupling mode by one quantum, the flux splits almost equally between the two channels. If we put more energy into the coupling mode, the wave packet dissociates primarily to the higher adiabatic limit. The branching ratio saturates at 25%/75% for $n_\gamma = 4$. Similar observations can be made for the series $(1,n_\gamma), n_\gamma = 0, 4$, see Fig. 5(c). In summary, we conclude that excitations along the coupling mode have a strong impact on the behaviour of the wave packet at the conical intersection. This fact can be used to tune the branching ratio between the two dissociation limits.
IV. CONCLUSIONS

As a first step towards a first-principles mechanistic understanding of the \(^1\pi\sigma^*\)-driven photochemistry of aromatic biomolecules, we have investigated the quantum wave-packet dynamics of a two-dimensional model of the \(^1B_1(\pi\sigma^*)\) excited state of pyrrole and its conical intersection with the electronic ground state. The photochemically reactive NH stretching mode and the vibronically active hydrogen out-of-plane bending model have been taken into account. We have investigated, in particular, the dependence of the branching ratio of the two hydrogen dissociation channels (corresponding to the \(^2\pi\) and \(^2\sigma\) pyrrolyl radicals) on the initial vibrational state. A considerable dependence of the branching ratio on the level of excitation of the bending mode has been found. This finding indicates that a control of the photodissociation dynamics of pyrrole via mode-specific IR excitation, as has recently been demonstrated for ammonia [25], should also be possible for pyrrole.

Control Strategies in the Presence of Conical Intersections

Regina de Vivie-Riedle and Dorothee Geppert
Department Chemie, LMU, Butenandstr. 11, D-81177 München, Germany

1. Introduction

The dynamics of chemical and physical processes can be monitored in real time using ultrashort laser pulses [1-7]. In combination with quantum dynamical calculations a detailed microscopic understanding of the reaction mechanisms can be achieved. Guided by this knowledge we design strategies for the control of complex molecular processes. Our basic tool is the optimal control theory (OCT) as proposed and developed by the groups of Rabitz [8,9] and Tannor, Rice and Kosloff [10,11]. The principle idea is to optimize the laser field with respect to amplitude and phase and guide the molecular processes from the initial to the final state. First experimental implementations were realized using ultrafast pulse shaping techniques in combination with genetic algorithms [12-14], followed by many experiments controlling more complex chemical reactions [15,16] and even biomolecules [17].

We illustrate the decoding of chemical reactions on the atomic scale and the subsequent design of control strategies for the photoinduced ringopening of cyclohexadiene. This reaction occurs within 200 fs in gas as well as in condensed phase [18-21] and is mediated via several conical intersections. After photoexcitation to the S2 state the molecule decays within a few femtoseconds to the S1 state from where the relaxation to the ground state is mediated by at least two conical intersections [22-26]. First the time evolution of the system subsequent to laser excitation is studied by means of wavepacket propagations on the ab initio potential reaction surfaces. We include the non-adiabatic coupling elements in the quantum dynamical calculations and follow the adiabatic approach to describe the complete relaxation process. Secondly the reaction is systematically driven through one of the conical intersections to optimize the resulting product distribution.

2. Non-adiabatic coupling elements in reactive coordinates

We introduced a reduced set of reactive coordinates to handle the ring opening reaction from the Franck-Condon (FC) to the product states and developed the corresponding Hamiltonian for the nuclear motion. The nuclear Hamiltonian for the reactive coordinates \( r, \theta, \varphi \) has the following form [27]:
\[ T_n = -\frac{1}{2} \left( \frac{B}{r} \partial_r^2 r + \left( \frac{B}{r^2} + \frac{B}{r^2} \right) \left( \frac{1}{\sin^2 \vartheta} \partial_\vartheta^2 + \partial_\varphi^2 + \cot \vartheta \partial_\varphi \right) \right) \] (1.1)

The motion in \( \vartheta \) is significantly weaker and less important than in \( r \) and \( \varphi \) direction, therefore \( \vartheta \) is kept constant throughout the calculations. The complete Hamiltonian including the non-adiabatic coupling between the two degenerate states reads:

\[
H = \begin{pmatrix}
T_n & K_{12} \\
-K_{12} & T_n
\end{pmatrix} \phi \begin{pmatrix}
V_1 & 0 \\
0 & V_2
\end{pmatrix}
\] (1.2)

where \( V_{1,2} \) denotes the adiabatic potentials. \( K_{12} \) is the non-adiabatic coupling term

\[
K_{12} = -\sum \frac{1}{m_j} \left( f_{12}^{(i)} \partial \phi_j + \frac{1}{2} g_{12}^{(i)} \right)
\] (1.3)

with \( m_j \) the mass of the \( j \)th atom and \( \phi_j \) Cartesian nuclear coordinates. The first- and second-order derivative (non-adiabatic) coupling elements for the electronic wavefunctions \( \Phi_{1,2} \) are given by

\[
f_{12}^{(i)} = \left\langle \Phi_1 | \partial \phi_j | \Phi_2 \right\rangle \quad \text{and} \quad g_{12}^{(i)} = \left\langle \Phi_1 | \partial^2 \phi_j | \Phi_2 \right\rangle
\] (1.4)

The NACs were calculated at the CASSCF-level using MOLPRO [28] and then transformed into the reactive coordinates. As the coupling is large in some degrees of freedom not explicitly included in our wavepacket propagation, we project them [27, 29] onto our subspace spanned by \( r \) and \( \varphi \). Exemplarily, the resulting NACs \( f_{12}^{\gamma \beta} \) at \( \text{C}_2\text{-CoIn} \) and \( f_{12}^{\gamma \varphi} \) at \( \text{CoIn}_{\text{min}} \) are shown in Fig. 1; they exhibit the typical spiky behavior.

The second derivative terms \( g_{12}^{\gamma \beta} \) of the non-adiabatic coupling are mostly much smaller than the first derivative terms but have to be included in the adiabatic description to conserve the hermiticity of the Hamiltonian.

3. Laser-molecule interaction and optimal control theory

To deal with photoinduced chemical processes the interaction between the molecule and the incident light pulses must be incorporated into the quantum mechanical description. Ultrashort laser pulses simultaneously provide many parameters to communicate with the internal molecular motion. The optimal shape to reach a selected target can be found with the help of optimal control algorithms. For instance the optimization of a laser field \( \tilde{e}(t) \) driving the system
Fig. 1 Non-adiabatic coupling elements around C$_2$-CoIn (right) spanning a region of $\Delta r = 0.06 \, \text{Å}$, $\Delta \phi = 1^\circ$ and around CoIn$_{\text{min}}$ (left) extending over $\Delta r = 0.02 \, \text{Å}$, $\Delta \phi = 0.42^\circ$.

from an initial state $\Psi_0(0)$ at time $t=0$ to the selected target area (defined by the projection operator $X$) at time $t=T$ can be reduced to maximizing the functional $L$ given by [9,30,31]:

$$L[\Psi_i(t), \Psi_f(t), \varepsilon(t)] = \left| \left\langle \Psi_i(T) | X | \Psi_f(T) \right\rangle \right|^2 - \alpha_0 \int_0^T \frac{\dot{\varepsilon}(t)^2}{s(t)} \, dt$$

$$- 4 \text{Re} \left\{ \left[ \frac{1}{i \hbar} \left[ H - \mu \varepsilon(t) \right] + \frac{\partial}{\partial t} \right] \Psi_j(t) \right\} dt$$

with the auxiliary wavefunction $\Psi_0$ being a Lagrange multiplier. Variation of this functional leads to a set of coupled differential equations, which is solved iteratively and leads to a laser field which is optimized for the given task. The first term defines the control aim, the second term is the integral over the laser fluent controlling the reaction and the third term guarantees the compliance of the wavepackets $\Psi_i$ and $\Psi_f$ with the Schrödinger equation under the influence of the laser field $\varepsilon(t)$. To satisfy the demand of a smooth switch on and off behavior of the laserfield the shape function $s(t)$ is introduced. The penalty factor $\alpha_0$ limits the time-averaged laser intensity and $T$ denotes the overall pulse duration.

4. Laser induced dynamics and control strategies

In a first approach laser pulses with various temporal width are employed for photoexcitation. In all cases the relaxation to the ground state takes place mainly
through the energetically higher lying conical intersection \( C_2 \text{-CoIn} \), the energetically lower conical intersection \( \text{CoIn}_\text{min} \) is also reached but less effective \[29\]. Shortening of the pulse duration just enhances the amount of the non-adiabatic transition. For instance an incident laser pulse with a FWHM of 11 fs prepares a localized wavepacket on the excited state which is dominantly accelerated and focused into the \( C_2 \text{-CoIn} \). Following the relaxation transfer of this localized wavepacket reveals that a pronounced stepwise transfer occurs mainly through this \( C_2 \)-symmetric conical intersection. Thus a certain amount of control is already achieved by just varying one parameter, the pulse duration.

The next step is to control the overall reaction from the initial state through one conical intersection into the target state. Therefore we employ our modified phase sensitive version of OCT \[32, 33\]. The optimal control calculations are performed for an analytic model which was constructed for the electrocyclic reaction of cyclohexadiene and its derivates on the basis of our ab initio data \[33\]. We selected the backward reaction, the ring closure starting from hexatriene. A gaussian type ultrafast laser pulse excites over 90 % of the wavepacket, and in contrast to the ringopening, the relaxation to the ground state takes place mainly via the \( \text{CoIn}_\text{min} \) forming already 80% of cyclohexadiene.

For the hexatriene \( \rightarrow \) cyclohexadiene reaction a control strategy is developed using an intermediate target on the excited state \( S_1 \). The target is close to the FC-region where the laser interaction between the two electronic states is still effective. It is selected as a gaussian wavepacket provided with special momentum. The wavepacket's momentum not only influences the dynamics in the excited state but also the dynamics on the ground state after the relaxation through the conical intersection. The task of the control functional was to find a laser pulse that drives the initial wavefunction to this intermediate target from where it evolves without laser correction to its final destination. The resulting optimal laser field exhibits a very high excitation efficiency of more than 97 %, It drives the wavepacket to the preselected geometry and achieves an enhanced product distribution of 91:9 cyclohexadiene:hexatriene.

5. Conclusion

The photoinduced electrocyclic ring opening reaction of cyclohexadiene provides an interesting example of a complex ultrafast reaction mediated by multiple conical intersections. For the short time domain we derived a realistic dynamical model and performed quantum dynamical calculations. It was necessary to adapt the adiabatic approach for the coupled dynamics in order to describe simultaneously the transfer through multiple conical intersections. On this basis it was possible to obtain a microscopic understanding of the relaxation process. Starting from cyclohexadiene, the return to the ground state takes place dominantly through the \( C_2 \text{-CoIn} \), starting from hexatriene the other conical intersection \( \text{CoIn}_\text{min} \).
is more favored. The final product yield for the ring closure reaction was optimized. The definition of an intermediate target on the excited state ensured that the reaction took place via one conical intersection and first results suggest that the possibility to define intermediate control objectives reduces the complexity of the optimal control field.

Acknowledgment

We want to thank Angelika Hofmann who has performed part of the dynamic calculations and Lena Seyfarth who was involved in the control calculations. Most of the work has been carried out on the IBM eServer p690 supercomputer of the RZG in Garching with financial support by the MPG and the DFG.

I. INTRODUCTION

Graph theory is a mathematical theory, which is concerned with sets of points that are connected by lines. It has a wide range of applications from combinatorics to computer science and physics. In chemistry we encounter graph theory in the atom-bond matrix which is one of the basic descriptors of molecular structure [1]. Already in 1968 Muetterties [2] realised that graph theory also was relevant to the description of dynamic chemical processes on a reaction surface: the nodes of the graph then correspond to the set of stable minima on the surface, and the lines are the feasible reactions or trajectories between the minima. The chemical literature offers many examples of reactivity patterns which exemplify famous graph structures such as the Petersen or Desargues-Levi graphs [3].

The study of conical intersections on a reaction surface enriches the graph-theoretical representation in an unexpected way. It draws attention to closed loops on the graph which may be identified as faces when the graph is embedded on a surface. In this contribution we will present the concepts of discrete topology that are involved here and then discuss an application to a conical intersection problem *par excellence*: the icosahedral $H\otimes h$ Jahn-Teller problem.

II. ELEMENTS OF DISCRETE TOPOLOGY

First let us overview some key elements of topological graph theory [4–6].

In principle a graph is a set of nodes and connections and has no topological meaning. Topology sneaks in though when one starts to wonder whether it is possible to draw a given graph on a piece of paper so that no two connections intersect. In 1929 Kuratowski [7, 8] proved the surprising result that a graph will be non-planar if it contains as a substructure at least the complete graph of 5 nodes, $K_5$, or the complete bipartite graph $K_{3,3}$. This result marks the start of topological graph theory, which is concerned with the actual drawing of a
graph on a surface, also denoted as the embedding. When a graph is embedded on a surface some of its closed loops will encircle a region of the surface which is called a *face*. Technically speaking a face is defined by a closed walk starting at a given directed edge or arc, and always taking the same rotation at the next vertex point to continue the walk [9].

The combination of the faces defines a polyhedron which encloses a finite region of space [10]. The underlying topology of the surface on which the polyhedron is drawn is expressed by the Euler characteristic, $\chi$, in the celebrated Euler theorem, which states that the numbers of vertices ($V$), edges ($E$), and faces ($F$) obey the following rule (see e.g. [11, 12]):

$$V - E + F = \chi \tag{1}$$

Here $\chi$ is a fixed integer which marks the topology of the surface on which the polyhedron is embedded. The family of surfaces can be divided into two classes: orientable and non-orientable surfaces. An orientable surface is one which has an inside and an outside, i.e. there does not exist a walk on the surface which takes you from the outside to the inside. Otherwise the surface is non-orientable. The orientable surfaces can be described as a sphere to which $p$ handles are attached, $S_p$. One has:

$$\chi(S_p) = 2 - 2p \tag{2}$$

Examples are the sphere itself ($S_0$) and the torus ($S_1$). A sphere with $q$ cross-caps forms a non-orientable surface $N_q$, with characteristic:

$$\chi(N_q) = 2 - q \tag{3}$$

with the projective plane, $N_1$, as an example. Euler’s theorem is a core result in discrete topology. It links the elements of a discrete polyhedral structure to the underlying surface.

*In what way is this now connected to conical intersections?* The connection is the following: when the wavefunction is transported adiabatically on a closed loop surrounding a conical intersection, its phase acquires a phase shift which is known as the Berry phase and amounts to $\pi$ when a single intersection line is encircled. This is the result of Berry which was already recognized in earlier studies of the Jahn-Teller effect by Longuet-Higgins and Herzberg [13, 14]. Hence the conical intersection is detected through closed loops and obviously draws attention to at least a two-dimensional region of the coordinate space that is encircled by these loops, i.e. it entails the *face* concept, and thus the problem of the embedding of the reaction graph. One way to formulate this problem is:

*Given a certain graph: what is the surface with the lowest Euler genus on which this graph can be embedded as a polyhedron?*
For some highly symmetrical graphs this problem has been solved. Such is the case for the complete graphs, $K_n$, which was successfully solved by Ringel [15] in 1968. For other graphs solutions can only be found by applying generating algorithms that however explode with the number of vertices [9].

III. APPLICATION: PHASE ENTANGLEMENT IN ICOSAHEDRAL JAHN-TELLER PROBLEM

Jahn-Teller systems offer paradigmatical cases of conical intersections, in which the point group symmetry is embedded in the continuous topological invariance groups. Particularly rich and intriguing cases are encountered in icosahedral symmetry [16], and the available icosahedral fullerenes, $C_{60}$ and $C_{80}$. A case of special interest is the ground state cross-over in the Jahn-Teller instability of an electronic quintuplet under trigonal distortions [17]. This case corresponds to the so-called $H \otimes h$ system. An icosahedron has ten threefold axes, each of which corresponds to the direction of a distortional minimum. Since the trigonal distortions are centro-symmetric, the spatial arrangement of the ten minima can be presented on a half sphere, which has the topology of the projective plane, $N_1$. The dynamic ground state of the system corresponds to the tunneling between the minima on this surface.

As is usual for Jahn-Teller problems the vibronic ground state has the same quintuplet symmetry as the original electronic ground state. However when the coupling strength is increased a ground state cross-over to a symmetric singlet state takes place. The reason is that at higher coupling strength the preferential tunneling path between the minima changes to a loop with vanishing Berry phase. A similar cross-over due to a change of tunneling path was also observed for the prototypical $E \otimes e$ problem with quadratic coupling [18]. Two research groups have attempted to describe the conical structure of the icosahedral surface, giving rise to this special phase entanglement [17, 19, 20]. They reached conflicting conclusions, due to the use of arbitrary 2D projections of the 5D loops. There is thus a need for an analysis of the entanglement which does not rely on projections of the base space [21].

A graph-theoretical treatment of this problem requires first the definition of a minimal cycle basis of the tunneling network. This is a minimal set of loops in which any loop can always be decomposed [22]. The dimension of this set is given by the Euler-like relation:

$$n = E - V + 1$$

For 10 minima ($V = 10$), which can tunnel to all neighbours ($E = 45$) the minimal cycle basis consists of $n = 36$ triangles. This basis is included in the full set of 120 triangles, that form the complete triangulated network which spans the Jahn-Teller surface. Taking into account icosahedral symmetry this
network contains five different types or orbits of triangles. We have scanned cross-sections of the surface for each orbit, and established the presence of conical intersections in three of these, while the other two did not have a cusp. All loops on the surface can be decomposed in sums of these triangles, and the absence or presence of Berry phase can immediately be verified by counting the number of cusps enclosed. In this way the absence of Berry phase in the loops that prevail at higher coupling strength could be related to the fact that these loops encircle two conical intersections. In comparison the earlier treatment of Moate et al. [17] explained the absence of Berry phase due to a tangential intersection of upper and lower electronic surface, while the work of Manini et al. [20] attributed the absence of Berry phase to a loop which encircles a conical intersection twice.

This graph-theoretical analysis points to a deeper graph-topological structure [23]. To understand this structure one can start from the highly symmetrical origin where all minima are equidistant neighbours and the hopping trajectories form the complete graph, $K_{10}$. The embedding with minimal genus for this graph can be found by the formula of Ringel and turns out to be $N_7$. The 10 trigonal minima can thus be placed on a closed surface with seven cross-caps. This polyhedral structure has 30 triangular faces ($F = 30$) and precise icosahedral symmetry. One can thus check the Euler equation:

$$\chi(N_7) = 2 - 7 = 10 - 45 + 30$$

The 30 triangles constituting the polyhedron form one icosahedral orbit of the fully triangulated net, and are all cusp-free. Hence it is possible to perform closed walks on this entire surface in the space of Jahn-Teller distortions, without ever encircling conical intersections. Since this surface is closed 29 out of the 30 triangles can be included in a minimal cycle basis; the remaining triangle can always be expressed as a sum of the 29 others. This leaves 7 more triangles for the minimal cycle basis. They match precisely the 7 cross-caps of $N_7$, since paths over these cross-caps are non-contractible.

IV. CONCLUSIONS

The study of conical intersections adds to chemical reaction graphs the notion of two-dimensional regions of space, encircled by reaction paths, that correspond to faces of a complex, and provide a connection to topological graph theory. It is expected that this theory will provide new tools for the study of the entanglement of electronic structures on multi-dimensional reaction surfaces.
Financial support from the Flemish Government (Concerted Action Scheme) and Fund for Scientific Research - Flanders (Belgium) is gratefully acknowledged.

[6] For a brief introduction into the field of Topological Graph Theory, see the survey by Dan Archdeacon on the webpage http://www.emba.uvm.edu/~archdeac/papers/papers.html.
I. INTRODUCTION

It is well-known that the electronic potential energy surfaces (PES) of polyatomic molecules can cross even if they are of the same symmetry. More precisely they form a conical intersection (CI) or a (3N-6-2)-dimensional hyperline in the nuclear coordinate space of an N-atom molecule. A very important consequence of the CI for reaction dynamics is that it provides an opportunity for a molecule to move facilely from one electronic PES to another.

Reaction mechanisms involving CI’s have recently been implicated in a number of well-known photochemical reactions and computational methods to characterize the PES in the vicinity of CI’s have been implemented and reviewed.[1] These computations have generally been quite enlightening both as to the nature of the PES and to possible dynamical consequences thereof. However, the gold standard for theoretical predictions, computational or otherwise, has always been experimental verification. Unfortunately, in the present case, it has been exceedingly difficult to apply this standard since most experimental measurements only probe the limits, i.e., reactants and products, of dynamics through the CI. Such measurements are relatively insensitive to the details of the CI.

There is however a clear exception to the above generalization and that is the CI caused by symmetry. Such CI’s have long been known and are referred to as Jahn-Teller effects.[2–5] From an experimental point of view, the uniqueness of the Jahn-Teller CI is that it is sampled by bound vibronic eigenfunctions that, along with their corresponding eigenvalues, can be precisely investigated by spectroscopic techniques.

In recent years, in our laboratory we have carried out a number of detailed spectroscopic investigations of the vibronic energy levels of Jahn-Teller active molecules. These experiments provide a gold-standard characterization of the molecular vibronic energy levels which are a sensitive function of the CI and the nearby PES. To apply this gold standard to the PES itself we utilize a somewhat modified version of the traditional analytical model of the PES, and determine
experimentally the parameters upon which it depends. This PES can then be compared with those resulting from various quantum chemistry calculations.

