

Accidental conical intersections of three states of the same symmetry. I. Location and relevance

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An efficient algorithm for locating conical intersections of three states of the same symmetry is presented. The algorithm, which derives its efficiency from the use of analytic gradient techniques, is used to locate a three state intersection for the excited $3p$ Rydberg states of the ethyl radical. The existence of a seam of three state conical intersections in a $3p$ Rydberg manifold is expected to be a general occurrence. © 2002 American Institute of Physics. [DOI: 10.1063/1.1513304]

I. INTRODUCTION

Photodissociation^{1,2} frequently involves excitation of a bright state, L_n , followed by electronic cascade to a lower state, L_1 or L_0 . It is reasonable to describe this electronic cascade as comprised of a sequence of pairwise nonadiabatic transitions, $L_m \rightarrow L_{m-1}$, with the nonadiabatic transitions attributed to the existence of conical intersections connecting each pair of electronic potential energy surfaces.^{3,4} This sequence of pairwise nonadiabatic transitions can be quite efficient. However this efficiency may be compromised when, for example, the regions of the nonadiabatic transitions are well separated. The impact of this type of bottleneck can be mitigated if multistate nonadiabatic transitions, $L_m \rightarrow L_{m-n}$, can occur. Conical intersections of three electronic states are germane in this regard since they provide a mechanism for a single step, two state nonadiabatic transition, $L_m \rightarrow L_{m-2}$. Thus such conical intersections, if they exist, can expedite radiationless decay.

Conical intersections of three states that are required by symmetry are well-known^{5,6} but of limited importance here since such high symmetry situations are comparatively rare. On the other hand, intersections that are not symmetry required, accidental intersections, which are relevant in the present context, have received much less attention. According to the noncrossing rule of von Neumann and Wigner,⁷ in the absence of any symmetry, a seam of such conical intersections can exist in a subspace of dimension $N^{\text{int}} - 5$, where N^{int} is the number of internal degrees of freedom. This should be compared with the $N^{\text{int}} - 2$ dimensional seam space for a two state conical intersection. The low dimensionality of the three state seam does not relegate this feature to obscurity since the “double cone” is five dimensional. For the two state conical intersection the double cone is only two dimensional.

The low dimensionality of the three state seam does

complicate the determination of its locus. The most detailed investigation of the seam for a three state conical intersection is that of Katriel and Davidson.⁸ They studied accidental three state intersections in CH_4^+ with a symmetry required three state intersection as the starting point and using Frost wave functions to describe the electronic states.⁸

In addition to the challenge of locating the seam space, three state intersections complicate the issue of the geometric phase⁶ as evinced by recent theoretical descriptions^{9(a),9(b)} of adiabatic transit observed in microwave cavities.^{9(c)} The three state problem in general, and the question of electronic phases in particular, has also been studied by Baer and co-workers,^{10,11} using the D -matrix method.

In this work we begin a systematic study of the possible role of three state conical intersections in radiationless decay. The present study was motivated by recent experiments in which excited $3s$ and/or $3p$ Rydberg states of organic radicals, including hydroxymethyl (CH_2OH),^{12,13} vinoxy (CH_2COH),^{14,15} allyl (C_3H_5),^{16,17} propargyl (C_3H_3)^{18,19} and ethyl (C_2H_5),^{20,21} were photodissociated. The close spacing of the Rydberg states and the well-known phenomenon of valence-Rydberg (avoided) intersections suggest consideration of this class of electronic states.

In order to carry out this study an efficient algorithm for locating conical intersections of three states is required. Previously we reported Lagrange multiplier based, analytic gradient driven, algorithms for locating two state conical intersections for the nonrelativistic or Coulomb Hamiltonian²² and for the electronic Hamiltonian with the spin-orbit interaction included²³ (within the zero pair²⁴ approximation). An extension of these algorithms that handles the nonrelativistic three state case is reported here.

Section II describes this algorithm in general terms, reserving a more detailed discussion for a subsequent work.²⁵ In Sec. III this algorithm is used to consider the existence and significance of a particular class of three state intersections in the ethyl radical. Section IV summarizes and suggests directions for future research.