II. NATURE OF THE EXPERIMENTS

The goal of experiments is to provide as complete a map as possible of the vibronic energy levels of a Jahn-Teller active state. For a comparison to calculated PES’s, it is desirable to utilize the lowest Jahn-Teller active state of a given symmetry. The most popular experimental approach[6, 7] has been to map the vibronic levels via the dispersed fluorescence thereto from a more highly excited state. Oftentimes the molecules are jet-cooled to reduce spectral congestion. Sometimes stimulated emission pumping experiments[8] have also been performed. If the active state of the lowest symmetry is itself excited, (non-dispersed) laser induced fluorescence can be used to characterize it.[9] For the ground state of ions, ZEKE and related spectroscopies have also been employed.[10–16] Naturally direct IR absorption to the excited vibronic levels of a Jahn-Teller active state is a powerful technique; however, the difficulty of achieving substantial populations of reactive, open-shell molecules makes the detection of IR absorption difficult, but not necessarily impossible.[17, 18]

The above experiments are all performed for isolated molecules. There is voluminous literature involving studies of Jahn-Teller molecules in condensed phases. However if comparison between experimental data and the calculated PES of the isolated molecule is desired, the condensed phase results are usually not appropriate. All too often, environmental effects in the condensed phase distort the PES comparably or greater than the intrinsic Jahn-Teller effect.[19]

Until about 25 years ago, there was little or no detailed gas-phase data for the vibronic energy levels of Jahn-Teller active molecules (nor for that matter, a computed PES worthy of comparison). This situation began to change with detailed spectroscopic determinations of the vibronic energy levels of the \( \tilde{X}^2E_g \) and \( ^2E \) states, respectively, of hexafluorobenzene and sym-trifluorobenzene (and related halobenzene) cations[7] and later methoxy.[20]

Although progress has been slow, there is now a substantial amount of precision data on a number of “families” of Jahn-Teller active molecules. In the “near-aromatic” family, the benzene cation[21] has recently joined its experimentally more accessible halobenzene “siblings.” In addition, the neutral radical “cousins,” cyclopentadienyl[22, 23] and tropyl[24] have also recently been investigated.

Arguably, the \( \tilde{X}^2E \) state of the methoxy family, CH\(_3\)O, CH\(_3\)S, CF\(_3\)O, and CF\(_3\)S has the most detailed experimental information presently available[2, 20, 25] of any of the organic families. Somewhat similar but a little less studied are the excited \( \tilde{A}^1E \) states of the organometallic family[2, 9, 26, 27] MCH\(_3\) (M=Mg, Ca, Zn, and Cd). Both these families introduce a complication into the PES that
the “nearly-aromatic” molecules lack. They have significant spin-orbit coupling that, strictly speaking, causes the CI at the symmetric point to become an avoided crossing.

All of the above Jahn-Teller active systems share a common characteristic. The two dimensions along which the electronic degeneracy of the CI is raised lie in a space spanned by several (3 or 4) doubly degenerate normal coordinates transforming according to a unique irreducible representative of the symmetry group characteristic of molecule at the CI. In Jahn-Teller language these are multi-mode problems.

The remaining Jahn-Teller active families for which there is presently considerable experimental data available[28] are the metal trimer systems. These fall into two categories, the alkali metal trimers (Li$_3$, Na$_3$, and K$_3$) and the coinage metal trimers (Cu$_3$, Ag$_3$, Au$_3$). There is a well-known spectroscopic transition $2E'' - ar{X}^2E'$, which has produced considerably more information on the excited state, although information on the $\bar{X}^2E'$ state is slowly forthcoming. Clearly these systems all have the possibility of spin-orbit coupling turning the CI into an avoided crossing. However they all also share an important simplifying feature. There is only a single normal mode of $e'$ symmetry that is Jahn-Teller active. Thus the problem of determining the orientation of the 2-dimensional Jahn-Teller distortion vector in the normal coordinate space is rendered trivial.

All the molecules discussed above have an $n$-fold symmetry axis where $n$ ranges from 3 to 7 and correspondingly a Jahn-Teller active state that transforms according to one of the doubly degenerate $E$ representations. For spectroscopic applications it has been traditional to represent the Jahn-Teller PES ($U_\pm$) as a function of the normal coordinates $i$ (in the vicinity of the CI) by an analytical expression of the form,[28]

$$U_\pm = \sum_{i=1}^{M-r} \frac{1}{2} \lambda_i Q_i^2 + \sum_{i=M-r+1}^{M} \frac{1}{2} \lambda_i \rho_i^2 \pm \rho_i k_i \left( 1 + \frac{2 g_{ii} \rho_i}{k_i} \cos(n \phi_i) + \frac{g_{ii}^2 \rho_i^2}{k_i^2} \right)^{1/2}$$

$$\approx \sum_{i=1}^{M-r} \frac{1}{2} \lambda_i Q_i^2 + \sum_{i=M-r+1}^{M} \frac{1}{2} \lambda_i \rho_i^2 \pm [k_i \rho_i + g_{ii} \rho_i^2 \cos(n \phi_i)]$$

(1)

where we have introduced for the $r$ degrees of freedom that remove the degeneracy, polar normal coordinates $Q_{i,\pm} = \rho_i e^{\pm \sqrt{-1} \phi_i}$ that span the space, $k_i = \left( \frac{\partial U}{\partial Q_{i,\pm}} \right)_0$, and $g_{ii} = \left( \frac{\partial^2 U}{\partial Q_{i,\pm}^2} \right)_0$ and reference the zero of energy to the vibrationless level of the $(M-r)$ modes that are not Jahn-Teller active. Note that $n$ in $\cos(n \phi_i)$ is determined by the point group symmetry of the molecule. The terms indicated above are typically included in the expression for the PES, although some may be zero for a particular molecule. In some cases additional terms are included[28, 29] in the expansion of the PES.
The form above corresponds to the traditional champagne bottle PES, in the space of the Jahn-Teller distortion coordinates. If $g = 0$ the CI lies above an equal potential moat (along $\phi$). The separation of the moat from the CI is the linear Jahn-Teller stabilization energy, $\epsilon^1$. For $g \neq 0$ the moat has barriers, $\epsilon^2$, separating equivalent local minima, caused by the quadratic Jahn-Teller effect. While the vibronic energy levels are sensitive to all aspects of the PES, it is usually considered to be characterized experimentally if values are obtained for the quantities $\epsilon^1$, $\epsilon^2$, and the geometry of the distorted minimum, the latter allowing the magnitude of the Jahn-Teller effect for each of the normal modes to be determined.

These same quantities are of course obtainable from quantum chemistry calculations of the PES and comparison of them to the experimental values constitutes an important benchmark for the computed surface. There are of course numerous procedures and programs (see below) for computing the electronic energies. Once that has been done, we have used three separate approaches to obtain values for comparison to experiments. (i) The simplest, but most computational intensive (oftentimes prohibitively intensive) is simply to calculate a grid of points over the entire portion of the PES of interest.[21] Given this grid, it is straightforward to extract values for $\epsilon^1$, $\epsilon^2$, the geometry of the global minimum, etc. (ii) A second approach is to calculate only the energies of the CI and the global minimum and the latter’s geometry.[30] The difference of the calculated energies gives the Jahn-Teller stabilization energy. The geometry of the global minimum gives the direction of the Jahn-Teller distortion. (iii) The third approach is to calculate the global minimum and distorted geometry.[30] Given that the geometry of the CI is known, all the desired quantities can be calculated using an assumed analytical form of the PES, e.g., Eq. (1). The last approach is computationally simplest and has been surprisingly successful in replicating experimental results, perhaps because the electronic computation involves only the global minimum, where it is expected to perform very well.

The choice of the computational method is of course highly dependent upon the molecule. Methods we have employed include density functional theory for the global minimum, the approach of Robb, et al.,[1] as contained in Gaussian 98 for the CI, and state-averaged CASSCF calculations using the Columbus package. Normal coordinate vectors at the CI also must be determined and CADPAC and ACESII have been employed for this purpose.

III. OUTLOOK

In the past few years the first notable successes have occurred with good agreement having been obtained between calculated PES’s and semi-empirical ones obtained from spectroscopic measurements. The results for the ground PES’s of $C_5H_5$ and $C_6H_6^+$ are excellent examples of such successes.
However many issues remain to be clarified. The general problem of computing a PES near a CI is far from a routine task. Many more molecules will need to be investigated before the best and least computationally expensive approaches can be selected with a degree of certainty.

Experimentally more data is needed but the open-shell nature of Jahn-Teller active states make the experiments difficult. Questions also abound concerning the sufficiency of the simple spectroscopic models to describe the actual PES of many molecules. Only more experiments and comparisons to calculations can answer these questions.

IV. ACKNOWLEDGMENT

The author gratefully acknowledges the support of the U. S. National Science Foundation via grant CHE-0211281.


I. Sioutis, G. Tarczay, and T. A. Miller, to be published.


H$_3^+$ in the Electronic Triplet State

António J. C. Varandas, Alexander Alijah,
Mihail Cernei, and Luís Pedro Viegas
Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal

I. INTRODUCTION

The H$_3^+$ ion has a fundamental importance in astrophysics and astrochemistry. Since it is the lightest triatomic molecule with only two electrons, many of its calculated ro-vibronic term values for the electronic ground state are known to about spectroscopic accuracy. This has become possible due to sophisticated theoretical methods for the calculation of both the electronic energy and the corresponding ro-vibrational bound states. For details on recent experimental and theoretical developments, see Refs. [1–6] and references therein.

Although investigations involving higher excited electronic states of H$_3^+$ are less abundant, there have been recent advances that justify the present review. Back in 1974, Schaad and Hicks [7] studied a large number of electronic states and found that the lowest triplet state is non-repulsive, with an energy minimum at symmetric linear configurations. The stability with respect to dissociation was obtained as 8.13 kcal mol$^{-1}$, likely to be sufficient to support a number of vibrational states. These findings were confirmed and the numerical data determined more precisely by Ahlrichs et al. [8], Wormer and de Groot [9] and Preiskorn et al. [10]. Wormer and de Groot were the first to publish a potential energy surface for this state, although their surface did not reach spectroscopic accuracy. In 1995, two papers have appeared by Tennyson [11] and McNab [12] that stated that information on the ro-vibronic levels supported by this electronic state would be highly desirable, as some of the yet unassigned lines in hydrogen plasmas might belong to the triplet state. Only in 2001 such information became available, when within just two weeks two of the present authors and their collaborators [13] and independently Sanz et al. [14] published the results of

*Electronic address: varandas@qtvs1.qui.uc.pt
†Electronic address: alijah@ci.uc.pt
bound state calculations based on new potential energy surfaces. It is on such developments that we focus on the present review.

II. POTENTIAL ENERGY SURFACES

The lowest electronic states of H$_3^+$ can be derived easily by initially assuming equilateral arrangement of the nuclei, i.e. D$_{3h}$ symmetry. The three hydrogenic 1s atomic orbitals can then be combined to form molecular orbitals of $a'_1$ and $e'$ symmetry. The electronic ground state, $X^1A_1$, is derived from the electronic configuration ($a'_1$)$^2$. The excited configuration $a'_1 e'$, however, leads to a singlet and a triplet state of $E'$ symmetry. These states are Jahn-Teller instable. We will consider here the triplet state, denoted as $1^3E'$. The potential energy surface of this state is split by vibronic interaction into a lower sheet, $a^3\Sigma^+_u$, with three equivalent minima at symmetric linear arrangements of the three nuclei, and an upper sheet, $2^3A'$, that resembles an upright cone. At symmetric equilateral arrangements there is a conical intersection of the two sheets.

While in principle the degeneracy of the two sheets at the conical intersection should be an automatic outcome of a surface fit, this requires in general the use of a $2 \times 2$ potential matrix, and hence roughly three times more labor than a fit to a single-sheeted surface. However, single-sheeted forms [15] are known to introduce small inaccuracies in describing the degeneracy locus. Although such inaccuracies did not manifest on the vibrational calculations, this may not be the case when the two sheets are simultaneously used to solve the dynamics problem, as when dealing with the full non-adiabatic problem. To overcome this difficulty, an extension of the popular double many-body expansion method has been proposed [16] to represent a double-valued potential energy surface that ensures the degeneracy at the intersection line to any degree of accuracy but employing a single-sheeted like formalism.

In their article, Sanz et al. [14] present a global fit based on the method of diatomics-in-molecules [17–19] with extra flexibility introduced by adding a three-body [20] energy term. Thus, their approach has some similarity with the DIM-3c [21] method employed for the XH$_2$ systems (X is an halogen atom). In turn, the surface used in our earlier work [22] is based on an expansion in hyperspherical coordinates. However, this was designed for bound state calculations, and hence no attempt has been made to accurately describe the dissociation channels. This issue has been carefully taken into consideration in subsequent papers [15, 16, 23], while the set of ab initio points has also been enlarged for a more accurate description of the full potential energy surface [16]. Specifically, 3621 ab initio points have been employed for each sheet of the surface, covering one sixth of the configuration space. In fact, because each of the three sectors containing two equivalent parts which are related by reflection through a plane of symmetry, it is sufficient to distribute the data points over just one
Figure 1: Vibronic states on the lower sheet. Shown by the dashed segments are the states that are mathematically allowed but physically forbidden.

Jahn-Teller distortion of the symmetric $D_{3h}$ nuclear configurations in the degenerate electronic state, $1^3E'$, leads to a linear equilibrium structure on the lower sheet, $\alpha^3\Sigma_u^+$, of the split potential energy surface. For symmetry reasons, there are three equivalent minima, which are related by permutation of the nuclei. The rovibronic wavefunctions of the lower sheet are therefore linear combinations of the three approximate wavefunctions $|\Psi_{1,11,111}^{\pm}\rangle$ localised sixth of the $H_3^+$ configuration space. Such electronic $ab\ initio$ energies were calculated in $C_s$ symmetry with the MOLPRO package, with a full CI being performed in the large basis of 165 functions generated from Dunning’s cc-pV5Z basis set. The best representation of the electronic energy for the two adiabatic sheets currently available is probably that reported recently [16] using a single-sheeted-type DMBE theory [24]; for a general multivalued DMBE approach, see Refs. [25, 26].

III. ROVIBRONIC STATES ON THE LOWER SHEET

Jahn-Teller distortion of the symmetric $D_{3h}$ nuclear configurations in the degenerate electronic state, $1^3E'$, leads to a linear equilibrium structure on the lower sheet, $\alpha^3\Sigma_u^+$, of the split potential energy surface. For symmetry reasons, there are three equivalent minima, which are related by permutation of the nuclei. The rovibronic wavefunctions of the lower sheet are therefore linear combinations of the three approximate wavefunctions $|\Psi_{1,11,111}^{\pm}\rangle$ localised...
Figure 2: Rotational structure, including \( \ell \)-type doubling, of the \((0,1^1,0) \pm \) states on the lower sheet. Shown by the dashed segments are the states that are mathematically allowed but physically forbidden.

in their respective minima. Superposition of such localised functions yields a one-dimensional representation

\[
|\Psi_A^{\pm}\rangle \sim |\Psi_I^{\pm}\rangle + |\Psi_{II}^{\pm}\rangle + |\Psi_{III}^{\pm}\rangle
\]

and a two-dimensional representation

\[
|\Psi_{E,\xi}^{\pm}\rangle \sim |\Psi_I^{\pm}\rangle + \omega |\Psi_{II}^{\pm}\rangle + \omega^2 |\Psi_{III}^{\pm}\rangle
\]

\[
|\Psi_{E,\eta}^{\pm}\rangle \sim |\Psi_I^{\pm}\rangle + \omega^2 |\Psi_{II}^{\pm}\rangle + \omega |\Psi_{III}^{\pm}\rangle
\]

where \( \omega = e^{\frac{2\pi i}{3}} \). The two components of the two-dimensional representation are related by complex conjugation. The symmetry classification of the functions defined above is with respect to the three-particle permutation inversion group \( S_3 \) or \( S_3 \times I \), a group isomorphic to the molecular symmetry group \( D_{3h}(M) \) [27]. The functions \( |\Psi^{\pm}\rangle \) on the other hand, which describe the localised linear structures, are classified according to irreducible representations of the linear
molecule symmetry group $D_{\infty h}(M)$. They can be expressed in terms of linear molecule basis functions as

$$|\Psi^\pm\rangle = \frac{1}{\sqrt{2}}|v_1v_2^\ell v_3\rangle \left(|N\ell m\rangle \pm |N - \ell m\rangle\right)$$  \hspace{1cm} (3)

For $\ell = 0$, only the function $|\Psi^+\rangle = \frac{1}{\sqrt{2}}|\Psi^\ell\rangle$ exists. $v_1$, $v_2$ and $v_3$ are the quantum numbers of the symmetric stretching vibration $\nu_1$, the double degenerate bending vibration $\nu_2$ and the antisymmetric stretching vibration $\nu_3$. $\ell$ is the vibrational angular momentum, which takes the values $\ell = v_2, v_2 - 2, \ldots, -v_2$. In the above equations, electronic spin has been neglected and $N$, where $N = J - S$, and its external projection $m$ are used in the rotational part. The internal projection has to be identical to the vibrational angular momentum $\ell$. The two states with $\ell \neq 0$ have opposite parity and are split in energy, an effect known as $\ell$-type doubling. The results expressed in Eqns. (1) and (2) show that for each rovibronic state as described in terms of traditional linear molecule quantum numbers, Eq. (3), a one-dimensional and a two-dimensional component arises due to delocalisation.

It has become apparent that for the calculation of the rovibronic states a method is required which treats the three equivalent structures on equal footing, such as a hyperspherical method. Indeed, all the results reported so far [13–16, 28, 29], for $\text{H}_3^+$ or $\text{D}_3^+$, were obtained with a hyperspherical method. For a long time, a drawback in the use of hyperspherical methods has been the difficulty of assigning the calculated states with spectroscopic quantum numbers. This problem has been solved due to the development of an algorithm for semi-automatic assignments [30]. The basis of this algorithm is the exact symmetry of the states, as derived for the present case in Ref. [29] and presented in Table 1 of that paper, and the recognition of vibrational or rotational progression patterns. Applying this algorithm, we have assigned all vibrational states up to the dissociation limit [15] and investigated the rovibronic structure of the lowest 19 bands [29]. Since there is a conical intersection between the two sheets of the potential energy surface, there should also be a topological effect due to the geometrical phase (Berry’s phase). Explicit calculations for the four lowest vibrational states showed that this effect is negligible [13].

Some of our results are summarised in Figures 1 and 2. In the first figure we have superimposed the vibrational structure with the curve of the energy minimum path that connects equivalent minima. The vibrational states of symmetries $A_1^\prime$ and $A_2^\prime$ are shown in the left and right stacks, respectively, while the states of symmetry $E'$ are arranged in the centre of the figure. Each of the states of a one-dimensional representation has a counterpart of $E'$ symmetry, with a small splitting between the two components. Only the lowest two vibrational states are below the barriers. Figure 2 shows the rotational structure of the state with $(v_1, v_2^\ell, v_3)$ equal $(0, 1^1, 0)$. For each rotational level we see not only the two counterparts of $A_1^\prime/A_2^\prime$ and $E'$ symmetry, but also the effect of $\ell$-type
doubling between the \((0,1^1,0)^+\) and \((0,1^1,0)^-\) states. The \pm\ sign corresponds to the sign in the definition of the functions in Eq. 3.

**IV. ROVIBRONIC STATES ON THE UPPER SHEET**

Figure 3 shows the positions of the quasi-bound vibrational cone states obtained in Ref. [23], as calculated without inclusion of the geometrical phase (NGP states) and with its inclusion (GP states). As expected, for the cone states the geometrical phase cannot be neglected. Nevertheless it is useful for the purpose of assigning spectroscopic quantum numbers to the calculated states to consider also the NGP case, since there is a correlation between the two sets of states. The states are assigned as \((v_1, v_2^j)\), where \(v_1\) is the symmetric stretch quantum number and and \(v_2\) that of the degenerate vibration. \(j\) is the pseudo-rotational quantum number defined as \(|j| = |\ell| + \alpha\) where \(\alpha = 0\) in the NGP case and \(\alpha = \frac{1}{2}\) in the GP case.
This work has the support of the Fundação para a Ciência e a Tecnologia, Portugal.

[18] P. J. Kuntz, in Dynamics of Molecular Collisions, Part B, edited by W. Miller (Plenum, New York, 1976), pp. 53-
A Continuous Representation of Seams of Conical Intersection – A Group Homomorphism Approach

Seungsuk Han
Department of Chemistry, Myong Ji University, Yongin, Kyunggido 449-728 Korea

and

David R. Yarkony
Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218, U.S.A.

I. Introduction

The vectors defining the branching space can fluctuate dramatically along a conical intersection seam. This problem can be resolved by exploiting a group homomorphism that arises from the freedom to mix the degenerate wave functions at the crossing point. This provides the basis for a smooth function representation of the seam.

The branching\(^1\) or g-h\(^2\) space is the subspace of nuclear coordinate space in which the linear dependence of the energy on displacements is evinced. The vectors defining this space are not uniquely defined since they are constructed from the degenerate wave functions at the conical intersection. These wave functions are in turn defined only up to a unitary mixing among themselves. This arbitrariness results in erratic behaviour of the matrix elements computed along the seam.\(^3\) In this review the problem is outlined, its consequences discussed and its resolution using a group homomorphism discussed. Three classes of two state conical intersections are considered: (a) the nonrelativistic or coulomb Hamiltonian, \(H^0(r; R)\); and two instances of intersections for Hamiltonians that include relativistic effects, (b) \(H'(r; R) = H^0(r; R) + H^{so}(r; R)\), with no spatial symmetry and (c) \(H'(r; R) = H^0(r; R) + H^{so}(r; R)\), with \(C_\text{s}\) symmetry imposed. Here \(r (R)\) denotes the electronic (nuclear) coordinates, \(H^{so}\) denotes the spin-orbit operator, and wave functions for the last two cases, referred to as relativistic wavefunctions, will be treated in the large component only approximation\(^4\) and will be restricted to molecules with an odd number of electrons. In section II degenerate perturbation theory\(^7\) is used to determine the relevant Hamiltonians in the vicinity of a point of conical intersection, \(R_x\). The relation between these Hamiltonians and the branching spaces is established. This relation permits the freedom to transform the degenerate wave functions amongst themselves to be related to a transformation of
the branching space. This final relation, a group homomorphism, provides for a
continuous description of the branching space along the seam.

II. Perturbative Determination of $H^e$ near $R_x$.

We begin by assuming that the adiabatic wave functions, $\Psi_f(r; R)$, which satisfy

$$[H^e (r; R) - E_f (R)]\Psi_f (r; R) = 0$$  \hspace{1cm} (1)$$

are expanded in a configuration state function (CSF) basis $\psi(r; R)$, that is

$$\Psi_f (r; R) = \sum c^f_a (R) \psi_a (r; R)$$  \hspace{1cm} (2a)$$

so that

$$[H_{\text{CSF}} (R) - IE_f] \psi(R) = 0$$  \hspace{1cm} (2b)$$

where $H_{\text{CSF}} (R)$ is the electronic Hamiltonian in the CSF basis. In case (a) the two
state intersection involves two adiabatic states, $\Psi^K$ and $\Psi^L$. Cases (b) and (c) are
more subtle. In those cases the two state intersection involves four wave functions
since time reversal symmetry renders each state doubly degenerate, Kramers’
doublets, that is $\Psi^K, \Psi^L$ and $T\Psi^K, T\Psi^L$ must be considered, where $T$ is the time
reversal operator. To account for this a time reversal adapted CSF bases is used.6 In
a time reversal adapted basis both $\Psi^K$ and $T\Psi^K$ are included in the basis.

II.A. $H^e$ near a conical intersection in the crude adiabatic basis

In the vicinity of a conical intersection of states $K, L$ at $R_x$ it is convenient
to replace the CSF basis with the crude adiabatic basis,

$$\Psi^k (r; R; R_x) = \sum c^k_a (R) \psi_a (r; R) \quad \text{for} \quad k = 1 - N_{\text{CSF}}$$  \hspace{1cm} (3)$$

Below $\Psi^k (r; R; R_x)$ will be abbreviated $\Psi^k (r; R)$ when no confusion will result.
Next, expand $\Psi^f (r; R)$ in the crude adiabatic basis as

$$\Psi_f (r; R) = \sum_k \eta^k (R) \Psi^k (r; R)$$  \hspace{1cm} (4)$$

and partition the crude adiabatic basis into a $Q$-space consisting of the $N_{\text{deg}}$
functions which are degenerate at $R_x$ and its orthogonal complement the $P$-space.
Then eq. (4) can be rewritten as

$$\begin{pmatrix}
H^{QQ} - E & H^{QP} \\
H^{PQ} & H^{PP} - E
\end{pmatrix}
\begin{pmatrix}
\eta^Q \\
\eta^P
\end{pmatrix} =
\begin{pmatrix}
0 \\
0
\end{pmatrix}$$  \hspace{1cm} (5a)$$
where \( H_{k,l}^{AB}(R) = H_{k,l}^{c}(R) = c_k(R_x)^{\dagger} H^{\text{CSF}}(R) c_l(R_x) \) for \( k \in A \) and \( l \in B \). Eq. (5a) can be solved for \( \eta^Q \) to yield

\[
[H^{QQ} + H^{PQ} (E - H^{PP})^{-1} H^{PO} - E] \eta^Q = 0
\]

Since we are interested in eq. (5b) to first order in \( \delta R \), displacements from \( R_x \), we expand \( H^{\text{CSF}}(R) \) in a Taylor series

\[
H^{\text{CSF}}(R) = H^{\text{CSF}}(R_x) + \nabla H^{\text{CSF}}(R_x) \cdot \delta R
\]

and transform to the crude adiabatic basis giving

\[
H_{k,l}^{c}(R) = E_k(R_x) \delta_{k,l} + c_k(R_x)^{\dagger} \nabla H^{c}(R_x) \cdot \delta R \ c_l(R_x)
\]

\[
\equiv E(R_x) + h^{k,l} \cdot \delta R
\]

where \( E(R_x) \) is the diagonal matrix of eigenvalues at \( R_x \). Thus \( H^{Q}, H^{PQ} \) begin at first order in \( \delta R \) and to first order in \( \delta R \) eq. (5b) becomes

\[
[h \cdot \delta R - \epsilon I] \eta^Q = 0
\]

where \( \epsilon = E - E_h(R_x) \) and the superscript 0 denotes the zeroth order contribution. Eq. (7) is the starting point of our analysis.

II. B. Explicit Hamiltonians

For case (a) and \( N_{\text{deg}} = 2 \) and \( h \) is a vector of symmetric (rather than hermitian) matrices so that eq. (7) becomes

\[
[(s^{K,L} \cdot \delta R) - \epsilon I + (g^{K,L} \cdot \delta R) \sigma_z + (h^{K,L} \cdot \delta R) \sigma_z = 0
\]

or

\[
[(s^{K,L} \cdot \delta R) - \epsilon I + \Gamma^a \cdot \Delta^a = 0
\]

where

\[
s^{K,L} = (h^{KK} + h^{LL})/2, \quad g^{K,L} = (h^{KK} - h^{LL})/2,
\]

\[
\Delta^a = (\sigma_a, \sigma_z).
\]

Cases (b) and (c) are less straightforward, since as noted above, \( \Psi_k \) and \( \Psi_l \) must be accompanied by the time reversed states \( T \Psi_k \) and \( T \Psi_l \), so that \( N_{\text{deg}} = 4 \). However, time reversal symmetry also serves to simplify the analysis by establishing relations among the \( h^{K,L} \). The details can be found in Refs. 6,8,9, where it is shown that eq. (7) becomes

\[
[(s^{K,L} \cdot \delta R) - \epsilon I + \Gamma^b \cdot \Delta^b = 0
\]

Here

\[
\Delta^b = (h^{KL}, -h^{K,L}, g^{KL}, -g^{K,L}, h^{KTL}, -h^{K,TL}) \cdot \delta R = (v^{(1)}, v^{(2)}, v^{(3)}, v^{(4)}, v^{(5)}) \cdot \delta R
\]

and
\[\Gamma^h = (\Gamma_x^h, \Gamma_y^h, \Gamma_z^h, \Gamma_y^h, \Gamma_w^h)\]  
(9c)

with \(\Gamma_k^h = [\sigma; 0], k = x,y,z, \Gamma_y^h = [0; i\sigma_z]\) and \(\Gamma_w^h = [0; \sigma_y]\) and

\[\{a; b\} = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}\]  
(10)

where \(a\) and \(b\) are \((2\times2)\) matrices. When \(C_s\) symmetry is present \(h^{KK}(R) = 0\) so that eq. (7) becomes

\[\left(\begin{array}{ccc} k^1 & k^2 & k^3 \\ a_{k^1} & a_{k^2} & a_{k^3} \end{array}\right) \cdot \delta R = 0\]  
(11a)

Since the \(\Gamma^h, k = x,y,z\) are block diagonal it is sufficient to consider

\[\left(\begin{array}{ccc} k^1 & k^2 & k^3 \\ a_{k^1} & a_{k^2} & a_{k^3} \end{array}\right) \cdot \delta R = 0\]  
(11b)

or

\[\left(\begin{array}{ccc} k^1 & k^2 & k^3 \\ a_{k^1} & a_{k^2} & a_{k^3} \end{array}\right) \cdot \Delta^c = 0\]  
(11c)

where

\[\Delta^c = (h^{K,L}, h^{K,L}, g^{K,L}) \cdot \delta R = (v^{(1)}, v^{(2)}, v^{(3)}) \cdot \delta R\]  
(11d)

II.C. Eigenvalues and Branching spaces

The \(v^{(k)}, k = 1-N^h\) constitute the branching space of the conical intersection at \(R_x\). From eqs. (8a), (9a) and (11c) it can be shown the eigenvalues of eq. (7) are given by

\[E(R + \delta R) = s^{K,L} \cdot \delta R \pm \sum_{i=1}^{N^h} (v^{(i)} \cdot \delta R)^2 \]  
(12)

where \(N^h\) is the dimension of the branching space, being 2, 5, 3 for cases (a), (b) and (c) respectively. Eq. (12) proves the previous assertion that it is in the branching space that the linear or conical topography is evinced.

Figure (1a) presents the branching space, \(h^{K,L}\) and \(g^{K,L}\), for a conical intersection of the \(^2\Sigma_1^+\) and \(^3\Pi_2^+\) states of BH2 at an \(R_x\) with \(C_{2v}\) symmetry. Figure (1b) presents the branching space, \(h^{K,L}\), \(h^{K,L}\) and \(g^{K,L}\), for a conical intersection of the \(^3\Sigma_1^+\) and \(^3\Pi_1^+\) states of HOH2 at an \(R_x\) with \(C_{2v}\) symmetry. In neither case do the \(v^{(i)}\) have the expected symmetry. The, tuning mode \(g^{K,L}\) are expected to be totally symmetric, while the coupling modes, the \(h^{K,L}\) are expected to have \(B_2\) or \(\Pi\) symmetry respectively. These expectations are based on the assumption that the degenerate wave functions are symmetry adapted. However this need not be the case, since the degenerate wave functions are determined only up to a unitary transformation of the degenerate states. Numerically one only gets very close to the
conical intersection so that the wave functions do not have the expected symmetry. This absence of symmetry is a disaster when it comes to describing the parameters of branching space, the magnitudes of the $v(0)$ and their directions, along the conical intersection seam. These, 'nascent' $v(0)$ vary erratically on the seam. They cannot be interpolated or extrapolated, that is, trends along the seam are unpredictable. Fortunately this problem can be solved using the same flexibility in the degenerate states that caused it. Below we describe how a unitary transformation of the degenerate electronic states can be chosen that automatically recovers any symmetry and makes the $v(0)$ continuous functions of the seam coordinates. We further explain how this can be accomplished without actually knowing the detailed form of the transformation!

![Figure 1](image.png)

**Figure 1.** Nascent vectors spanning branching spaces for (left) a conical intersection of the 1 $^2A_1$ and 1$^2$B$_2$ states in BH$_2$ and (right) a conical intersection of $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ states in collinear HOHH.

### II.D. Invariances and a group homomorphism

At $R_x$ the $N_{\text{deg}}$ degenerate electronic wave functions are defined up to an orthogonal (or unitary) transformation, $u$. Since the $\Gamma$ are basis for the Hamiltonians in question $u^\dagger (\Gamma \Delta) u = (u^\dagger \Gamma u) \Delta' = \Gamma' \Delta'$

where

$$\Delta' = R(u) \Delta$$

and

$$u^\dagger \Gamma_j u = \sum_k \Gamma_{j,k} R(u)_{k,l}$$

(13a)

(13b)
Note that the transformation $\mathbf{R}(u)$ should not be confused with the nuclear coordinates $\mathbf{R}$ and $\delta \mathbf{R}$. Factoring out the $\delta \mathbf{R}$ from the definition of $\Delta$ in eq. (13a) gives
\[
\Delta^{(i)} = \sum_j R(u)_{k,j} \Delta^{(j)}.
\] (13c)

Eq. (13c) is a central result of this work. Before discussing its significance it is useful to determine the explicit form of $\mathbf{R}(u)$.

For case (a)
\[
u^a = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}, \quad \mathbf{R}(u) = \begin{pmatrix} \cos 2\theta & -\sin 2\theta \\ \sin 2\theta & \cos 2\theta \end{pmatrix}.
\] (14a)

This is readily seen from eq. (13b) since
\[
u^a \sigma_x u^a = \cos 2\theta \sigma_x + \sin 2\theta \sigma_z \quad \text{(14b)}
\]
\[
u^a \sigma_z u^a = \sin 2\theta \sigma_x + \cos 2\theta \sigma_z \quad \text{(14c)}
\]

For case (c)
\[
u^c = \begin{pmatrix} e^{-i(\alpha+\gamma)/2} \cos \theta & -e^{i(\alpha+\gamma)/2} \sin \theta \\ e^{-i(\alpha-\gamma)/2} \sin \theta & e^{i(\alpha-\gamma)/2} \cos \theta \end{pmatrix},
\]
\[
\mathbf{R}(u) = \begin{pmatrix} c2\theta \cos \alpha - s2\theta \sin \alpha & c2\theta \cos \gamma \sin \alpha + s2\theta \cos \gamma \\ -c2\theta \cos \gamma \sin \alpha - s2\theta \cos \gamma & c2\theta \cos \alpha + s2\theta \sin \alpha \end{pmatrix}
\] (15)

which follows from eqs. (14a), (14b), and the following observations
\[
u^c \sigma_y u^c = \sigma_y \quad \text{(16a)}
\]
\[
u^c \sigma_z u^c = \sigma_z \quad \text{(16b)}
\]
\[
u^c \sigma_x u^c = \cos 2\gamma \sigma_x - \sin 2\gamma \sigma_y \quad \text{(16b)}
\]
\[
u^c \sigma_y u^c = \sin 2\gamma \sigma_x + \cos 2\gamma \sigma_y \quad \text{(16b)}
\]

\[
\begin{pmatrix} e^{-i\alpha} & 0 \\ 0 & e^{i\alpha} \end{pmatrix} \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} e^{-i\gamma} & 0 \\ 0 & e^{i\gamma} \end{pmatrix} = \begin{pmatrix} e^{-i(\alpha+\gamma)} \cos \theta & -e^{i(\alpha-\gamma)} \sin \theta \\ e^{-i(\alpha-\gamma)} \sin \theta & e^{i(\alpha+\gamma)} \cos \theta \end{pmatrix}
\] (16c)

where $u^c = \begin{pmatrix} e^{-i\gamma} & 0 \\ 0 & e^{i\gamma} \end{pmatrix}$, and $c = \cos \alpha$ and $s = \sin \alpha$.  

43
Finally $u^\gamma$ is constructed from products of $[u^\delta; 0], [u^\epsilon; 0]$ and the permutation $1/2[\sigma_1 + 1; 1 - \sigma_2]$. It is straightforward to see that $R([u^\delta; 0])$ and $R([u^\epsilon; 0])$ are elements of $O^+_5$.

The $R(u)$ in eqs. (14a) and (15) are seen to be the most general elements of $O'(2)$ and $O'(3)$, the groups of rotations two and three dimensional vectors respectively. A similar result is obtained in case (b) with $R(u^b)$ being the most general element of $O'(5)$. This result is proven in Ref. 9. Further the $u$ form a group, so that $u^{-1}u^{x^2} = u^{x^2}$, for $x = a, b, c$. Then from eqs. (13a)-(13c), $R(u^{x^2}) = R(u^{x^2})$. Thus $R(u)$ is a group homomorphism between a group of unitary ( or orthogonal in case (a) ) matrices in the wave function space and a rotation group in the branching space. In particular for cases (a), (b) and (c) respectively, $u$ an element of $O^+_2$, $SU(2)$ (the group of 2x2 unitary matrices with determinant +1) and Sp(4) (the symplectic group of order 4, a subgroup of SU(4)), while $R(u)$ is an element of $O^+_2$, $O^+_3$ and $O^+_5$.

Since $R(u)$ spans all of $O^+_x$, given an $R(u)$ there is a corresponding $u$ that generates any desired rotation. The problem of the erratic behaviour of the representation of the branching space can be addressed using that observation. Recall that in the examples discussed above, point group symmetry required the branching space vectors to be orthogonal. While the nascent $v^{(i)}$ are not mutually orthogonal this property can be imposed. Using eq. (13c), with the superscript $t$ denoting the transpose, so that $v^{(i)}_t$ is a row vector, we have

$$v^{(k)}_t M v^{(j)} = \sum_i R(u)_{k,i} v^{(j)}_t M \sum_i R(u)_{i,l} v^{(l)} = (R(u) S R(u)^t)_{k,l}$$

(17a)

where the overlap matrix $S = v^{(i)}_t M v^{(i)}$. Here, for generality, we have introduced $M$, a metric matrix, which, although it may be $I$, depends on the choice of internal coordinates. Then the requirement that the $v^{(k)}_t$ be orthogonal is achieved by choosing $R(u) = \tilde{R}(u)$ to diagonalize $S$

$$S_{k,l} = (\tilde{R}(u) S \tilde{R}(u)^t)_{k,l}$$

(17b)

The orthogonal $v^{(k)}_t$ are then obtained from eq. (13c). Thus the affect of the transformation $u$ on the g-h space can be determined without explicitly determining $u$ itself! For a given point of conical intersection two distinct sets of nascent $v^{(i)}_t$ that are possible must be related to each other by an $R(u)$. Thus the $v^{(k)}_t$ determined by eqs. (17a), (17b) are unique up to trivial rearrangements and overall phases. Consequently this transformation extracts the intrinsic, continuous, variation in the branching space along a seam from its ‘random’ background.

Case (a) is particularly simple and revealing. Here (suppressing the superscript $K,L$)

$$S = \begin{pmatrix} h' \cdot h & h' \cdot g \\ g' \cdot h & g' \cdot g \\ \end{pmatrix}$$

(18a)
is diagonalized by the rotation $R(u^\theta)$ with the rotation angle $2\theta$ obtained from

$$\tan 4\theta = \frac{2h' \cdot g}{h' \cdot h - g' \cdot g} \quad \text{(18b)}$$

This result was previously obtained from the requirement that $g' \cdot h = 0$ using the explicit form for the primed vectors obtained eq. (14). The later approach, while simple in case (a), becomes tedious or even intractable for cases (b) and (c). The approach presented here obviates those problems.

The utility of this transformation is evinced from a computational perspective in Figs. (2a) and (2b) which report the $v^{d,b}$, the orthogonal vectors, corresponding to the nascent vectors in Fig. (1a) and (1b) respectively. In these figures the requisite symmetry adaptation is clearly evident. Because this representation is unique, up to sign changes and ordering of the eigenvectors, it can be readily chosen continuous along the seam. Note that orthogonalization procedures such as the Schmidt orthogonalization would not achieve the desired symmetrization or continuity along the seam. This continuity has been used to expedite convergence of algorithms that locate energy minimized conical intersections.  

Figure 2. Vectors defining branches spaces described in Fig. (1a) and (1b) following rotation based on eq. (13b).

III Summary

We have proven in general that the branching space of a two state conical intersection can be represented by a set of mutually orthogonal vectors that change
continuously along the seam of conical intersections. This result applies to branching spaces of dimension 2, 3 and 5. While this result may seem intuitively obvious it should not be so construed. Recently we have developed algorithms to locate three state conical intersections. These intersections have a branching space of dimension 5 but the three degenerate wave functions are determined only up to a three parameter rotation. Thus there are not enough parameters to make the five vectors mutually orthogonal.

Acknowledgement

This work was made possible, and reviews work sponsored, by National Science Foundation, Air Force Office of Scientific Research, and Department of Energy Office of Basic Energy Science grants to D. R. Y.

Quantum Dynamics at Conical Intersections Treated Within the Multi-mode Vibronic Coupling Approach and its Generalizations

Horst Köppel

Theoretical Chemistry, University of Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

I. INTRODUCTION

Vibronic coupling, i.e. the interaction of different electronic states through the nuclear motion, is of paramount importance for spectroscopy, collision processes, photochemistry etc., and quite general for electronically excited state processes of even small polyatomic molecules. One of its most important consequences is the violation of the Born-Oppenheimer, or adiabatic, approximation [1] whereby the nuclear motion no longer proceeds on a single potential energy surface but rather on several surfaces simultaneously. Nonadiabatic coupling effects are of singular strength at degeneracies of these surfaces, in particular at conical intersections, which have emerged in recent years as paradigms of nonadiabatic excited-states dynamics in quite different fields [2, 3].

In the Heidelberg and Munich groups we have developed over the past decades simple, but also efficient and rather flexible methods to deal with the nuclear dynamics in such systems, based on the so-called linear vibronic coupling approach [4–7]. It relies on the well-established concept of diabatic electronic states [8–10], where the singularities of the adiabatic electronic wavefunctions at the intersection are removed by a suitable orthogonal transformation and the off-diagonal, or coupling, elements arise from the potential rather than kinetic energy (at least to a sufficiently good approximation). The potential coupling terms can be expanded in a Taylor series, and the truncation after the first (or second) order immediately gives the linear (or quadratic) vibronic coupling scheme. The resulting model potential energy surfaces turn out to be sufficiently flexible to cover a variety of interesting phenomena and be applicable to different molecular systems [4, 6, 7]. To generalize the approach, it has been suggested more recently to be applied only to the adiabatic-to-diabatic mixing angle (see below) [11, 12]. This leads to an enormous increase in flexibility and renders it applicable also to photochemical problems, at least in principle. The methodological developments are briefly surveyed in Sec. II below. Sec. III gives two selected
applications and Sec. IV concludes with a short summary.