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II. LOCATING THREE STATE CONICAL INTERSECTIONS

At $\mathbf{R}^{x,ijk}$, a point of conical intersection of states i, j , and k , $\Delta E_{ij}(\mathbf{R}^{x,ijk}) = \Delta E_{jk}(\mathbf{R}^{x,ijk}) = 0$, where $\Delta E_{mn}(\mathbf{R}) = E_m(\mathbf{R}) - E_n(\mathbf{R})$,

$$(\mathbf{H}(\mathbf{R}) - E_k(\mathbf{R})\mathbf{I})\mathbf{c}^k(\mathbf{R}) = \mathbf{0} \quad (1a)$$

and

$$\Psi_i(\mathbf{r}; \mathbf{R}) = \sum_{\alpha=1}^{N^{CSF}} \psi_{\alpha}(\mathbf{r}; \mathbf{R}) c_{\alpha}^i(\mathbf{R}). \quad (1b)$$

In words, the electronic wave functions, Ψ_i which depend parametrically on the nuclear coordinates \mathbf{R} , are expanded in a basis of configuration state functions (CSFs) and the geometry dependent coefficients of combination, the $\mathbf{c}^i(\mathbf{R})$, are the eigenvectors of \mathbf{H} , the Hamiltonian in the CSF basis. In this work the Ψ_i will be state-averaged multiconfigurational self-consistent field (SA-MCSCF)/configuration interaction (CI) wave functions.²⁶ This class of multireference CI (MRCI) wave function can provide an even-handed description of several electronic states while including both dynamic and nondynamic correlation.

Using degenerate perturbation theory^{27,28} it can be shown²⁵ that in the vicinity of $\mathbf{R}^{x,ijk}$ as far as states i, j , and k are concerned, the electronic Hamiltonian, $\mathbf{H}(\mathbf{R})$ can be written, to first order in $\delta\mathbf{R}$, the displacements from $\mathbf{R}^{x,ijk}$, as a 3×3 Hamiltonian

$$\mathbf{H}^{(1)}(\mathbf{R}) = (E_j(\mathbf{R}^{x,ijk}) + \mathbf{h}^{jj} \cdot \delta\mathbf{R})\mathbf{I} + \begin{pmatrix} \mathbf{g}^{ji} \cdot \delta\mathbf{R} & \mathbf{h}^{ij} \cdot \delta\mathbf{R} & \mathbf{h}^{ik} \cdot \delta\mathbf{R} \\ \mathbf{h}^{ij} \cdot \delta\mathbf{R} & 0 & \mathbf{h}^{jk} \cdot \delta\mathbf{R} \\ \mathbf{h}^{ik} \cdot \delta\mathbf{R} & \mathbf{h}^{jk} \cdot \delta\mathbf{R} & \mathbf{g}^{kj} \cdot \delta\mathbf{R} \end{pmatrix}, \quad (2a)$$

where

$$\mathbf{h}^{jk}(\mathbf{R}) = \mathbf{c}^j(\mathbf{R}^{x,ijk})^{\dagger} \nabla \mathbf{H}(\mathbf{R}) \mathbf{c}^k(\mathbf{R}^{x,ijk})$$

$$\mathbf{g}^{mn}(\mathbf{R}) = \mathbf{h}^{mn}(\mathbf{R}) - \mathbf{h}^{nn}(\mathbf{R}). \quad (2b)$$

Here $\mathbf{g}^{mn}(\mathbf{R})$ is the energy difference gradient for states m and n , and $\mathbf{h}^{mn}(\mathbf{R})/\Delta E_{mn}(\mathbf{R})$ is approximately the derivative coupling vector for states m and n . Note that in the definition of $\mathbf{h}^{jk}(\mathbf{R})$ the \mathbf{R} -dependence originates entirely from $\nabla \mathbf{H}(\mathbf{R})$, and ∇ denotes the gradient with respect to nuclear coordinates only. At $\mathbf{R} = \mathbf{R}^{x,ijk} + \delta\mathbf{R}$, $\mathbf{H}^{(1)}(\mathbf{R})$ in the adiabatic representation $\tilde{\mathbf{H}}^{(1)}(\mathbf{R}) \equiv \mathbf{U}^{\dagger}(\mathbf{R})\mathbf{H}^{(1)}(\mathbf{R})\mathbf{U}(\mathbf{R})$ is given by

$$\tilde{\mathbf{H}}^{(1)}(\mathbf{R}) = E_j(\mathbf{R})\mathbf{I} + \begin{pmatrix} \Delta E_{ij}(\mathbf{R}) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \Delta E_{kj}(\mathbf{R}) \end{pmatrix}. \quad (2c)$$