II. VIBRONIC HAMILTONIANS

A. The linear (and quadratic) vibronic coupling Hamiltonian

As stated in the introduction, we start from a diabatic electronic representation and expand the potential energy matrix elements $W_{nm}(Q)$ (for the electronic states $n$ and $m$) in a Taylor series in the nuclear displacement coordinates $Q = (Q_1, Q_2, \ldots, Q_f)$. Taking the expansion to be around the origin $Q = 0$ we can write the vibronic matrix Hamiltonian as follows [4, 6, 7]

$$\mathcal{H} = T_N 1 + W.$$  \hspace{1cm} (1)

Here $1$ is the unit matrix in electronic function space and the matrix elements of $W$ read

$$W_{nn} = V_0(Q) + E_n + \sum_i \kappa_i^{(n)} Q_i + \sum_{i,j} \gamma_{ij}^{(n)} Q_i Q_j + \ldots$$  \hspace{1cm} (2a)

$$W_{nm} = \sum_i \lambda_i^{(nm)} Q_i + \sum_{ij} \eta_{ij}^{(nm)} Q_i Q_j + \ldots \quad (n \neq m).$$  \hspace{1cm} (2b)

In Eq. (2), $V_0(Q)$ represents some 'unperturbed' potential energy term which is often identified with that of the electronic ground state and treated in the harmonic approximation. The $E_n$ denote vertical excitation (or ionization) energies, the quantities $\kappa_i^{(n)}$ and $\lambda_i^{(n)}$ are first-order coupling constants (intra- and inter-state, respectively) while the parameters $\gamma_{ij}^{(nm)}$ and $\eta_{ij}^{(nm)}$ represent second-order coupling constants. In the linear vibronic coupling (LVC) approach the latter terms in Eq. (2) are neglected.

The LVC approach embodied in Eq. (2) has been applied for a long time to analyze the vibrational structure of electronic spectra and time-dependent (electronic and vibrational) dynamics of vibronically coupled systems [4, 6, 7]. Strong nonadiabatic coupling effects associated with conical intersections of potential energy surfaces could be unequivocally established in this way. We refer to this literature for a survey of these examples and also for a further discussion of the meaning and implications of the various terms in the Hamiltonian (2).

Over the time, the strict LVC approach has been extended by including selected, or even all, second order terms in Eq. (2). In some cases their effect on the spectrum turned out to be surprisingly large [13]. Fitting the LVC spectra to a result obtained with the inclusion of second order terms, implies effective LVC coupling constants which incorporate some of the higher-order effects. The use of second-order coupling terms may reduce the need for parameter adjustment.
when using ab initio calculated coupling constants to reproduce an experimental spectrum [14]. The ab initio determination of the coupling constants is relatively easy with and without second order terms since no multi-dimensional grid and only a small number of energy points per mode are required owing to the model assumptions underlying Eq. (2).

Finally we point out the close relation of the general Hamiltonian (2) and model Hamiltonians frequently used in Jahn-Teller (JT) theory [15, 16]. There, an analogous Taylor series is used, but many interrelations between the various coupling terms exist due to symmetry. Formally, these JT Hamiltonians are thus a special case of Eq. (2) and are recovered by imposing these restrictions. They have been successfully used to analyze and interpret even high-resolution molecular JT spectra [17]. For similar applications and extensions to cover also couplings to nearby nondegenerate electronic states, see the article by S. Mahapatra in this booklet.

B. The concept of regularized diabatic states

The concept of regularized diabatic states [11, 12] can be understood as a generalization of the ‘conventional’ LVC approach (as outlined above) by applying it to the adiabatic-to-diabatic (ATD) mixing angle only. For illustrative purposes consider the case of two potential energy surfaces \( V_1(Q) \) and \( V_2(Q) \) intersecting at a point \( Q_g = Q_u = 0 \) in two-dimensional nuclear coordinate space. Let their behavior near the origin be described by \( E_0 + \kappa Q_g \pm \delta \kappa Q_g \) along a symmetry-preserving coordinate \( Q_g \) (no interaction between the states) and by \( E_0 \pm \lambda Q_u \) along a symmetry lowering coordinate \( Q_u \) (inducing an interaction). The corresponding LVC Hamiltonian (2) can be written as follows:

\[
\mathcal{H} = (T_N + V_0 + E_0 + \kappa Q_g)1 + \left( \begin{array}{cc} \delta \kappa Q_g & \lambda Q_u \\ \lambda Q_u & -\delta \kappa Q_g \end{array} \right) \quad (3a)
\]

\[
= H_01 + W^{(1)}. \quad (3b)
\]

The corresponding ATD angle \( \alpha(Q) \) is defined through the eigenvector relation

\[
S = \begin{pmatrix} V_1^{(1)} & 0 \\ 0 & V_2^{(1)} \end{pmatrix} \quad (4a)
\]

\[
S = \begin{pmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{pmatrix} \quad (4b)
\]

where \( V_1^{(1)} \) and \( V_2^{(1)} \) are the adiabatic potential energy surfaces in first order, inherent to the LVC model Hamiltonian (3). For convenience the coordinate-dependence of the various quantities is suppressed in Eq. (4) and also below. The concept of regularized diabatic states consists in applying the LVC mixing
angle $\alpha$ of Eq. (4) to the general adiabatic potential surfaces $V_1$ and $V_2$. After some elementary algebra this leads to the following result [11, 12]:

$$H_{reg} = \left( T_N + \frac{V_1 + V_2}{2} \right) 1 + \frac{V_1 - V_2}{V_1^{(1)} - V_2^{(1)}} \left( \delta \kappa Q_g \quad \lambda Q_u \quad -\delta \kappa Q_g \right).$$  \hspace{1cm} (5)

This expression is seen to reduce to the usual LVC result close to the intersection (when $V_1 \to V_1^{(1)}$ and $V_2 \to V_2^{(1)}$) but, for configurations far away from it (when the adiabatic approximation is valid) recovers the general surfaces $V_1$ and $V_2$. It thus interpolates ‘smoothly’ between the two limits.

A theoretical justification of this procedure is obtained by noting that the linear terms of Eq. (3) determine the singular part of the full derivative couplings [11, 12] (corresponding to the full surfaces $V_1$ and $V_2$) near the intersection at $Q_g = Q_u = 0$. Thus, within the concept of regularized diabatic states, Eq. (5), the singular derivative couplings are eliminated, which motivates the nomenclature adopted. Note that all derivative couplings cannot be eliminated in the general case [10, 18, 19]. Thus, the concept of regularized diabatic states constitutes a natural extension of the usual adiabatic, or Born-Oppenheimer, approximation to intersecting electronic surfaces: all the singular couplings are eliminated and the others are neglected (group Born-Oppenheimer approximation).

The above scheme has been generalized to cover seams of symmetry-allowed conical intersections, where likewise all information needed for the construction can be obtained from the potential energy surfaces above [12]. Further generalizations to also cover accidental intersections, where symmetry plays no role, are currently underway in my group. We mention in passing that virtually all other schemes, proposed in the literature for constructing approximately diabatic states, rely on information on the adiabatic electronic wavefunctions [10]. Finally we point out that the concept of regularized diabatic states has been tested numerically for a number of different symmetry-allowed [12] and Jahn-Teller [11] conical intersections and very good agreement on dynamical quantities with reference data from the literature has been obtained. The neglect of nonsingular coupling terms apparently constitutes a very good approximation in these cases, where the concept appears to be not only simple, but also efficient and accurate. Applications of the scheme have been reported for H$_3$ [20] and NO$_2$ [21], see also below.

III. VIBRONIC PHENOMENA AND EXAMPLES

In this section I briefly illustrate typical nonadiabatic phenomena associated with conical intersections of potential energy surfaces, namely, an irregular, and anomalously dense, line structure in electronic spectra and an ultrafast electronic population decay. These are chosen from two different examples treated by us
in recent (and current) work and obtained by utilizing either of the theoretical approaches outlined in the previous section.

A. The $\tilde{X}^2A_1 - \tilde{A}^2B_2$ electronic manifold of NO$_2$

The $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$ electronic states of NO$_2$ represent one of the earliest examples of a conical intersection known in the spectroscopic literature [22–24]. It is responsible for the highly congested visible absorption spectrum and severely affects even the lowest electronic transition of this radical, exciting the system from the $\tilde{X}^2A_1$ to the $\tilde{A}^2B_2$ state (vertical excitation energy $\sim$3.4 eV, adiabatic excitation energy $\sim$1.0 eV). The presence of a conical intersection was predicted by Gillespie et al., and Jackels and Davidson [23, 24] ab initio and confirmed later by simulating the highly irregular visible absorption spectrum [25]. We refer to these papers for references to the large amount of other literature on this problem.

![Calculated vibronic line spectra for photodetachment and photoabsorption probing the coupled $\tilde{X} - \tilde{A}$ electronic manifold of NO$_2$. The energy scale is relative to the $\tilde{X}$ state minimum of the system. The intensities are normalized to unity when summing over all spectral lines of the electronic transition.](image)

More recently, the low-energy vibronic structure of the same electronic tran-
sition has been investigated using high-resolution excitation [26, 27] and also photoelectron spectroscopic [28] techniques. Corresponding theoretical efforts relied on the wave-packet propagation method [21] and are currently being extended to obtain also the vibronic line structure. An example is presented in Fig. 1 which displays in comparison the line structures for both the photoabsorption and photodetachment processes. They differ mostly because of the different equilibrium bond angles in the neutral and anionic ground states (of \( \sim 134^\circ \) and \( \sim 117^\circ \), respectively). The underlying diabatic potential surfaces are the same as described in Ref. [21], employing the concept of regularized diabatic states.

The lines, especially of the photodetachment spectrum, are seen to form groups or 'bunches' which can each be associated to a bending vibrational level of the \( \tilde{A}^2B_2 \) electronic state (the first group actually corresponds to \( v_b = 3 \), see Ref. [21]). This one-to-one relationship points to a moderate coupling strength between the \( \tilde{X} \) and \( \tilde{A} \) state vibrational levels. It is consistent with the relatively small vibronic coupling constant \( \lambda \) near the minimum of the intersection seam. However, \( \lambda \) increases with the energy [21] and for higher energies the photoabsorption line structure in Fig. 1 indeed becomes increasingly dense and erratic. The latter is in line with the trends observed experimentally [26, 27] and can be considered a generic feature of the singular nonadiabatic derivative couplings at conical intersections [3].

B. The low-lying singlet excited states of furan

The low-lying excited states of furan, a prototype heteroaromatic molecule [29], have been investigated quite intensively from an experimental and theoretical point of view [30–33]. Based on the EOM-CCSD method we have recently investigated stationary points of their potential energy surfaces, selected cuts along normal mode coordinates and a full set of coupling constants according to the LVC model (note that the latter comprise all vibrational modes of furan) [30, 34]. A number of conical intersections between close-lying electronic states could thus be established, comprising all adjacent singlet states, i. e. \( S_1 - S_2 \), \( S_2 - S_3 \), and \( S_3 - S_4 \). We mention that these are all composed of \( \pi - \pi^* \) and \( \pi \)-Rydberg excitations, with a vertical ordering of \( ^1A_2 - ^1B_2 - ^1A_1 / ^1B_1 \) symmetry (in the \( C_{2v} \) point group).

These results have been employed to conduct wave-packet dynamical calculations on the absorption spectrum and electronic population dynamics of furan [34], the largest ones relying on the so-called MCTDH method [35]. Upon adjusting a single quantity (the vertical excitation energy of the \( ^1B_1 \) state) the experimental spectrum of Ref. [33] could be very well reproduced. Here we employ the same model and parameters to obtain the time-dependent populations in Fig. 2. These assume broadband excitation to the \( ^1A_1(S_3) \) state and thus complement those presented in Ref. [34] where the initial wave-packet has been
FIG. 2: Time-dependent electronic populations of furan following broad-band excitation to the $^1A_1(S_3)$ state. The vibronic Hamiltonian is the same as described in Ref. [34], including coupling to the $^1B_1$ electronic state. However, the population of this state always remains below 0.05 and is suppressed in the figure for the sake of clarity.

assumed to be located on the $^1B_2(S_2)$ state surface. By populating the higher excited $^1A_1$ state at $t = 0$, an even richer population dynamics results, as is revealed by Fig. 2. Very short times, up to $t \approx 10 – 20$ fs, are characterized by a rapid population decay of the $^1A_1$ state, excited initially. The population is transferred temporarily to the next lower, the $^1B_2(S_2)$ state which exhibits a low-energy intersection with the $S_3$ state. This ultrafast population transfer, proceeding on the time scale of less than a typical vibrational period, can be considered to be the hallmark of the time-dependent dynamics at conical intersections, and is typical for many other cases as well [3]. In addition, Fig. 2 displays the phenomenon of a stepwise, or sequential, decay to lower electronic states, namely, the $^1A_2(S_1)$ excited state of furan. This is a (relatively) new feature which is being investigated currently also for other multi-state vibronic coupling systems, with co-existing seams of conical intersections [36]. In the case of furan and other five-membered heterocycles it provides a pathway to the $S_1$ state on which the photochemistry is believed to proceed [37], although the $S_0 – S_1$ transition is dipole-forbidden; the above ultrafast internal conversion processes precede, and are a prerequisite of, the first photochemical reaction steps of this system.
IV. CONCLUDING REMARKS

In this article I have outlined a specific ab initio-based approach to treat the quantum dynamics on conically intersecting potential energy surfaces. Some salient features of electronic spectra and time-dependent population dynamics treated in this way have been pointed out. Observables of the nuclear motion have likewise been studied in this way, and relations to time-resolved pump-probe spectroscopy been established [5]. Also, electron transfer processes have been studied along these lines [38].

More recently, the original vibronic coupling approach has been extended to refer only to the ATD mixing angle, thus yielding the concept of regularized diabatic states. Current applications are focussing on (seams of) symmetry-allowed conical intersections where all information can be extracted from the potential energy surfaces alone. Further ongoing work will establish generalizations to cover also fully accidental intersections. This is hoped to lay the grounds for an ab initio quantum treatment of general photophysical and photochemical processes.

Acknowledgments

It is a pleasure to acknowledge a long-term collaboration with L. S. Cederbaum, W. Domeke and S. Mahapatra on the vibronic coupling problem. The author is grateful to E. Gromov, A. Trofimov, J. Schirmer and H.-D. Meyer for a fruitful collaboration on vibronic coupling in furan, pyrrole and thiophene.

The Use of Elementary Reaction Coordinates in the Search of Conical Intersections

Yehuda Haas and Shmuel Zilberg
Department of Physical Chemistry and the Farkas Center for Light Induced Processes, the Hebrew University of Jerusalem, Jerusalem, Israel

This paper reviews the principles of a universal method that locates singularities on the ground state potential surface of a molecular system. The singularities considered are locations at which the ground electronic state (as defined by the BO approximation) is degenerate with the first electronic state, leading to their key role in the crossing between the two surfaces. The model presented is based on the concept of a chemical reaction as a two-state system, that appears to be uniquely appropriate for this purpose, especially for large polyatomic systems, in which several degeneracies are common.

In the two-state model of chemical reactions, the electronic wave functions (EWFs) of the transition states of elementary reactions can be constructed as the combinations of the EWFs of the reactant and product. If the combination is in-phase the reaction is sign preserving (p) and if out-of-phase – sign inverting (i). Using this method, the whole landscape of a molecular system can be partitioned into domains containing in general two or three minima that are bordered by reaction coordinates of elementary reactions. Each loop defines a separate 2-D domain in this plot which is defined by the two coordinates spanning it. The domain includes all points enclosed by the loop, as well as points along the reaction coordinates forming the loop. Its 'border' is defined by the change in curvature of the potential energy surface normal to the trajectory defined by the reaction coordinates. Sign inverting loops are of two types = i^2 and ip^2 and by the Longuet-Higgins sign inverting theorem they contain an odd number of conical intersections. We showed that two-fold and three-fold degeneracies can be located by a simple, straightforward procedure, starting at minima on the ground state potential surface.

The central theorem of this paper is an extension of the LH sign-inverting theorem: if the loop formed by two or three elementary reactions is sign-inverting, it encircles one and only one conical intersection. The proof is by contradiction as shown in Figure 1 for domains in which there are two separate minima connected by a sign-inverting loop having two transition states lying on reaction coordinate Q_1 and Q_2. In Figure 1 we plot the diagram as a function of two coordinates Q_+ and Q_-. 

56
\[ Q_z = Q_1 + Q_2 \]
\[ Q_z = Q_1 - Q_2 \]

For a sign-inverting loop, the EWF’s sign is preserved for motion along \( Q_z \) and inverted for motion along \( Q_z \). By construction, the loop passes through two minima (A and B) differing in their spin-pairing arrangements. In Figure 1 \( Q_z \) connects the reactant and the product and \( Q_z \) connects the two transition states. \( TS_1 \) is the in-phase transition state and \( TS_2 \) is the out-of-phase one. A conical intersection \( CI_0 \) lies at the origin of the \( Q_z \) and \( Q_z \) axes. Any other conical intersection must be off the \( Q_z = 0 \) axis, as it must have a contribution from both an in-phase combination of \( |A\rangle \) and \( |B\rangle \) (the area above the line connecting \( |A\rangle \) and \( |B\rangle \)) and also the out-of-phase combination (area below that line). A second CI on the top half of the figure is (denoted as \( CI_1 \) (diamond) is impossible, as it is surrounded by a sign-preserving loop A-\( TS_1 \)-B-\( TS_{0,1} \)-A. The proof is identical for \( CI_2 \) – a presumed conical intersection in the lower half.

**Figure 1**: A graph used to prove the uniqueness theorem, see text.

The proof for a 3-legged domain is analogous. Several examples are presented including the photo-isomerization of ethylene, one of the formaldehyde cation, one of furane, one of the 1,3 sigmatropic shift in propene and the ring closure reaction of the allyl radical to the cyclopropyl radical. In the latter system, four conical intersections are possible by symmetry.

57
A photochemical reaction can proceed via two CIs encircled by two conrotatory (or two disrotatory) transition states, suggesting the observation of interference effects.

In conclusion, we show that (1) reaction coordinates of elementary reactions are natural coordinates for finding conical intersections involved in photochemical reactions. (2) The complete molecular landscape can be partitioned into 2-D domains; each bordered by a loop formed from reaction coordinates of elementary reactions. (3) The conical intersection lies at a higher energy than neighboring minima or transition states.

Extremely Narrow Photofragment Distributions due to Conical Intersections.

Marc C. van Hemert  
*Theoretical Chemistry Group, Leiden Institute of Chemistry, Leiden University, Postbox 9502, 2300 RA Leiden, Netherlands*

Rob van Harrevelt  
*Theoretische Chemie, Technische Universität München, Lichtenberstrasse 4, 85748 Garching, Germany, and Theoretische Chemie, Universität Bielefeld, Postfach 100131, 33501 Bielefeld, Germany*

Some four years ago Xueming Yang\(^1\) observed that OD (\(A^2\Sigma,v=0\)) photofragments formed by photodissociating HOD with Ly\(_D\) radiation showed an extreme preference for a single rotational state with the high angular momentum value \(N=28\). Immediately two questions arose, i) how could this be explained, ii) why had this never been observed before.

The key to the understanding is the remarkable shape of the potential energy surface of the water \(\tilde{B}\) state. In figure 1 is presented the adiabatic potential energy surface\(^2\) for a fixed OH distance of 1.8 Bohr. The O and H atoms are located at \((x,y)=(0,0)\) and \((-1.8,0)\) respectively. The energies are in units of eV and the contour lines are drawn at 6.5, 7.0, 7.5, ... eV. The Franck-Condon point is indicated with X. The origin of the shape with its deep minima, both at linear HOH and at linear HHO geometry, is a conical intersection caused by the intersection of the curves for the \(1\Sigma^+\) and \(1\Pi\) states of linear water.\(^2,3\)

The dynamics on this surface can be simply explained in classical trajectory terms: the parting H atom will be accelerated towards the minimum at linear HOH geometry causing an end over end rotation of the two fragments. Angular momentum conservation leads to an angular momentum in opposite direction of the OH fragment. At the same time there is an increase in distance between the oxygen atom and the parting H atom. From the contour plot it is seen that photodissociation is possible for photon energies higher than \(~(8.9 - 0.3) = 8.6\ eV\) (0.3 eV is the zeropoint energy change). The excess energy, for Ly\(_D\) equal to \(~1.5\ eV\), is distributed over translation, vibration and rotation of the fragments. For each \(v_{OH}\) there is a specific threshold for each OH \(N\) value. The centrifugal potential \(V_{cent}(R)\) corresponding to the end over end rotation gives rise to a rotational barrier. Assuming zero initial total angular momentum,
\[ V_{\text{centr}}(R) = \frac{N(N+1)}{2\mu_R R^2}. \]

\( \mu_R \) is the reduced mass of the OH-H complex and \( R \) is the H to OH center of mass distance. When the barrier is sufficiently high, it prevents dissociation in a particular OH N level, even when the photon energy is above the corresponding threshold. E.g. for \( v_{\text{OD}} = 0 \) at \( N \geq 30 \) the barrier energies are already \( > 0.15 \) eV above the asymptotic energies which explains the observation of the absence of fragments with \( N > 28 \) in the experiments even though at \( \text{Ly}_\alpha \) all states with \( N \leq 31 \) are energetically accessible. The near absence of levels with \( N < 28 \) is also made plausible in this picture. All fragments are initially formed with a too high formal angular momentum to overcome the barrier. At later times in the trajectory rotational energy is transferred internally to translational energy until the rotational barrier is lowered sufficiently such that the H atom can ultimately escape.

\textbf{Figure 1.} Contour plot of the potential energy surface for water in the \( \tilde{B} \) state.

Although this picture explains the Yang experiment, it can not be completely correct, because at other wavelengths, satisfying the criteria of sufficiently high energy to create a rotational barrier with a maximum above the threshold, only a clear population inversion is observed, but no single-N phenomenon. Strong population inversions in rotational distributions also have been observed in the photodissociation of \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \), although not as extreme as found for HOD.
The single N phenomenon can be considered as a case of extreme population inversion. The population inversions for H2O and D2O4 and HOD1 could be well described with 3D quantum dynamical calculations using the wave packet approach, provided the full aspects of a conical intersection were taken into account.4 Here the diabatic potentials and couplings as provided by Dobbyn and Knowles2 were used. Specifically, for HOD the single N phenomenon in the Ly range can be nicely reproduced. However it is found that the single N-phenomenon only occurs in narrow energy intervals with a width of ~0.03eV. Outside these intervals just the population inversion is found. The intervals are exactly in between the positions of subsequent maxima in the quantum mechanically formulated rotational barrier heights.

These barriers are obtained as follows. For a grid of R values the two dimensional Hamiltonian for the remaining degrees of freedom, the Jacobi angle γ and the fragment internuclear distance r, is diagonalized using a Fourier grid for r and a basis set expansion in Legendre polynomials for γ. The eigenvalues V_vN(R) form the set of rovibrationally adiabatic potentials that have barriers for sufficiently high N values. The locations of the barriers at R > 6 Bohr are far enough outside the strong interaction region to justify the inherent approximation of decoupling motion in the R, r and γ degrees of freedom.

The wave packet formalism that was used has been described in Refs. 5 and 6, and takes angular momentum coupling properly into account. It also gives the opportunity to the determine the β parameter that is used when expressing the cross section σ as a function of the angle θ between the polarization of the radiation and the recoil direction by

\[ σ(θ) = σ_{tot} \{ 1 + β \left( \frac{1}{2} - \frac{3}{2} \cos^2 θ \right) \} \]

Here we present results for θ = 0° (“parallel detection”) and θ = 90° (“perpendicular detection”). In experiments where the rotational distributions of the OH or OD fragments are determined from the A to X fluorescence, the populations correspond to the average over the angle θ. The calculation of β requires very long propagation times.

In figures 2 and 3 the rotational distributions for OD A 2Σ are given as functions of energy for parallel and perpendicular detection respectively. In accord with the experiment the phenomenon is predominant for parallel detection.
Figures 2, 3 and 4. $P_N(E)$ functions for HOD $\rightarrow$ OD + H with parallel, perpendicular and averaged detection. The four lines correspond to $N$ values of 29, 30, 31 and 32.

From our calculations it follows that only OD resulting from the photodissociation of HOD and OH resulting from the photodissociation of H$_2$O will show the single $N$-phenomenon. For OD from D$_2$O and OH from HOD there is a weak single $N$-phenomenon for parallel detection, but it is absent after averaging over $\theta$. The absence or presence of single $N$ is closely related to the locations of the barriers in the rotationally adiabatic potentials that of course depend on the reduced masses of both the complex and the fragment.

The single-$N$ phenomenon for H$_2$O(000) occurs at rather high energies, in the tail of the absorption spectrum. An experimental detection will be difficult because of the presence of a strong background from other excited electronic states. Our calculations show that also in vibrationally mediated photodissociation (VMP) the phenomenon should be observable, but now at much lower photon energies. In figures 5 and 6 the predicted OH fragment distributions are shown for H$_2$O(301) $\rightarrow$ OH + H with parallel detection and averaged over $\theta$.
Figures 5 and 6. \( P_N(E) \) functions for \( \text{H}_2\text{O}(301) \rightarrow \text{OH} + \text{H} \) with parallel and averaged detection. The four lines correspond to \( N \) values of 20, 21, 22 and 23.

At these energies \( \text{OH}(A) \) fragments can only be formed via photodissociation of water in the \( \tilde{\text{B}} \) state. There will however be many \( \text{OH}(X) \) fragments, both from the water \( \tilde{\text{A}} \) and \( \tilde{\text{B}} \) bands. These results suggest that VMP of \( \text{H}_2\text{O} \) with \( \text{OH}(A) \) detection via either KER or fluorescence should be a valuable method to study the Single N phenomenon.

It is thus seen that the occurrence of the single N-phenomenon critically depends on
the shape of the potential and on the (reduced) masses of the fragments. To our
knowledge only in one other triatomic dihydride a dramatic population inversion
has been observed, namely in the photodissociation of NH₂ in the second continuum
band where highly rotationally excited NH fragments in the excited A \(^3\Pi\) state are
produced.\(^7\) The adiabatic potential energy surface of the excited state held
responsible, in C\(_2\)\(_v\), labeling \(^1\Sigma_2^+\), has exactly the same topology as the surface for
H₂O displayed in figure 1. Preliminary calculations indicate that the single-N
phenomenon should be observable at the higher excitation energies. Presumably,
the experimentalists have just missed the phenomenon by analyzing only for a few
excitation wavelengths the NH fragment distribution through the NH \(^3\Pi\) fluorescence. A definitive quantum dynamical study waits for proper treatment of
the couplings between electronic states that are for NH₂ much more numerous than
for H₂O. For NH₂ at least three conical intersections have to be taken into account
in the relevant energy range, while there is only one for H₂O.

First Principles Ab Initio Multiple Spawning Dynamics of Electronically Excited trans-1,3-Butadiene with Wavefunction and Density Functional Theory

Benjamin Levine and Todd J. Martinez

Department of Chemistry, University of Illinois at Urbana-Champaign
Urbana, IL 61801, U.S.A.

I. Introduction

Photoisomerization of conjugated organic molecules represents one of the simplest means of converting optical energy to mechanical motion on the molecular scale. These processes provide a great challenge to theoretical chemistry on a number of levels. While quantum chemistry, i.e. electronic structure theory, alone can answer some questions, only accurate dynamical simulations can determine which reaction paths are important and which are not. Accurate simulation of photochemistry requires a description of the quantum mechanical behavior of both electrons and nuclei. The quantum behavior of the nuclei is particularly important at or near conical intersections where nonadiabatic effects are large. Full quantum mechanical treatment of the electrons is required in order to obtain accurate global descriptions of the ground and excited state potential energy surfaces (PESs). To these ends we use Ab Initio Multiple Spawning (AIMS) dynamical simulations, which solve the electronic and nuclear Schrödinger equations simultaneously. In this report, we focus on our recent studies of trans-1,3-butadiene. Trans-1,3-butadiene is the smallest conjugated organic molecule, and therefore offers a paradigm for photochemistry in these molecules.

In general, our dynamical simulations utilize multi-reference ab initio methods to calculate the PESs and their couplings “on the fly,” i.e. simultaneously with the evolving nuclear dynamics. In an effort to reduce the computational cost of our simulations without losing accuracy, we have also considered alternative approaches to the electronic structure problem. In this report, we detail our investigation of Time Dependent Density Functional Theory (TDDFT) as such an alternative. TDDFT is well known to be a highly accurate predictor of vertical excitation energies of singly excited electronic states, but little is known about its ability to predict the shape of PESs and to describe doubly excited states. Using butadiene and other small organic molecules as test cases, we explore the potential of TDDFT as a general and low cost tool for photochemical studies.
II. Ab Initio Multiple Spawning

AIMS is a hierarchy of approximations which allows for fully quantum dynamical molecular dynamics simulations on ab initio PESs calculated “on the fly.” The nuclear wavefunction in AIMS is expanded in a basis of frozen Gaussian basis functions, each of which is associated with a single Born-Oppenheimer surface. The center of each basis function is propagated according to the classical equations of motion appropriate for the electronic state with which it is associated. However, each basis function carries a complex amplitude and basis functions are allowed to exchange population through the solution of the nuclear Schrödinger equation. Additionally, the nuclear basis set expands adaptively throughout the simulation. This basis set expansion and the coupling of the nuclear basis functions allows for the proper description of nonadiabatic effects. For instance, when a basis function reaches a region of space where the nonadiabatic coupling with another electronic state is large, a new basis function is created (“spawned”) on the other electronic state to accept population. The matrix elements between basis functions which are required to solve the nuclear Schrodinger equation are approximated by a truncated Taylor expansion around the point between two basis functions which forms the center of the product of the two basis functions. Thus, AIMS only requires energies, forces, and nonadiabatic coupling vectors calculated at single points in nuclear configuration space, which can be provided by ab initio quantum chemistry.

III. First Principles Study of trans-1,3-Butadiene

Considerable experimental and theoretical work on 1,3-butadiene suggests that after photoexcitation the molecule quickly leaves the Franck-Condon region and decays to the ground state by a radiationless process.4-12 Early work suggests the importance of charge transfer to the excited state dynamics of butadiene.13-17 However, the commonly accepted mechanism for this decay, proposed by Olivucci, Robb, and coworkers, involves an almost instant decay from the bright 1 1Bu state to the nearby dark 2 1Ag state, followed quickly by decay to the ground state via a conical intersection (the transoid intersection, vide infra) between covalent states that is twisted about all three carbon-carbon bonds.18,19

We developed a method for optimizing minimal energy conical intersection points (MECIs) at levels of theory where nonadiabatic couplings are not readily available and used it to optimize S1/S0 MECIs for butadiene at the Multi-State Complete Active Space Second Order Perturbation Theory20 (MS-CASPT2) level of theory with 4 active electrons in 4 active orbitals. All MS-CASPT2 calculations were performed using MOLCAS.21
Olivucci have utilized CASSCF nonadiabatic couplings to perform MECI optimizations at the CASPT2 level of theory. Results of our MS-CASPT2 optimizations as well as Complete Active Space Self Consistent Field (CASSCF) optimizations are shown in Figure 1. All CASSCF calculations are performed using MOLPRO. We find the covalent transoid intersection and two other intersections involving states of charge transfer character, all of which are comparable in energy. The two charge transfer intersection geometries are characterized by twisting about one of the terminal carbon-carbon bonds and pyramidalization about either the terminal carbon of the twisted bond, or the central carbon of the twisted bond. The pyramidalized carbon is negatively charged in both cases, and the planar carbon of the same bond is positively charged, while the other ethylene unit remains neutral. We refer to these two MECIs the Methyl\(^{+}\) (Me\(^{+}\)) and Methyl\(^{-}\) (Me\(^{-}\)) intersections according to the charge on the twisted terminal methyl group.

![Figure 1](image-url)  
*Figure 1.* Relative energies at the Frank-Condon (FC) point and three important MECI geometries of butadiene at three levels of theory. Notice that CAS(4/4) favors the transoid intersection by more than 1 eV relative to the charge transfer intersections. Despite significant effort we were unable to locate the Me\(^{-}\) intersection at the CAS(4/4) level of theory. CAS(4/3) slightly disfavors the transoid intersection but reproduces the MS-CASPT2 finding that all three intersections exist and are comparable in energy.

The ab initio work of Olivucci and coworkers which suggested the importance of the transoid intersection was primarily based on CASSCF calculations with an active space of 4 electrons in 4 orbitals, i.e. CAS(4/4). When we search for the three intersections using SA-3-CAS(4/4), we find that the transoid intersection is favored compared to the Me\(^{+}\) intersections, and despite significant effort we are unable to locate a conical intersection of Me\(^{-}\) character. This failure of
CAS(4/4) persists when using 6-31G, 6-31G*, and 6-31G** basis sets. However, using SA-3-CAS(4/3) with the 6-31G basis set, we find MECIs for all three cases and furthermore find these to have comparable energies, in agreement with MS-CASPT2. Another well known failure of CAS(4/4) is the prediction of a large energy gap between the two lowest lying valence excited states in the Franck-Condon region. Calculations including dynamical electron correlation agree that these two states are nearly degenerate. CAS(4/3) also accurately reproduces this feature of the potential surface, predicting an S1/S2 energy gap of 0.05 eV at the Franck-Condon point. Thus, we choose SA-3-CAS(4/3) as the electronic structure method to provide the PESs and nonadiabatic couplings for our AIMS simulations.

It is important to note that CAS(4/3) is neither the more intuitive choice of active space nor the larger. However, by comparison with MS-CASPT2, which includes both static and dynamic electron correlation effects, we have determined it to be the most accurate of the two active spaces investigated. It is well known that CASSCF calculations with reasonably-sized active spaces include a large amount of the static correlation energy without including very much dynamical correlation. This strongly favors states of covalent character. By choosing a smaller active space we achieve a better balance of correlation effects and therefore a more accurate PES.

Figure 2. Pump-photoionization probe signal calculated from AIMS dynamics, calculated at a probe energy of 2.99 eV. The signal is highly non-exponential, but agrees well with the experimentally observed lifetime of 35-110 fs. The signal we observe is gated not by a nonadiabatic transition, but by the increase in the ionization potential resulting from twisting on the S2 electronic state.

Ten AIMS simulations are run for trans-1,3-butadiene, each starting from one nuclear basis function whose average position and momentum are chosen from the ground state Wigner distribution in the harmonic approximation, with ground state geometry and normal modes calculated at the BLYP/6-31G** level of theory. After excitation to the optically bright 1^1B_u state, the molecule relaxes along a bond
alternation coordinate. At this point, most of the population resides on $S_2$ (our labeling of adiabatic states follows the usual photochemical nomenclature where states are numbered strictly according to their energetic ordering\textsuperscript{25}) which is the adiabatic label for the bright $1^1B_u$ state in these geometries. On $S_2$, the molecule twists about a single terminal carbon-carbon bond. From our dynamical simulation, we calculated the expected signal from a time resolved pump-photoionization probe experiment. These results can be compared to recent experimental data.\textsuperscript{6,7,26} Our results are shown in figure 2. We find excellent agreement between our calculated lifetime of 50-80 fs and the experimental lifetimes, measured to be 35-110 fs. This lifetime is often suggested to correspond to internal conversion, but we find that our signal decays as a result of the increased ionization potential which results from adiabatically twisting on $S_2$.

Once twisted, the energy gap between $S_2$ and $S_1$ becomes small and the molecule quickly decays to $S_1$. After reaching $S_1$, the molecule moves towards the various $S_1/S_0$ intersections discussed above. In our simulation, decay through the Me$^+$ intersection is the dominant path, even though the Me$^+$ and Me$^-$ MECIs are nearly degenerate both at the CAS(4/3) and MS-CASPT2 levels of theory. Our results suggest that charge transfer plays a very significant role in the photochemistry of butadiene in the gas phase. One would expect that decay paths involving states of charge transfer character would be even more important for molecules in a polarizable or charged environment, as would be found in the solution phase or for a chromophore embedded in a protein.

IV. TDDFT as a General Tool for the Study of Photochemistry

As demonstrated above, CASSCF can be a very powerful electronic structure method for the study of photochemical reaction dynamics, but its neglect of dynamical correlation effects can lead to qualitatively incorrect results if not applied carefully. Explicit inclusion of dynamic electron correlation within the framework of ab initio quantum chemistry is very computationally expensive, so we analyze TDDFT as a potentially accurate and low cost alternative. TDDFT includes dynamical correlation effects through a functional of the electron density. Though exact in principle, currently available functionals are grossly approximate and TDDFT is formally very similar to single reference methods like Single-Excitation Configuration Interaction (CIS).\textsuperscript{27} Such methods ignore doubly excited states and are often inaccurate in describing the potential energy surface outside the Frank-Condon region, where the ground state wavefunction is no longer well described by a single closed shell determinant. Throughout this work all TDDFT calculations are performed using the GAUSSIAN 98 software package.\textsuperscript{28}

In order to assess the ability of TDDFT to accurately predict the shape of singly excited potential energy surfaces near the Frank-Condon region, we have
carried out dynamical simulations on the valence (V) and 3s Rydberg (R3s) states of ethylene. From these simulations we calculate electronic absorption spectra according to the time-dependent formalism of Heller, shift the V and R3s states by .06 and .18 eV respectively to best match the experimental absorption spectrum, and add them with weights corresponding to the calculated TDDFT oscillator strengths. In Figure 3, we compare to the experimental spectrum, finding good agreement. The TDDFT spectrum accurately reproduces the width of the broad V band, as well as the progression observed in the R3s band. From this we conclude that TDDFT is capable of describing the potential energy surface of singly excited states in the Frank-Condon region with impressive accuracy.

Figure 3. The electronic absorption spectrum of ethylene calculated from dynamical simulations run on B3LYP/6-31+G excited state potential energy surfaces (blue) with the experimental spectrum (red). Notice that the overall width of the spectrum, which is the result of the dynamics on the V state, agrees well with experiment. The spacing of the progression resulting from dynamics on the R3s state is also in good agreement, though the peaks in the calculated are not split as they are in the experimental spectrum. This splitting is often assigned to torsional motion, which would not be expected in our simulations which use a single wavepacket basis function restricted to planarity by symmetry.

To assess the ability of TDDFT to describe states with doubly-excited character in the Frank-Condon region, we calculate potential energy surfaces for the low lying valence excited states of butadiene along a bond alternation coordinate. The low lying 2^1A_g state of butadiene has significant doubly excited character, but this state is clearly missing at the TDDFT level of theory, suggesting that TDDFT cannot be expected to describe doubly excited states.

To analyze TDDFT outside the Frank-Condon region we optimize intersections between electronic states and examine the potential energy surface in their vicinity. We utilize the same conical intersection optimization scheme
discussed above in the context of MS-CASPT2 to search for intersections between TDDFT response states and the DFT ground state. We chose starting conditions from ab initio optimized $S_1/S_0$ MECI geometries for six intersections from three small conjugated organic molecules. In all cases intersections were found very near to the ab initio intersections, including the Me$^+$ intersection which we do not find at the CAS(4/4) level of theory. Unfortunately, the shape of the PES in the region of these intersections is grossly flawed, as seen in Figure 4. In reality conical intersections exist in $N$-2 dimensional seams (where $N$ is the number of nuclear degrees of freedom), but at the TDDFT level of theory intersection seams are $N$-1 dimensional. This is a direct consequence of the absence of coupling between the DFT ground state and TDDFT excited states (Brillouin’s theorem).

Figure 4. Potential energy surfaces of H2O in the vicinity of a linear conical intersection calculated at the CASSCF (left) and B3LYP/6-31G (right) level of theory. The correct behavior is demonstrated by the CASSCF surface. Specifically, there are two independent directions which break the degeneracy of the intersection, making the intersection seam $N$-2 dimensional. The degeneracy of the TDDFT surfaces is only broken by one independent direction, yielding an $N$-1 dimensional intersection seam.

V. Conclusions

Trans-1,3-butadiene decays to the ground state through three different channels, two of which involve states of charge transfer character. Our simulations suggest that the Me$^+$ channel is the most important for dynamical reasons, in spite of energetic considerations. Previous work which concludes that butadiene decays via a covalent state was the result of the poor performance of CAS(4/4), which is the intuitive choice of CASSCF method for this problem. In general, comparison to a higher level of theory is necessary when choosing an active space for such
TDDFT offers an alternative to CASSCF for calculation of singly excited electronic states in the Frank-Condon region. Unfortunately, TDDFT with the currently available array of functionals is incapable of describing doubly excited states and the potential energy surface around conical intersections. Developments such as improved functionals and multireference DFT methods will likely correct these problems and allow DFT to become a general tool for the study of photochemistry.

Spectroscopy and Reactive Scattering Dynamics at Conical Intersections of Potential Energy Surfaces

Susanta Mahapatra*
School of Chemistry, University of Hyderabad, Hyderabad, 500 046, India

The conical intersections (CIs) of electronic potential energy surfaces (PESs) is a well established concept and is recognized to play important mechanistic role in the spectroscopy, photochemistry and reaction dynamics of polyatomic molecules [1-4]. CIs are characterized by a (N-2)-dimensional seam (a hyperline) of degeneracy of the two PESs in the N-dimensional vibrational space of the molecule and a lifting of degeneracy in first-order with respect to nuclear displacement in the two-dimensional branching space [2]. The existence of CIs of PESs causes a breakdown of the adiabatic or Born-Oppenheimer approximation [5], and therefore, electronic transitions take place during nuclear vibration. Apart from this, the associated nonadiabatic coupling elements exhibit a singularity at the seam of CIs in an adiabatic electronic representation making it unsuitable for the dynamical studies [2]. The complementary diabatic electronic representation is preferred for the latter purpose in which the coupling elements exhibit a smooth behavior [6-8].

The typical dynamical outcomes of CIs of PESs are femtosecond decay of the excited molecular states [2], seemingly diffuse and highly complex optical spectrum, the phenomenon of geometric phase [9], bifurcation of the wave packet [10] and dissipative molecular vibration [11]. Besides spectroscopic studies, the impact of CIs on the thermal reactive scattering [see, for example, Refs. 19-30 of Ref. [12]] and photoinduced hydrogen elimination [13] processes have been paid attention only recently. Furthermore, the interplay of the electronic and relativistic spin-orbit (SO) coupling has currently become an interesting topic of research in this area of chemical dynamics [14-16]. In the discussion that follows, I will briefly highlight some static aspects of CIs of PESs and their effects on the quantum dynamics of a wide variety of molecular systems studied by us in the recent past. In particular, I focus on the static and dynamic aspects of the Jahn-Teller (JT) [2, 17, 18] and pseudo-Jahn-Teller (PJT) [2, 19, 20] CIs, probing the CI of PESs through photodetachment spectroscopy of bound and

*Email: smsc@uohyd.ernet.in, Fax: +91-40-23012460
scattering systems and the impact of CIs on the thermal bimolecular reactive scattering.