From these observations we can deduce, again using perturbation theory,²⁵ the relations that define the core of our algorithm for locating three state conical intersections. Let $\mathbf{R}^1 = \mathbf{R}^0 + \delta\mathbf{R}$, with $\mathbf{R}^1 \sim \mathbf{R}^{x,ijk}$ then comparing Eqs. (2a) and (2c) we require

$$\Delta E_{ij}(\mathbf{R}_0) + \mathbf{g}^{ij}(\mathbf{R}_0) \cdot \delta\mathbf{R} = 0 \quad \text{and} \quad \mathbf{h}^{ij}(\mathbf{R}_0) \cdot \delta\mathbf{R} = 0 \quad (3a)$$

$$\Delta E_{kj}(\mathbf{R}_0) + \mathbf{g}^{kj}(\mathbf{R}_0) \cdot \delta\mathbf{R} = 0 \quad \text{and}$$

$$\mathbf{h}^{mn}(\mathbf{R}_0) \cdot \delta\mathbf{R} = 0 \quad \text{where} \quad mn = jk, ki. \quad (3b)$$

Equations (3a) and (3b) specify five conditions. The two conditions in Eq. (3a) are those used to locate a two state conical intersection. When $N^{\text{int}} > 5$ additional constraints on the internal coordinates are required. We specify these conditions as geometrical constraints

$$K^i(\mathbf{R}) = 0, \quad i = 1 - N^{\text{con}}, \quad (3c)$$

for example fixing a bond distance or internal angle—and/or the requirement that in addition to Eqs. (3a)–(3c) the energy of the crossing point is minimized.

These conditions can be imposed by finding an extremum of the Lagrangian:²²

$$L(\mathbf{R}, \xi, \bar{\xi}, \lambda) = E_i + \xi_1 \Delta E_{ij} + \xi_2 \Delta E_{kj} + \bar{\xi}_1 H_{ij} + \bar{\xi}_2 H_{ik} + \bar{\xi}_3 H_{kj} + \sum_{i=1}^{N^{\text{con}}} \lambda_i K^i. \quad (4)$$

An extremum of L is obtained by requiring \mathbf{L}' , the gradient of Eq. (4) with respect to all the independent variables \mathbf{R} , ξ , and λ , to vanish. Then expanding \mathbf{L}' through *first* order about $\mathbf{R}^1 = \mathbf{R}^0 + \delta\mathbf{R}$ and assuming that $\mathbf{R}^1 \sim \mathbf{R}^{x,ijk}$ gives the following Newton–Raphson equations:

$$\begin{pmatrix} L^{RR} & \mathbf{g}^{ij\dagger} & \mathbf{g}^{kj\dagger} & \mathbf{h}^{\dagger} & \mathbf{k}^{\dagger} \\ \mathbf{g}^{ij} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{g}^{kj} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{h} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{k} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \delta\mathbf{R} \\ \delta\xi_1 \\ \delta\xi_2 \\ \delta\bar{\xi} \\ \delta\lambda \end{pmatrix} = - \begin{pmatrix} \nabla L \\ \Delta E_{ij} \\ \Delta E_{kj} \\ \mathbf{0} \\ \mathbf{K} \end{pmatrix} = -\mathbf{L}', \quad (5a)$$

where $\mathbf{k}^i = \nabla K^i$, $\mathbf{L}^{RR} = \nabla(\nabla L)$, $\mathbf{h}^{\dagger} = (\mathbf{h}^{ij\dagger}, \mathbf{h}^{jk\dagger}, \mathbf{h}^{ik\dagger})$ everything in Eq. (5a) is evaluated at \mathbf{R}_0 and

$$\nabla L = \nabla E_j + \xi_1 \mathbf{g}^{ij} + \xi_2 \mathbf{g}^{kj} + \bar{\xi}_1 \mathbf{h}^{ij} + \bar{\xi}_2 \mathbf{h}^{ik} + \bar{\xi}_3 \mathbf{h}^{kj} + \sum_{i=1}^{N^{\text{con}}} \lambda_i \mathbf{k}^i. \quad (5b)$$

Equation (5a) is solved iteratively until the right hand side vanishes. Therefore the right hand side must be readily evaluated each iteration. The computational cost for evaluating \mathbf{k}^i is negligible as explicit expressions for the \mathbf{k}^i are obtained algebraically. Key here is that the potentially costly \mathbf{g}^{mn} and \mathbf{h}^{kl} can, for MRCI wave functions, be efficiently evaluated using analytic gradient techniques.²⁶ On the other hand \mathbf{L}^{RR} which is evaluated by divided difference of ∇L can be quite costly to compute. Fortunately it need not be

computed at each iteration and need not be known exactly. See below.