The $1^2E^0$ ground electronic manifold of $H_3$ is the simplest representative of a $(E \times e)$-JT class of CIs. The latter is directly probed in the measurement of the emission spectrum of $H_3$ from its $n = 3$ Rydberg electronic state which terminates in the vicinity of the CIs of the $1^2E^0$ electronic state at the $D_{3h}$ equilibrium configuration. The emission spectra of $H_3$ and its deuterated isotopomers recorded by Bruckmeier et al. [21] revealed highly diffuse and structureless bimodal profiles with two maxima at $\sim 240$ nm and $\sim 310$ nm. This amounts to a JT splitting of $\sim 9600$ cm$^{-1}$ in the $1^2E^0$ electronic manifold of $H_3$. We examined theoretically the impact of the CIs on the time-evolution of $H_3$ in the vicinity of its $D_{3h}$ conformation [22, 23] by numerically solving the time-dependent Schrödinger equation (TDSE) in a coupled diabatic electronic representation. The details of the diabatization procedure can be found in the article by H. Köppel in this booklet. In actual computation the adiabatic sheets of the double many-body expansion (DMBE) PES of Varandas et al. [24] are used. The calculated Rydberg emission spectrum of $H_3$ and its deuterated isotopomers has been found to be in good accord with the experimental recording. This reveals the accuracy of the DMBE PES as well as the diabatization procedure at and near the seam of CIs. The maxima at $\sim 240$ nm and $\sim 310$ nm are found to be due to a transition to the lower $V_-$ and upper $V_+$ adiabatic sheets of the $1^2E^0$ electronic manifold, respectively. The JT effect of the single degenerate vibrational mode is particularly very strong and as a result the bound vibrational levels of the uncoupled upper adiabatic sheet $V_+$ transforms into highly overlapping resonances when the coupling to the lower sheet is activated [22]. This results into an extremely fast decay of the electronic population of $V_+$ occurring on a time scale of $\sim 3-6$ fs only [23] and perhaps represents the fastest femtosecond decay process studied in the literature to date.

A strong interplay of JT and PJT effects is immediately visible from the photoionization spectrum of cyclopropane (CP) [25]. The experimental data exhibit a bimodal structure centered around $\sim 11$ eV, a broad band at $\sim 13.2$ eV and two strongly overlapping bands at $\sim 15.7$ and $\sim 16.5$ eV. The twin band at $\sim 11$ eV is due the ionization from the $3e'$ molecular orbital of CP forming its radical cation (CP$^+$) in the electronic ground $\tilde{X}^2E'$ state. Neutral CP belongs to the $D_{3h}$ symmetry point group at the equilibrium geometry of its electronic ground state. Elementary symmetry selection rule suggests that its four degenerate vibrational modes of $E'$ symmetry can exhibit the $(E \times e)$-JT activity in the $\tilde{X}^2E'$ electronic manifold of CP$^+$. The multimode JT interactions in the electronic ground manifold of CP$^+$ have recently been investigated by us with the aid of an $ab$ initio quantum dynamical method [26]. In the theoretical approach we employed a model diabatic Hamiltonian with $ab$ initio calculated parameters within linear and quadratic vibronic coupling schemes [2] and examined the vibronic structure of the twin band. A careful inspection revealed the excita-
tion of the C-C stretching ($A'$), CH$_2$ scissoring ($A'_1$), CH$_2$ wagging ($E'$), ring deformation ($E'$) and CH$_2$ scissoring ($E'$) vibrational modes in the photoelectron band. The theoretically calculated spectrum is found to be in very good overall agreement with the experimental data. The strong JT activity of the degenerate CH$_2$ wagging and ring deformation modes leads to the appearance of two distinct maxima in the band indicating transitions to both the sheets of the so-called Mexican hat PES of the $X^2E'$ electronic manifold. Also, these two modes mainly form the progression in the low-energy wing of the envelope. The overall width of the band and the separation between the two maxima of $\sim 0.76$ eV (compared to the experimental value of $\sim 0.78$ eV [25]) are reproduced quite well by the linear vibronic coupling model. Despite this overall agreement, the average spacing in the low-energy progression of the band estimated from the theoretical results is $\sim 40$ meV higher than its experimental value [25]. This discrepancy is reduced when a quadratic coupling scheme is employed. Unfortunately, in this case the apparent regularity of the progression is lost [26]. The reason for this discrepancy is presently being examined.

The three doubly degenerate vibrational modes of CH$_3$F molecule can exhibit $(E \times \epsilon)$-JT activity in the doubly degenerate ground ($X^2E'$) and excited electronic state ($B^2E'$) of its radical cation. The same vibrational modes may also couple the degenerate and the nondegenerate ($A^2A_1$) electronic states and can exhibit $(E + A) \times \epsilon$ PJT activity. The JT and PJT interactions in the ground and excited electronic states of CH$_3$F$^+$ are revealed in the photoelectron spectrum of CH$_3$F, which indicated resolved vibrational structures at low energies and highly diffuse and structureless profile at high energies [28]. The static and dynamic aspects of the JT and PJT interactions in the ground and excited electronic manifold of CH$_3$F$^+$ have been investigated by us recently with the aid of an $ab$ initio quantum dynamical approach [27]. The JT activity of the degenerate vibrational modes is found to be weak in both the $X^2E'$ and $B^2E'$ electronic states. Despite some details, the agreement between the theoretical and experimental results on the $X^2E'$ and $B^2E'$ photoelectron bands at low and high energies, respectively, is satisfying [27]. The resolved vibrational structures at low energies are caused by the C-F stretching ($A_1$), CH$_3$ deformation ($E$) and C-F bending ($E$) vibrational modes in accord with the experimental [28] and previous theoretical results [29]. Although the $X^2E'$ and the $A^2A_1$ states are $\sim 3.81$ eV apart at the vertical configuration, still the PJT activity of the C-F bending ($E$) vibrational mode is found to have significant effect on the $X^2E'$ photoelectron band at low energies. It is found that a linear-plus-quadratic $(E \times \epsilon)$-JT model is clearly inadequate in describing the observed diffuse and structureless appearance of the $B^2E'$ band at high energies. The condon activity of the C-F stretching ($A_1$) and the JT activity of the CH$_3$ deformation ($E$) modes dominates in the nuclear dynamics of the latter electronic manifold. The linear PJT coupling strengths of the CH$_3$ deformation ($E$) and C-F bending ($E$)
vibrational modes in the $\tilde{A}^2A_1-\tilde{B}^2E$ electronic manifold are nearly identical and small. However, these electronic states are nearly degenerate and therefore, even a relatively weak coupling can have significant effects on the nuclear dynamics on them.

The photodetachment spectroscopy is an attractive technique to probe the vibronic structure of the neutral electronic states by photodetaching its stable anion [30]. This technique has been successfully used in probing the CIs of excited molecular electronic states, transition states and the prereactive van der Waals wells in chemical reactions.

Even though the crucial roles of $^2B_2$ and $^2A_1$ electronic states have been realised in the photochemistry of ClO$_2$, their existence remained unconfirmed experimentally for a long time! They can not be probed in an optical absorption experiment because, the $^2B_2$ state is optically dark and the $^2A_1 \leftrightarrow \tilde{X}^2B_1$ transition has extremely low oscillator strength [31]. Although an indirect evidence of the existence of a $^2A_1$ state emerged from the combined experimental and theoretical studies on the resonance Raman spectrum of OCIO [33], the existence of a $^2B_2$ state solely relied on the theoretical predictions [32]. Wang and Wang [34] recorded the photodetachment spectrum ClO$_2^-$ with increasing photon energy and observed the appearance of a diffuse and highly overlapping band structure in the 4.0-5.5 eV electron binding energy range. This diffuse structure is predicted to be due to the ionisation of ClO$_2^-$ to the $^2B_2$, $^2A_1$ and $^2A_2$ electronic states of ClO$_2$ [34].

In order to understand the observed diffuse structure of the photodetachment spectrum and to add to the evidence in favor of the existence of a $^2B_2$ state in ClO$_2$, we devised a theoretical model and simulated the nuclear dynamics on the coupled multiple electronic states with the aid of a time-dependent wave packet approach [35]. We established a symmetry allowed CI between the $^2B_2$ and $^2A_1$ electronic states in the vicinity of the Franck-Condon zone for the photodetachment process [35]. The SO interactions between the $^2A_1$ and $^2A_2$ is estimated to be weak ($\sim 2$ cm$^{-1}$) [33] and is not considered in the dynamical simulations. Our theoretical results [35] are found to be in good agreement with the experimental observations [34]. Our analysis revealed that the humplike structure at low energies corresponds to the vibronic structure of the $^2B_2$ electronic state and the diffuse structure at high energies corresponds to that of the $^2A_1$ and $^2A_2$ electronic states [35]. A close look at the theoretical results indicated a small contribution of the $^2A_2$ electronic states to the spectral intensity in par with the estimated low magnitude of the SO coupling between the $^2A_1$-$^2A_2$ states [33]. Examination of the time-dependence of the adiabatic and diabatic electronic populations revealed that the population transfer from the $^2A_1$ to the $^2B_2$ electronic state occurs to within $\sim$250 fs [35]. This estimate is in excellent agreement with the recent time-resolved experimental findings of Stert et al. [36].

The simplest Cl atom reaction Cl+H$_2$ is slightly endothermic (endothermicity $\sim$0.045 eV) and proceeds on a late barrier type of PES (barrier height $\sim$0.366
The geometry of ClH\textsubscript{2}\textsuperscript{−} is far away from the barrier configuration and is close to the van der Waals well region of the reactive Cl+H\textsubscript{2} PES [37]. The latter is probed by the photodetachment spectroscopy which provide an experimental evidence (for the first time!) of the existence and importance of a van der Waals well in the reagent asymptote of a reacting system [38]. The dynamics of the Cl+H\textsubscript{2} reaction in the ground electronic state is influenced by the electronic and SO coupling with the excited electronic states. The approach of a Cl(2\textit{P}) atom to the H\textsubscript{2} molecule splits the three-fold degeneracy of the 2\textit{P} state. The resulting two electronic states, 1\textit{2}\textit{A}' and 2\textit{2}\textit{A}'' (correlating to the \textit{2}\Sigma and \textit{2}\Pi, respectively, in the linear geometry), correlate adiabatically to the ground state Cl(2\textit{P}_{3/2}) atom, while the third state 2\textit{2}\textit{A}' (\textit{2}\Pi species in the linear geometry) correlates adiabatically to the SO excited Cl\textsuperscript{+}(2\textit{P}_{1/2}) atom. Of these, only the 1\textit{2}\textit{A}' state correlates with the electronic ground state of the products [HCl(\textit{X}\Sigma\textsuperscript{+})+H(\textit{2}\textit{S})]. The remaining two electronic states correlate with the electronically excited state of the products [HCl(\textit{3}\Pi) + H(\textit{2}\textit{S})]. The two 2\textit{A}' states form CIs at the linear geometry. The SO coupling of the Cl atom further splits these states and hereafter we refer to them as 2\textit{2}\Sigma\textsubscript{1/2}, 2\textit{2}\Pi\textsubscript{3/2} (correlating with the Cl(2\textit{P}_{3/2} asymptote) and 2\textit{2}\Pi\textsubscript{1/2} (correlating with the Cl\textsuperscript{+}(2\textit{P}_{1/2}) asymptote) [16].

Based on a time-dependent wave packet approach and \textit{ab initio} calculated PESs of ClH\textsubscript{2} [16] and ClH\textsubscript{2} [37] we investigated the photodetachment dynamics of ClH\textsubscript{2} [39]. The calculations are carried out for the lowest value of the partial wave \textit{J}=0.5 and considering both the electronic and SO couplings. Our final theoretical results have been shown to be in good accord with the experimental results of Neumark and coworkers [38]. The two large peaks are \textasciitilde0.102 eV apart when compared with the experimental value of \textasciitilde0.111 eV and correspond to the SO splittings of \textasciitilde0.109 eV of the Cl atom. The widths of the individual peaks are also of comparable magnitude with the experiment. The two satellite peaks (one at low energy and the other in between the large peaks) has been found to get intensities mostly from the transition to the 2\Pi\textsubscript{1/2} state of ClH\textsubscript{2}. A detailed analysis revealed that the individual peak structures are quite complex and each peak originates from highly overlapping transitions to all the SO states of ClH\textsubscript{2}. The fine structures under each peak revealed van der waals progression (motion along Cl...H\textsubscript{2} coordinate) as well as progression along the ClH\textsubscript{2} bending motion and H\textsubscript{2} vibration. A strong effect of the SO coupling is found and the electronic coupling arising from the \textit{Σ}−\textit{Π} CIs has practically no influence on the dynamics [39].

The H+H\textsubscript{2} exchange reaction proceeds on the repulsive lower adiabatic sheet (\textit{V}_{\perp}) of its degenerate 1\textit{2}\textit{E}' ground electronic manifold. The impact of the CIs of this JT split electronic manifold on its reaction dynamics has recently been investigated by us with the aid of a quantum flux operator formalism and a time-dependent wave packet approach [12, 40]. The possible impact of the CIs on the reactive scattering dynamics of H+H\textsubscript{2} has been studied in the literature in terms
of the geometric phase change of the adiabatic electronic wavefunction [41, 42]. In our approach we explicitly considered both the sheets of its degenerate ground electronic state and their coupling in order to investigate the reaction dynamics. This in a way extends the previous studies on this system by going to higher energies and incorporating the geometric phase effects and the nonadiabatic coupling in a coherent fashion. The initial wavefunction pertinent to the H+H$_2$ reacting system is located in the asymptotic reactant channel of $V_-$ and then propagated in a diabatic representation (mentioned above). The final analysis is carried out by representing the flux operator both in the adiabatic and in the diabatic electronic representations (see, Eqs. 11 and 26 of Ref. [40]). The minimum of the seam of CIs of this degenerate ground electronic manifold occurs at $\sim$2.74 eV. It is found that the reaction probabilities for H$_2$(v = 0, j = 0) differ only slightly from the uncoupled surface results beyond this energy, which can be essentially reproduced by adding the diagonal correction term (the Born-Huang term) to the single surface adiabatic Hamiltonian. The fact that the minimum energy path of the H+H$_2$ exchange process occurs at the collinear configuration, and the seam of CIs occurs at the $D_{3h}$ configuration, the CIs do not have any major impact on its reactive scattering dynamics [12, 40].

Following this work on the H+H$_2$ reactive scattering we extended our flux operator formalism for three electronic states with electronic and SO coupling within a time-dependent wave packet approach and applied it recently to the realistic case of Cl(2P)+H$_2$ reaction dynamics [43] for the lowest value of the partial wave $J$=0.5. The excited SO states viz., $^2$II$_{3/2}$ and $^2$II$_{1/2}$ are nonreactive in the adiabatic limit. The theoretical results revealed a huge impact of the SO coupling on the reaction dynamics. The electronic coupling due to the CIs on the other hand has only minor impact on the dynamics of the $^2$II$_{1/2}$ diabatic electronic state. Analysis of the reactivity of different SO states revealed that the II state reacts via the nonadiabatic transition to the $^2$II$_{1/2}$ state and is mostly mediated by the C – II SO coupling. The SO excited Cl*(2P$_{1/2}$) is less reactive compared to its SO ground state, in agreement with the available theoretical results [16] but in apparent contradiction with the experiment [44].

A concise account of the quantum dynamics at CIs of PESs is presented emphasizing on a wide variety of molecular processes with increasing complexity ranging from spectroscopy to reactive scattering. The spectroscopic probing of the CIs of PESs is discussed. The interplay of the electronic and SO coupling in the quantum molecular dynamics has been considered and treated. The multimode effects, huge increase in the spectral line density and the ultrafast nonradiative decay of the excited molecular states due to the nonadiabatic coupling associated with the CIs of PESs are delineated.
Acknowledgments

It is a great pleasure to acknowledge fruitful collaborations with Professors H. Köppel, L. S. Cederbaum, W. Domcke, Drs. C. Woywod and V. Vallet and Mrs. T. S. Venkatesan, S. Ghosal and G. M. Krishnan on various topics presented in this account. Financial supports from the AvH stiftung, VW stiftung (Germany) and the DST, CSIR (New Delhi) are gratefully acknowledged. Thanks are also to the UGC, New Delhi for the computational facilities provided in the University of Hyderabad under the UPE program. A travel support from the Indian National Science Academy to participate in this meeting is gratefully acknowledged.

The Geometric Phase and the Hydrogen Exchange Reaction

Juan Carlos Juanes-Marcos and Stuart C. Althorpe
School of Chemistry, University of Nottingham,
University Park Nottingham, NG7 2RD, U.K.

I. WHY H + H₂?

The hydrogen exchange reaction (H + H₂ → H₂ + H) is the simplest prototype of a bimolecular reaction [1]. Conveniently, it is also the simplest reaction to possess a conical intersection (CI). The CI lies 2.7 eV above the minimum in the potential energy surface, which makes it inaccessible to most reactive scattering experiments (which probe the reaction in the range E=0.4–2.5 eV). However, the path around the intersection, which passes over the three H-H-H transition states, is energetically accessible. The H₃ reaction dynamics ought therefore to manifest the effects of the Geometric (or Berry) phase (GP) [2–4], and can therefore be used as a prototype, to investigate how the GP affects the dynamics of bimolecular reactions.

The difference between a bimolecular and unimolecular reaction is, of course, that the former has a sense of direction, defined by the collision vector of the reagents. This produces a characteristic angular distribution of the products, as a result of the large number of superposed total angular momentum (J) states. One of the main reasons for studying GP effects in H + H₂ is to find out how the GP can affect this superposition of J-states and hence the directionality of the reaction mechanism. The most interesting outcome would be that the GP caused radical changes in the directionality of the mechanism, giving rise to striking features in the angular distribution of the products, which could be detected experimentally.

Such a result was predicted some years ago by Kuppermann and co-workers [5], in pioneering calculations on the H + H₂ reaction that included the GP. However, the striking changes they predicted in the product angular distributions have not been found experimentally [6]. Moreover, these predictions were contradicted recently by a series of calculations by Kendrick [7]. The latter included the GP using the vector potential method of Mead and Truhlar [3], and predicted an intriguing but negative result: In the individual fixed-J calculations, the GP produces noticeable changes in, for example, the rovibrational...

81
product distributions, but when the fixed-$J$ wave functions are superposed (to give the full bimolecular scattering wave function) all the changes produced by the GP ‘magically’ cancel. As a result, Kendrick predicts [7] that there are no measurable GP effects in either the differential cross sections (DCS—the angular distributions of the products) or the integral cross sections (ICS—the total amount of product scattered into a given $H_2$ rovibrational product state). It is not yet known what is the cause of this striking result (symmetry effects have been suggested [7] but not proved); neither is it known whether the cancellation is a general effect, applicable to all bimolecular reactions, or specific to $H + H_2$.

Furthermore, this prediction contradicts directly the predictions made earlier by Kuppermann and co-workers [5].

II. RECENT WAVE PACKET CALCULATIONS

Recently, we performed time-dependent wave packet calculations [8–13] on the $H + H_2$ reaction, with the aim of deciding which of Kuppermann’s and Kendrick’s predictions were correct, and of using the wave packets to explain how (or whether) the GP changes the reaction dynamics. In a preliminary calculation [10], we computed the full wave packet for the bimolecular $H + H_2$ reaction, without inclusion of GP effects, and plotted the packet in terms of hyperspherical coordinates. These coordinates [14] represent very clearly the motion of the wave packet around the CI. The packet failed to encircle significantly the CI, at any scattering angle, demonstrating that GP effects are expected to be small in the $H + H_2$ reaction.

Subsequently [12, 13], we computed the DCS and ICS, both with and without inclusion of the GP. The results agreed with the predictions of Kendrick [7], showing a perfect cancellation in the GP effects, when individual $J$-states were superposed to give the ICS. Given that the methods [8, 11] of our calculations differ in almost every respect from those of Kuppermann [5] and Kendrick [7] (time-dependent versus time-independent, Jacobi versus hyperspherical coordinates, grid basis functions versus hyperspherical surface functions, different definitions of the encirclement angle and vector potential), the close agreement with Kendrick’s results suggests almost conclusively that the prediction that the GP effects cancel is the correct one.

Nevertheless, our calculations [12, 13] do predict that GP effects are experimentally observable in $H + H_2$, in the DCS, at energies above 1.8 eV. Kendrick [7] did not report results for the full DCS in this energy range. We find that oscillations that are present in the non-GP differential cross sections (for some particular final rovibrational quantum states) change noticeably upon inclusion of the GP. In the corresponding integral cross sections, the cancellation discussed above still holds rigorously.

Hence new experimental measurements of the DCS in $H + H_2$ are required,
above 1.8 eV. This will establish whether the predictions made here are indeed correct. It is also necessary to establish theoretically the cause of the cancellation between different $J$ states, and to determine whether this is a general effect, which will prevent the GP from influencing the ICS or the rate constant of any bimolecular chemical reaction.

Acknowledgements

This research is funded by a grant from the UK Engineering and Physical Sciences Research Council. SCA acknowledges the award of a Royal Society University Research Fellowship.

For the accurate study of non-adiabatic systems it is necessary to solve the
time-dependent Schrödinger equation. The most direct and visual way of doing
this is wavepacket dynamics in which the nuclear wavefunction is expanded in a
basis set
\[ \Psi(Q, t) = \sum_{N_1 \ldots N_f} A_{N_1 \ldots N_f}(t) \phi_{N_1}(Q_1) \ldots \phi_{N_f}(Q_f) \]  
(1)
and equations of motion are now set up for the time-evolution of the expansion coe-
cfficients. The basis functions usually used effectively discretise the coordinate
space, with the wavefunction being represented on a multi-dimensional grid built
up from the product of one-dimensional grids. This method has been used to
provide much detailed information about how a molecular system passes through
a conical intersection \cite{1, 2}. It, however, suffers from the serious drawback that
the number of grid points increases exponentially with the number of degrees of
freedom of the system - restricting us to 4-6 in practice.

To extend wavepacket dynamics to larger systems the multi-configuration
time-dependent Hartree (MCTDH) method was introduced \cite{3}. The basis func-
tions are now time-dependent:
\[ \Psi(Q, t) = \sum_{n_1 \ldots n_f} A_{n_1 \ldots n_f}(t) \varphi_{n_1}(Q_1, t) \ldots \varphi_{n_f}(Q_f, t) \]  
(2)
and equations of motion are now set up for the time-evolution of the expansion coefficients and the functions. A variational principle is used for the derivation
and so the basis functions optimally describe the wavepacket at all times. The
“single-particle functions”, as the basis functions are called, are described using
the same time-independent “primitive” basis functions used in the standard
method. This has the effect of contracting the basis set, and the full product
basis is only set up where the evolving wavepacket requires it. Details of the
method and its relationship to standard wavepacket dynamics are to be found
in recent reviews \cite{4, 5}.
In its simplest form one-dimensional single-particle functions are used. The computational effort is thereby reduced from $N^f$ to $n^f$, where $N$ is the number of time-independent basis functions per degree of freedom (of which there are $f$) and $n$ the number of single-particle functions required. The variational character of the method ensures that $n << N$. A further flexibility of the method is that one can use multi-dimensional single-particle functions (a coordinate $Q$ in Eq. (2) is then a set of real coordinates). This reduces the effective dimensionality of the system, and can give a further gain in efficiency [4].

The MCTDH method is completely general and can be applied to all quantum dynamics calculations. In conjunction with the vibronic model Hamiltonian, it has proved especially powerful in treating non-adiabatic systems [6]. Our calculation on the absorption spectrum of pyrazine including all 24-modes is becoming a standard benchmark [7].

While this is a big step forward, the exponential scaling found in wavepacket dynamics is still present, and more than 30 degrees of freedom are still only possible in special cases. To break this exponential scaling further developments such as the cascading method [5], selecting important configurations [8], and using localised single-particle functions that follow trajectories [9] have been proposed.

Another variant, which we are presently developing, is called the G-MCTDH method. In this, single-particle functions can be replaced by multi-dimensional Gaussian functions, $g$. Thus the wavefunction ansatz is

$$\Psi(Q, t) = \sum_{n_1 \ldots n_f} A_{n_1 \ldots n_f}(t) \varphi_{n_1}^{(1)}(Q_1, t) \ldots \varphi_{n_s}^{(s)}(Q_s, t) g_{n_{s+1}}^{(s+1)}(Q_{s+1}, t) \ldots g_{n_f}^{(f)}(Q_f, t)$$

and equations of motion for the parameters of the single-particle Gaussians are now required in addition to those for the coefficients and usual MCTDH single-particle functions [10]. The use of Gaussian functions reduces the scaling as, although more of these non-orthogonal functions will be required than single-particle functions, the number of parameters will be far fewer than the number of primitive grid functions needed. Being free from a primitive basis grid also means that it is not necessary to define a priori limits to the evolving system.

The efficiency of the Gaussian functions however is only useful if we can solve the integrals required cheaply. The simplest way to do this is to use a local harmonic approximation (LHA) to the potential about the midpoint of each Gaussian function. The dynamics of a system attached to a bath has been treated by this method [11].

A further step towards approximate, but reasonable, quantum dynamics would then be to treat the whole system by a set of multi-dimensional Gaussian functions, i.e.

$$\Psi(Q, t) = \sum_n A_n(t) g_n(Q, t)$$

This we call the variational multi-configuration Gaussian (vMCG) method.
In contrast to other Gaussian Wavepacket methods (see e.g. the Martinez and Levine article in this volume or the brief review in [12]), the vMCG functions do not follow classical trajectories. The variational derivation for the parameter equations of motion means that the functions are coupled and move so as to avoid each other. As a result, the space is optimally covered, and convergence will be fast. A further feature of the variational coupling is that the functions are able to describe tunelling. This has been demonstrated on a 4-dimensional Henon-Heiles potential [13].

Like all Gaussian wavepacket based methods that require only local information about the potential energy surface, the vMCG method also opens the opportunity to provide a quantum dynamics method with the surfaces calculated “on-the-fly” where and when they required by the evolving wavepacket. This is really the only feasible approach for systems with many degrees of freedom. It also opens up the door to using quantum dynamics as an everyday tool in the manner quantum chemistry is used today.

A demonstration of this approach has been published using the butatriene radical cation as a suitable test [14]. A very small basis set was seen to qualitatively reproduce the main features of the dynamics (wavepacket bifurcation, a recurrence in the adiabatic populations). Combined with the GAUSSIAN program to calculate the surfaces, the direct dynamics version, DD-vMCG, is then shown to be a feasible scheme.

Reaction Dynamics on Conical Intersections for the OHF System

Octavio Roncero\textsuperscript{a}, Susana Gómez-Carrasco\textsuperscript{b,c}, Lola González-Sánchez\textsuperscript{a,b}, Miguel Paniagua\textsuperscript{c} and Alfredo Aguado\textsuperscript{c}
\textsuperscript{a}) Unidad Asociada UAM-CSIC, Instituto de Matemáticas y Física Fundamental, C.S.I.C., Serrano 123, 28006 Madrid, Spain
\textsuperscript{b}) Departamento de Química Física, Facultad de Química, Universidad de Salamanca, 37008 Salamanca, Spain and
\textsuperscript{c}) Unidad Asociada UAM-CSIC, Departamento de Química Física, Facultad de Ciencias C-XIV, Universidad Autónoma de Madrid, 28049 Madrid, Spain

I. INTRODUCTION

In atmospheric chemistry open shell species, like oxygen atoms, play an important role. The collisions among those species involve several degenerate electronic states correlating either to reactants or products, which may cross along the minimum energy reaction path, leading to conical intersections. The study of the reaction dynamics at these conical intersections is therefore of great interest in the modeling of the atmosphere.

The reactions of hydrogen halides, HX, with oxygen atoms contribute in the catalytic ozone destruction cycle\cite{1}, and because its larger abundance, the chlorinated compounds have been the most widely studied\cite{2-12}, most of them in single adiabatic potential energy surfaces (PES). The realistic modelization of three-dimensional coupled potential energy surfaces for studying reaction dynamics requires high level \textit{ab initio} calculations of large complexity and the development of new methods for their fitting and for the study of the dynamics. O+HF system may be considered as a benchmark model system for this kind of reactions because of its relatively simple electronic structure, presenting most of the features of the O+HX family. Among them, the first triplet states present several curve crossings along the minimum energy path at collinear configuration as shown in Fig.1, leading to conical intersections of special interest in this work.

The HF+O(\textit{3P}) \rightarrow OH+F reaction is very endoergic, by \(\approx 1.5 \text{ eV}\), in contrast to the analogous HCl+O(\textit{3P}) reaction, which is nearly thermoneutral. The reverse OH+F reaction involves two radical species and, until now, only few experimental kinetic studies on the temperature effect on the rate constants\cite{13} and
FIG. 1: Collinear minimum Energy Path (in eV) for some electronic states of OHF including several asymptotic rearrangement channels.

infrared chemiluminescence spectra for final vibrational states of HF products[14] are available, under multiple collision conditions.

An alternative source of experimental information about this system was obtained in the photoelectron detachment spectroscopic studies performed by Neu-mark and co-workers[15]. In these experiments the OHF$^-$ anion, of linear equilibrium configuration, is excited by detaching an electron, and several electronic states of the neutral OHF system are reached in the region of the transition state. Nearly all previous theoretical simulations[15, 16] have been restricted to collinear OHF geometries and the ground electronic state.

Later, the three-dimensional PES for the ground triplet $1^3\Pi$ state has been proposed[17] and the photodetachment spectrum was simulated[18]. In contrast to previous 2D simulations, the spectrum showed many resonances. Below the OH+F threshold, the resonances were attributed to the collinear O+HF products well. Above this threshold, however, the resonances correspond to the light hydrogen atom oscillating between the heavier ones, exploring the two wells existing in the entrance and exit channels, respectively, and the region of the saddle point. Such resonances also appeared in the OH+F reactive collisions[17], both in Wave-Packets (WP) and Quasiclassical Trajectory (QCT) simulations, thus demonstrating the importance of quasi periodic orbits at the transition state for low translational kinetic energies. After average over partial waves, the individual trace of these Heavy-Light-Heavy (HLH) resonances disappears, but
the total cross section showed a fast increase at low translational energies, due to the presence of those HLH resonances. The good agreement obtained in the total reaction cross sections between WP and QCT calculations[17], justifies the use of the last method for comparing with the experimental available data. Thus, the experimental final vibrational and rotational distribution of HF products at nearly room temperature[14] were very nicely reproduced by QCT results[19]. Also, the thermal rate constant obtained with the ground electronic state was slightly larger than the experimental ones[13]. Neglecting the spin-orbit effects and assuming that the three triplet states have the same reactivity, multiplying by the electronic partition function for triplets, 9/24, the simulated rate constant becomes slightly lower than the experimental one.

More recently, the PES’s for the other two triplet states, 2^3\Sigma^+ and 1^3\Pi, were obtained[20]. The simulated photodetachment spectra[21], obtained using these three three-dimensional PES’s for triplet states, and four two-dimensional PES’s for singlet states, reproduced in an excellent way all the structures of the experimental spectrum[15]. However, the reaction cross section for the OH+F collision on the excited triplet states were found to be too small[20]. Thus, with only the ground triplet state contributing to the reaction, the partition function becomes 3/24, producing a simulated rate constant too small with respect to the experimental one. This could be attributed to the PES’s. However, the quality of the \textit{ab initio} calculations and the accuracy of the fits does not seem that this could be the responsible for the whole disagreement.

Another reason may be the possibility of non adiabatic transitions due to the existing conical intersections. At collinear geometries, the triplet states correlate with a \(^3\Sigma^+\) and two \(^3\Pi\) states. These states cross several times along the minimum energy path, as shown in Fig. 1, so that the wells in the reactant and product channels correspond to the \(^3\Sigma^+\) state, while the lower transition state correlates to the \(^3\Pi\) states. Such situation is clearly shown in Fig.2, where the crossing seams between the two triplet states at collinear geometry are shown. This geometry plays a central role in the simulation of the photodetachment spectrum since the initial wavepacket is on the top of the saddle point for the collinear equilibrium geometry of the parent OHF\(^-\) anion in its ground vibrational state, as also shown in Fig.2. This wavepacket evolves towards reactants and products passing through the intersection seams. Moreover, in the collision, to reach HF+O products from OH+F, the wavepacket should cross the intersection seams twice.

As long as the system bents, the \(^3\Sigma^-\) state interacts with one \(^3\Pi\) state, yielding two \(^3\Pi\) states and one \(^3\Sigma^+\) state. The two \(^3\Pi\) cross at collinear geometry, and at bent configuration near the crossing seams of Fig.2 important \(\Sigma - \Pi\) vibronic effects should appear, which could be the responsible of an increase of the reactivity in the excited triplet states. Moreover, the resonances appearing in the reactive collision and photodetachment spectrum of the ground \(^3\Sigma^-\), are attributed to the two wells, corresponding to the \(^3\Sigma^-\) state, passing over the
lower saddle point of the $^3\Pi$ states. Therefore, such resonances, which mediate the reactivity in collisions at low translational energies, should be very much affected by the $\Sigma - \Pi$ vibronic couplings.

II. DIABATIC REPRESENTATION

The study of the dynamics near conical intersections presents the problem of singularities in the non-adiabatic couplings when using the adiabatic representation. It is more convenient to transform to a diabatic representation, in which the couplings vary smoothly with the nuclear configuration. However, for polyatomic systems the difficulty is that there is no a strict diabatic representation, as it is well known[22]. For this reason many quasidiabatization schemes are possible. In the present case a quite complete description is formed by considering a two state model, what provides an important simplification. The transformation between the adiabatic and diabatic representation is then governed by a mixing angle $\alpha$ which can be obtained in many different ways[23–25].

By similarity with the Renner-Teller effect and $\Sigma - \Pi$ vibronic coupling[26], a perturbative approach could be followed to determine the effective Hamiltonian to extract the proper adiabatic/diabatic transformation. However, when treating a reaction from reactants to products it is difficult to establish a equilibrium
geometry. Instead of this, here we propose a new model which yields equivalent results[27].

The reaction to be studied is given by

\[ \text{OH}^{(2\Pi)} + \text{F}^{(2\,P)} \rightarrow \text{HF}^{(1\Sigma^+)} + \text{O}^{(\beta\,P)}, \]  

(1)

while the third rearrangement channel to form \text{OF} products is energetically closed. The transfer of the \text{H} atom is produced at quite short distances, so that along the reactant and product channels the diatomic HF or OH fragments can be considered to be at their corresponding equilibrium distances. Both diatomic fragments have a significant ionic character, and at a zero order approach, they can be considered as \text{H}^+\text{F}^- and \text{O}^-\text{H}^+. Under this assumption, the reaction can be described as

\[ \text{O}^{-}(2\,P)\text{H}^+ + \text{F}^{(2\,P)} \rightarrow \text{H}^+\text{F}^{-}(1\,S) + \text{O}^{(\beta\,P)}, \]  

(2)

where \text{H}^+ is a proton with no structure and:

- \text{O}^{-}(2\,P) anion is described by one electron hole in a \text{p} atomic orbital with the restriction that the \text{p}_z component does not exist,
- \text{F}^{(2\,P)} atom is described by one electron hole in a \text{p} atomic orbital,
- \text{F}^{-}(1\,S) is an atomic spheric anion with a closed shell, and
- \text{O}^{(\beta\,P)} atom can be described by two electron holes in a \text{p} atomic orbital.

The reaction can then be visualized by an exchange of a proton and an electron hole between the two heavier atomic fragments. The \text{OF} axis thus form a quite natural quantization axis, and the proton and two electron-holes move around it. Being a two electron-hole model, the electronic spin part can be separated from the orbital part. The basis set orbital functions are classified separated by the projection of the orbital angular momentum on the \text{OF} axis, \lambda. In this crude model, the orbital electronic-hole functions basis set for triplet states is formed by functions with \lambda = 0,

\[
\begin{align*}
    & p^O_1(1)p^F_{-1}(2) - p^O_1(2)p^F_{-1}(1) - p^O_1(1)p^F_1(2) & p^O_1(2)p^F_1(1) & \text{ for reactants} \\
    & p^O_1(1)p^O_{-1}(2) - p^O_1(2)p^O_{-1}(1) & \text{ for products}
\end{align*}
\]

or with \lambda = 1,

\[
\begin{align*}
    & p^O_1(1)p^F_0(2) - p^O_1(2)p^F_0(1) & \text{ for reactants}
    & p^O_1(1)p^O_0(2) - p^O_1(2)p^O_0(1) & \text{ for products}
\end{align*}
\]

and with \lambda = -1, are equivalent to those written for \lambda = 1, but with \text{p}^O_{1} instead of \text{p}^O_{1}.
In the expressions above (i) refers to electron-holes 1 or 2. Under reconnection through the x-z body-fixed plane these functions have an eigenvalue $-1$, thus giving rise to the $^3\Sigma^-$ state.

We can then consider the total electronic Hamiltonian, $\hat{H}_e$, as being that of the OF$^-$ fragment plus the electrostatic terms of the proton with the rest of the particles of the OHF system. These last terms can be factorized in an isotropic contribution, corresponding to the proton in the OF axis, from the anisotropic term, $V_e$, which account for the couplings arising when the proton leaves the OF axis. The electronic Hamiltonian then becomes $\hat{H}_e = \hat{H}_e^0 + V_e$. A diabatic representation can be formed by eigenfunctions of $\hat{H}_e^0$, expressed in the electronic basis set functions expressed above, which have a defined projection. Here we will consider the lower state for $\Lambda = 0, \pm 1$, and denote them as $\phi_\Lambda$, with eigenvalues $E_\Lambda$.

Within this $3 \times 3$ subspace, the diabatic states are coupled through the $V_e$ potential term, so that the Hamiltonian matrix in this $(\phi_{-1}, \phi_0, \phi_1)$ representation becomes:

$$
\begin{pmatrix}
E_{-1}(r, R, \gamma) & V_1(r, R, \gamma)e^{i\chi} & 0 \\
V_1(r, R, \gamma)e^{-i\chi} & E_0(r, R, \gamma) & -V_1(r, R, \gamma)e^{i\chi} \\
0 & -V_1(r, R, \gamma)e^{-i\chi} & E_1(r, R, \gamma)
\end{pmatrix}
$$

where $E_1 = E_{-1}$ and the direct coupling between $\phi_1$ and $\phi_{-1}$ is zero by two reasons. First, the direct coupling is not possible because $V_e$ includes mono-electronic-hole terms, so it can not change simultaneously the projection of the orbital angular momentum of the two electron at the same time. Second, indirect couplings could appear due to some other states, but in the present simple model, with three diabatic states, this is not possible. The direct $(\phi_1 | \hat{H}_e | \phi_{-1})$ coupling, similar to that appearing in treating Renner-Teller effects, is expected here to be rather small. The $V_e$ coupling term can be expanded in spherical harmonics[28], from where it is deduced that the coupling terms $V_1(r, R, \gamma)$ goes to zero as $\gamma \to 0$ or $\pi$ as it is also found in other treatments for the $\Sigma - \Pi$ vibronic effects[26].

The matrix elements in Eq.(3) depends on the coordinates required to specify the geometry of the molecule. Here we consider two Jacobi vectors $r$, the OF internuclear vector, and $R$ joining the OF center-of-mass to hydrogen, with $\gamma$ being the angle between them. We consider a body-fixed frame with the $z$-axis being parallel to $r$. The orientation of this frame with respect to the space-fixed frame is specified by two Euler angles $(\phi_r, \theta_r, 0)$. Finally, the orientation of $R$ vector in the body-fixed frame is specified by the angles $(\gamma, \chi)$.

Eq.(3) is completely analogous to those used before for treating $\Sigma - \Pi$ vibronic effects[26]. Because the system presents a plane of symmetry, this diabatic representation can be transformed to a new symmetry adapted diabatic basis.
\((\phi_Y, \phi_Z, \phi_X)\), in which the transformation brings \(\mathbf{R}\) to the \(x\)-\(z\) plane as

\[
(\tilde{\phi}_Y \tilde{\phi}_Z \tilde{\phi}_X) = (\phi_{-1} \phi_0 \phi_1) \begin{pmatrix}
e^{i\chi/\sqrt{2}} & 0 & e^{i\chi/\sqrt{2}} \\
0 & 1 & 0 \\
-e^{-i\chi/\sqrt{2}} & 0 & e^{-i\chi/\sqrt{2}}
\end{pmatrix}.
\]

(4)

In this representation the Hamiltonian becomes block diagonal

\[
\tilde{\mathbf{H}}_c = \begin{pmatrix}
E_1(r, R, \gamma) & V_1(r, R, \gamma)\sqrt{2} & 0 \\
V_1(r, R, \gamma)\sqrt{2} & E_0(r, R, \gamma) & 0 \\
0 & 0 & E_1(r, R, \gamma)
\end{pmatrix},
\]

(5)

which eigenvalues are

\[
E_{\pm} = \left(E_1 + E_0 \pm \sqrt{(E_1 - E_0)^2 + 8V_1^2}\right)/2 \quad \text{and} \quad E_1
\]

(6)

which are the ones obtained in the \textit{ab initio} calculations.

In this model, the diabatic Hamiltonian matrices only depend on three quantities, \(E_1, E_0\) and \(V_1\), which vary as a function of the internal coordinates. \(E_1\) corresponds to the eigenvalues of the \(1^3A'\) electronic state, which fit as a function of internal coordinates is described elsewhere\([20]\).

\(E_0\) and \(V_1\) can be directly obtained from the eigenvalues of the \(1^3A''\) and \(2^3A''\) states. This is done in a sequential procedure by fitting first \(E_0 = E_+ + E_- - E_1\), using the method of Aguado and Panagia\([29]\). Later the \(V_1^2 = \left[(E_+ - E_-)^2 - (E_1 - E_0)^2\right]/8\), in which the dependence of the coupling on \(\sin \gamma\) is included to account for the proper symmetry conditions of the Hamiltonian matrix, using a modification of the standard fitting procedure used for the other terms\([29]\).

\section*{III. QUANTUM WAVEPACKET DYNAMICS}

The coordinate system used to describe the diabatization model is not valid to describe any of the two rearrangement channels. Instead, we used either reactant or product Jacobi coordinates in a body-fixed frame, in which \(\mathbf{r}'\) is the BC internuclear vector, BC=OH or HF, and \(\mathbf{R}'\), which joins the BC center of mass to the A atom, A=F or O (the primes are introduced to distinguish from those coordinates used in the diabatization model). The body-fixed frame chosen is also formally different, with the \(z'\)-axis parallel to the new \(\mathbf{R}'\), being the two Jacobi vectors on the \(x'-z'\) plane. Hydrogen is very light and always attached to one of the heavier atoms, and it is a good approximation to consider that \(\mathbf{R}'\) nearly coincides with the quantization axis used for the diabatization model \(\mathbf{r} = \mathbf{R}_{OF}\), specially at long distances \(\mathbf{R}'\). Because of this approximation, the electronic diabatic functions can be referred to the present \(\mathbf{R}'\) axis.
In these coordinates the wavepacket for a total angular momentum $J$, with projection $\Omega$ on the body-fixed $z$-axis, is represented in a finite basis set as

$$\psi_i^{JMS}(r', R', t) = \sqrt{\frac{2J+1}{4\pi}} \sum_{j, \Omega, \Lambda} D_{M\Omega}^{J*}(\phi', \theta', 0) \ Y_{j\Omega}(\gamma', \chi') \ \phi_{\Lambda}^{S\Sigma}$$  

(7)

and

$$\frac{\psi_i^{JS}(r, R, t)}{rR}$$  

(8)

where $i$ refers to the quantum numbers needed to specify the initial wavepacket, either in a collision or photodetachment simulation. $\phi', \theta'$ are the polar angles of $R'$ in the space-fixed frame while $\gamma', \chi'$ are the polar angles of $r'$ in the corresponding body-fixed frame.

The Hamiltonian operator of the system is analogous to that of Rebentrost and Lester[30], and if electronic couplings due to the Coriolis terms are neglected, the $X$ state, equivalent to the adiabatic $1^3A^0$ state, is separated from the case of the $Y, Z$ couple, corresponding to the $1^1A^0$ electronic states.

FIG. 3: Population of the diabatic electronic states obtained in the F+OH($\Lambda = Z, v = 0, j = 1, J = 0$) collision.

Wavepacket calculations performed for the F+OH($\Lambda = Y$ or $Z, v = 0, j = 1, J = 0$) reactive collisions indicate that the electronic population is transferred
essentially in the vicinity of the transition state, where the two conical inter-
sections take place. Starting in the asymptotic OH+F reactant channel, the
wavepacket becomes very broad as it evolves, because its large energy distribu-
tion. As a consequence, when it arrives to the crossing region its width is much
larger than the transition state region. The dynamics cannot then distinguish
the effects due to a particular crossings, either in the reactants or the prod-
ucts channels. As a consequence, the electronic population transfer presents a
smooth variation, as shown in Fig.3. Because of the HLH character of the re-
action, and the small skewing angle, the reaction takes place preferentially at
nearly collinear geometry, where the Σ – Π vibronic couplings are more impor-
tant. This explains the high efficiency of the population transfer, which yield to
a nearly equal population of the two diabatic electronic states. For this reason
the reaction probabilities are very similar for collisions starting in different elec-
tronic diabatic states. When the calculation is performed in the corresponding
adiabatic representation, however, the reaction probability for the $1^3A''$ is much
higher than that obtained for $2^3A''$, which is nearly negligible. The sum of the
reaction probabilities obtained in the diabatic representation is not equal to the
sum for the adiabatic representation, thus demonstrating the important effects
of non adiabatic transitions in the presence of conical intersections. Neverthe-
less, the total reaction cross sections should be calculated to better determine
the relevance of this effect.

Another feature is that the reaction probabilities present resonances in the
collision for the two different initial electronic diabatic states. In the adiabatic
representation only the ground $1^3A''$ shows resonances. This can also be taken
as an indirect evidence that the resonances are associated to quasibound states
distributed in the two diabatic states.

The situation in the photodetachment spectrum simulations is somehow differ-
cent. The initial wavepacket is placed on the top of the two conical intersections,
as shown in Fig. 2. The wavepacket vibrates several times in the transition state
region passing several times across the two conical intersections, so that the elec-
tronic populations versus time present several oscillations as shown in Fig. 4. As
in the collisional case, the final populations of the two diabatic states become
similar. As a consequence, the spectra corresponding to initial excitation to ei-
ther of the two diabatic states share most of the features. In particular, the HLH
resonances discussed before are present in the two spectra, while in the adiabatic
representation they only appear in the $3A''$ ground electronic state. Also, the
resonances, located on the conical intersection seams, have components on the
two electronic diabatic states.
FIG. 4: Population of the diabatic electronic states obtained in the $\text{OHF}^- + \hbar \nu \rightarrow \text{OHF}(^3\Sigma^-) + e$ photodetachment simulations.

IV. ACKNOWLEDGMENT

This work has been supported by Ministerio de Ciencia y Tecnología (Spain), under grants no. BFM2001-2179 and BQU2001-0152.


97
I. INTRODUCTION

The study of complexes containing open-shell atoms and/or open-shell diatomic molecules is an active field of research. The theoretical description of these complexes is more involved than the description of complexes containing closed-shell molecules because in general the interaction between the fragments is determined by multiple, asymptotically degenerate, potential energy surfaces. Usually, the explicit inclusion of nonadiabatic couplings between the (nearly) degenerate electronic states is avoided by switching to a diabatic basis. Another source of complication in an open-shell complex is the presence of electronic orbital and/or spin angular momentum.

The derivation of the rotational kinetic energy operator and its matrix elements for, e.g., a complex consisting of an open-shell diatomic molecule and a closed-shell atom is a relatively straightforward extension of the derivation for open-shell diatomic molecules. Although the final expressions are simple, the derivation involves two-angle embedded angular momentum operators that satisfy awkward commutation relations. Several rigorous derivations dealing with two-angle embedded frames that can be found in the literature[1–4] do not use the full power of angular momentum theory. In Secs. II and III we will review the rotation operator formalism that we used in recent work [5–7]. The method is rather formal, but it is rigorous and compact and it simplifies the notorious phase convention problems[8] in the definition of the parity operator, as we will show in Sec. IV.

There are certain constraints on the angular expansion of diabatic potentials. For the case of an open-shell diatomic molecule with a closed-shell atom the proper functional form was derived by considering the multipole expansion of...
the interaction energy[9]. For the open-shell atom + closed-shell diatom the expressions were also derived by assuming that an open-shell atom in, e.g., a \( P \)-state may be treated as if it were a closed-shell diatomic molecule in a \( l = 1 \) state [10–12]. We derived the same functional forms in a more formal way, by requiring the interaction operator to be invariant under rotation, inversion, and hermitian conjugation [5, 6]. Recently it was shown that in the case of two interacting open-shell atoms the analogy between an open-shell atom and a diatomic molecule breaks down, whereas the formal approach still applies[13], as we will explain in Sec. V. All angular momentum theory used here can be found in Ref. [14], much of which is reviewed in Ref. [15].

II. ROTRONIC WAVE FUNCTIONS FOR NONLINEAR RIGID MOLECULES

Space-fixed and body-fixed electronic coordinates are related through

\[
\mathbf{r}^{\text{SF}} = \mathbb{R}(\alpha, \beta, \gamma)\mathbf{r}^{\text{BF}},
\]

where the \( 3 \times 3 \) orthogonal matrix \( \mathbb{R} \), expressed in \( zyz \) Euler angles, defines a so-called three-angle embedded frame. Following Wigner’s convention, we have, for an electronic wave function expressed in body fixed electronic coordinates,

\[
\Phi^{\text{elec}}(\mathbf{r}^{\text{BF}}) = \Phi^{\text{elec}}(\mathbb{R}(\alpha, \beta, \gamma)^{-1}\mathbf{r}^{\text{SF}}) = \hat{R}(\alpha, \beta, \gamma)\Phi^{\text{elec}}(\mathbf{r}^{\text{SF}}). \tag{2}
\]

Since we wish to include electronic spin it is convenient to switch to Dirac notation for the electronic wave function

\[
|\mathbf{n}S\Sigma\rangle^{\text{BF}} = \hat{R}(\alpha, \beta, \gamma)|\mathbf{n}S\Sigma\rangle^{\text{SF}},
\]

where the superscript indicates to which axis (or frame) the spin-projection quantum number \( \Sigma \) and possibly other electronic quantum numbers \( \mathbf{n} \) refer. The rotation operator \( \hat{R}(\alpha, \beta, \gamma) \), in the active rotation convention has the explicit form

\[
\hat{R}(\alpha, \beta, \gamma) = e^{-i\alpha\hat{j}_z}e^{-i\beta\hat{j}_y}e^{-i\gamma\hat{j}_z}, \tag{4}
\]

where \( \hat{j} \) is the space-fixed total electronic angular momentum operator. Matrix elements of this operator in the standard basis \( \{|JM\rangle, M = -J, \ldots, J\} \) are the familiar Wigner D-functions

\[
D_{M,\Omega}^{J}\,(\alpha, \beta, \gamma) = \langle JM|\hat{R}(\alpha, \beta, \gamma)|J\Omega\rangle. \tag{5}
\]

For a rigid, nonlinear molecule we may now write an (unnormalized) rotronic wave function as

\[
D_{M,\Omega}^{J}\,(\alpha, \beta, \gamma)|\mathbf{n}S\Sigma\rangle^{\text{BF}} = \hat{R}(\alpha, \beta, \gamma)|\mathbf{n}S\Sigma\rangle^{\text{SF}}. \tag{6}
\]
Without the rotation operator in the middle the rotronic wave function would be a direct product of a pure nuclear rotational wave function and a purely electronic wave function and all rotational properties would follow from elementary angular momentum theory. Only two fundamental relations involving the rotation operator, given below, are required to derive the rotational properties of the body-fixed wave function. Note that the body-fixed electronic function $(nS\pi)_{BF}$ depends on the nuclear coordinates via the choice of a frame attached to the nuclei.

The space-fixed total angular momentum operator $\hat{J}$ is given by

$$\hat{J} = \hat{\mathbf{L}} + \hat{\mathbf{j}},$$

(7)

with the nuclear angular momentum operator $\hat{\mathbf{L}}$ given by

$$\hat{L}_x = i \cos \alpha \cot \beta \frac{\partial}{\partial \alpha} + i \sin \alpha \frac{\partial}{\partial \beta} - i \frac{\cos \alpha}{\sin \beta} \frac{\partial}{\partial \gamma},$$

(8)

$$\hat{L}_y = i \sin \alpha \cot \beta \frac{\partial}{\partial \alpha} - i \cos \alpha \frac{\partial}{\partial \beta} - i \frac{\sin \alpha}{\sin \beta} \frac{\partial}{\partial \gamma},$$

(9)

$$\hat{L}_z = -i \frac{\partial}{\partial \alpha}.$$ 

(10)

Body fixed components of this angular momentum operator are defined by

$$\hat{L}^\text{BF} \equiv \Re(\alpha, \beta, \gamma)^T \hat{\mathbf{L}}$$

(11)

and similarly for $\hat{j}^\text{BF}$ and $\hat{J}^\text{BF}$. The action of $\hat{\mathbf{L}}$ and $\hat{L}^\text{BF}$ on the rigid rotor functions $D_{M,\Omega}^{J_\pi}$ is known from elementary angular momentum theory. The two fundamental relations involving the rotation operator are the defining property of a vector operator

$$\hat{R}(\alpha, \beta, \gamma)\hat{j} \hat{R}(\alpha, \beta, \gamma)^\dagger = \Re(\alpha, \beta, \gamma)^T \hat{j}$$

(12)

and

$$\hat{L} \hat{j} \hat{R}(\alpha, \beta, \gamma) = -\hat{j} \hat{R}(\alpha, \beta, \gamma).$$

(13)

This last relation may not be as familiar. For the $z$ component it is easily verified by applying $\hat{L}_z$ [see Eq. (10)] to the the rotation operator defined in Eq. (4). The proof for the other components involves repeated use of Eq. (12). Actually, taking the complex conjugate of a matrix element $\langle J M | \ldots | J' \Omega \rangle$ to the left and the right of Eq. (13) gives the familiar action of $\hat{\mathbf{L}}$ on $D_{M,\Omega}^{J_\pi}(\alpha, \beta, \gamma)$. Eq. (12) may be rewritten as

$$\Re^T \hat{j} \hat{R} = \hat{j} \hat{R}.$$ 

(14)
where we omitted the Euler angles for clarity, and together with Eq. (13) this gives

$$R_T^* \hat{L} \hat{R} = -R_T^* \hat{j} \hat{R} = -\hat{R} \hat{j}.$$  

Adding Eqs. (14) and (15) gives

$$R_T^* \hat{J} \hat{R} = 0$$

and hence $\hat{J} \hat{R} = 0$.  

This proves that

$$\hat{J} |n \Sigma\rangle_{BF} = \hat{J}_{BF} |n \Sigma\rangle_{BF} = 0,$$

i.e., the body fixed electronic wave function is invariant under simultaneous rotation of the electrons and the nuclei. Furthermore, since the electronic angular momentum operator $\hat{j}$ does not act on $D_J^M$, we find that applying $\hat{J}$ or $\hat{J}_{BF}$ to the rotronic wave function of Eq. (6) amounts to acting with $\hat{L}$, respectively $\hat{L}_{BF}$ on $D_J^M$.

### III. ROTRONIC WAVE FUNCTIONS FOR DIATOMIC MOLECULES

For a diatomic molecule we take $\beta$ and $\alpha$ in Eq. (1) to be the polar angles defining the body-fixed $z$-axis of the molecule and we set $\gamma$ to zero, which results in a two-angle embedded frame. The end-over-end angular momentum operator $\tilde{L}$ is obtained from the operators $\hat{L}$ by dropping the terms involving $\hat{\omega}$. The expression equivalent to Eq. (14) for the $\tilde{L}$ operator, however, is more complicated [see Eq. (A28) in [7]] and it would seem that the derivation of the rotational properties of the (unnormalized) two-angle embedded rotronic functions

$$D_J^M (\alpha, \beta) \hat{R} (\alpha, \beta, 0) |n \Lambda \Sigma\rangle_{SF},$$

where we explicitly included the electronic orbital angular momentum projection quantum number ($\Lambda$) is also more complicated. For this reason the two-angle embedded case is usually treated separately [1–4]. We observe, however, that for $\Omega = \Lambda + \Sigma$ we have

$$\hat{R} (\alpha, \beta, 0) |n \Lambda \Sigma\rangle_{SF} = \hat{R} (\alpha, \beta, \gamma) |n \Lambda \Sigma\rangle_{SF} e^{i \Omega \gamma}$$

and with $D_J^M (\alpha, \beta, 0) e^{i \Omega \gamma} = D_J^M (\alpha, \beta, \gamma) \tilde{L} D_J^M (\alpha, \beta, \gamma) \hat{R} (\alpha, \beta, \gamma) |n \Lambda \Sigma\rangle_{SF}$

To evaluate the matrix elements of the $\tilde{L}^2$ operator one commonly substitutes

$$\tilde{l}^2 = \hat{j}^2 - 2 \hat{j}_{BF} \cdot \hat{J}_{BF} + \hat{j}^2,$$
where for a linear molecule \( J \equiv j + l \). A previous derivation of this relation was cumbersome because of the complicated commutation relations between \( \hat{J}^{BF} \) and \( \hat{J}^{BF} \) [1]. However, the corresponding expression for space fixed operators is easily derived by observing that \([\hat{j}_i, \hat{J}^{BF}] = 0\). Next, switching to the body-fixed expression requires \([\hat{j}_i^{BF}, R_{j;k}(\alpha, \beta, \gamma)] = 0\), which is trivial, since the electronic operator \( \hat{j}^{BF} \) does not act on the rotation matrix. One should be aware, however, that sometimes the body-fixed operators are defined by a rotation from the right, in which case the order of \( \hat{j}^{BF} \) and \( \hat{J}^{BF} \) should be reversed. Finally, note that we do not have to rewrite \( \hat{J}^2 \) in body-fixed operators to compute the matrix elements, as was shown in the previous section.

IV. PARITY

The spatial inversion operator \( \hat{i} \) inverts the space fixed electronic and nuclear coordinates and leaves the space fixed spin functions invariant. Since the body-fixed frame is attached to the nuclear coordinates, \( \hat{i} \) also acts on the Euler angles. One axis of the body-fixed frame should be defined as the cross-product of the other two, in order to keep a right-handed frame. As a result, \( \hat{i} \) maps a right-handed frame onto another right-handed frame and the action of \( \hat{i} \) on the Euler angles follows from

\[
i\mathbb{R}(\alpha, \beta, \gamma)\hat{i}^\dagger = \mathbb{R}(\alpha', \beta', \gamma').
\]

For example, in the case of the two-angle embedded frame define above we find

\[
\alpha' = i\alpha i^\dagger = \alpha + \pi,
\]
\[
\beta' = i\beta i^\dagger = \pi - \beta.
\]

When evaluating the effect of this transformation on the rotation operator in the case of half-integer spin we should be aware that rotations over \( 2\pi \) radians do not correspond to the identity operator and we should use the relations for the rotation operator in function space

\[
\hat{R}(\alpha, \beta, \gamma)\hat{R}(\mathbf{n}, \phi)\hat{R}^\dagger(\alpha, \beta, \gamma) = \hat{R}(\mathbb{R}(\alpha, \beta, \gamma)\mathbf{n}, \phi),
\]

where a rotation over an angle \( \phi \) around the rotation axis \( \mathbf{n} \) is written as \( \hat{R}(\mathbf{n}, \phi) = e^{-i\phi \hat{n}} \), and

\[
\hat{R}_x(\pi)\hat{R}_y(\pi)\hat{R}_z(\pi) = 1.
\]

This procedure is shown in some detail in Ref. [7]. One can prove Eq. (26) using Eq. (25).
V. FUNCTIONAL FORM OF DIABATIC POTENTIALS

As a first example we consider the interaction between a closed-shell molecule and an atom in a $P$-state. In this case the interaction potential can be modeled by treating the atom in the $P$-state as if it were a diatomic molecule in a $l=1$ state [11]. The potential is then expanded just as in the diatom-diatom case. The same expansion can be found by a more formal approach[6]. Denoting the degenerate electronic states by $|\lambda, \mu\rangle, \mu = -\lambda, \ldots, \lambda$, we introduce the electronic projection operator $\hat{P} = \sum_\mu |\lambda, \mu\rangle \langle \lambda, \mu|$ and we define the potential operator by

\[ \hat{P} \hat{V} \hat{P} = \sum_{\mu' \mu} |\lambda, \mu'\rangle V_{\mu', \mu}(R, r)(\lambda, \mu)|, \]

(27)

where $R, r$ are the usual atom-diatom Jacobi coordinates. The proper expansion for $V_{\mu', \mu}(R, r)$ can now be found by requiring the operator $\hat{V}$ to be invariant under rotation, inversion, hermitian conjugation, and time reversal

\[ \hat{R} \hat{V} \hat{R}^\dagger = \hat{V}, \quad i\hat{V} \hat{t}^\dagger = \hat{V}, \quad \hat{V}^\dagger = \hat{V}, \quad \text{and} \quad \hat{\theta} \hat{V} \hat{\theta}^\dagger = \hat{V}. \]

(28)

The potentials obtained in this way are called diabatic. The eigenvalues of the matrix with the elements $V_{\mu', \mu}(R, r)$ correspond to the adiabatic potentials that can be obtained in quantum chemistry calculations. In a dynamical calculation the diabatic basis is preferred because the diabatic electronic states may be assumed (approximately) independent of the nuclear geometry. This procedure has also been applied to the case of open-shell diatom + closed-shell atom[5].

To perform the rotation in Eq. (28) it is convenient to express the electronic operators $|\lambda, \mu\rangle (\lambda, \mu)$ in irreducible tensor operators defined by

\[ \hat{T}_Q^L(\lambda) \equiv \sum_{\mu' \mu} |\lambda, \mu'\rangle (\lambda, \mu) (-1)^{\lambda - \mu'} \begin{pmatrix} \lambda & L & \lambda \\ -\mu' & Q & \mu \end{pmatrix} \sqrt{2L + 1}. \]

(29)

When the electronic functions $|\lambda, \mu\rangle$ are modeled as spherical harmonics $Y_{\lambda \mu}(\theta, \phi)$ we find that the tensor $\hat{T}_Q^L(\lambda)$ is simply proportional to a spherical harmonic multiplicative operator $Y_{LQ}(\theta, \phi)$ in the space spanned by $\{Y_{\lambda \mu}(\theta, \phi), \mu = -\lambda, \ldots, \lambda\}$,

\[ Y_{LQ}(\theta, \phi) = \hat{T}_Q^L(\lambda)c_L(\lambda), \]

(30)

with

\[ c_L(\lambda) = (-1)^\lambda \frac{2\lambda + 1}{\sqrt{4\pi}} \begin{pmatrix} \lambda & L & \lambda \\ 0 & 0 & 0 \end{pmatrix}. \]

(31)

This coefficient is only non-zero when $L$ is even. When the complex contains a single open-shell atom only terms with even $L$ appear in the expansion of
the potential. Hence, in that case, the formal expansion of the potential in irreducible tensor operators and the expansion where the open-shell atom is treated as an effective diatomic molecule are equivalent.

In the case of two open-shell atoms it has been shown[13] that direct products of tensor operators of odd rank appear in the expansion. In this case the formal expansion does not correspond to an effective diatom-diatom model. In a long range expansion of the potentials the odd-rank terms actually do not contribute in first order. However, when these terms are not included, the number of degrees of freedom in the diabatic model is not equal to the number of adiabatic states, which makes it impossible to construct a diabatic model consistent with the adiabats for the full range of interatomic separations.

In recent work on the OH\(^{(2)}\) + HCl complex it was found that also the time-reversal invariance condition in Eq. (28) is essential[16].