III. THREE STATE CONICAL INTERSECTIONS: THE ETHYL RADICAL

We consider the possibility that molecular structures exist for which the three $3p$ Rydberg states of the ethyl radical, $\text{CH}_3\text{CH}_2\cdot$, become degenerate. At its ground X^2A' state (using C_s symmetry labels) equilibrium geometry, $\mathbf{R}^e(X^2A')$, the highest occupied molecular orbital (HOMO) of the ethyl radical, is a singly occupied valence orbital, while, the low-lying excited electronic states and their corresponding HOMOs, are Rydberg in character. Both the $3s$ (Refs. 21, 29) and the $3p$ (Ref. 20) states have been probed experimentally. If the molecule were effectively a point the $3p$ Rydberg states would be degenerate. Since this is not the case the $3p$ Rydberg states are split. Here we are concerned with whether the molecule can distort in such a way as to restore this degeneracy. The three state conical intersection could, depending on the energy and geometrical structure, significantly influence the photochemistry of the highest $3p$ Rydberg state.

A. Electronic structure description

The five lowest states of the ethyl radical, with energies E_n , $n = 1-5$, are described at the SA-MCSCF/CI level, that is, the wave functions are determined from multireference CI expansions based on molecular orbitals determined from a SA-MCSCF procedure. In this initial work ($6s4p1d$) and ($4s1p$) bases are used on carbon and hydrogen respectively. Both the hydrogen and carbon bases are polarized double zeta bases. The carbon basis is augmented with two s and two p Rydberg functions following Dunning.³⁰ In the SA-MCSCF molecular orbital optimization procedure the active space consists of one electron in five orbitals, nominally the half-filled orbital of the ground state and the $3s$, $3p_{x,y,z}$ Rydberg orbitals. The MRCI wave functions include all CSFs obtained as single and double excitations relative to these five reference CSFs. This MRCI space, denoted SOMRCI, is comprised of 1.2 million CSFs. No spatial symmetry is assumed in these calculations. This level of treatment is expected to provide a reasonable description of the five lowest states near $\mathbf{R}^e(X^2A')$. The reliability of this description is considered below.

B. Ground state geometry and vertical excitation energies

Table I reports the values of representative internal coordinates at $\mathbf{R}^e(X^2A')$ (atom labelling $\text{C}^3\text{H}^1\text{HH}-\text{C}^2\text{HH}$ with each HH pair symmetry equivalent in C_s symmetry) and compares them with a previous theoretical study that treated only the ground electronic state using MP2 wave functions and extended atomic orbital basis sets.³¹ The agreement with the previous theoretical work is quite good. Also provided in that table are the vertical excitation energies, $T_v(I)$, to the I th state. The vertical excitation energy to the $2^2A'$ ($3s$ Rydberg) state, $T_v(2^2A') = 38\,740\text{ cm}^{-1}$ is in good accord with the known absorption feature in the region $37\,800-40\,920$

TABLE I. Internal coordinates and energetics at $\mathbf{R}^e(X^2A')$ and $\mathbf{R}^{x,345}$ using SOMRCI expansion.

	$R^e(X^2A)$	$R^{x,345}$
$R(\text{C}^3-\text{C}^2)$	1.494(1.482)	1.345
$R(\text{C}^3-\text{H}^1)$	1.096(1.097)	1.156
$R(\text{C}^3-\text{H})$	1.089(1.091)	1.09(± 0.01)
$R(\text{C}^2-\text{H})$	1.079(1.079)	1.046
$\angle \text{HC}^2\text{H}$	117.3(117.5)	109.6
E_1	0	10996
E_2	38740	44845
E_3	45251	52443
E_4	45834	52443
E_5	46985	52443

^aDistances in Å and energies in cm^{-1} relative to $E_1 = -78.896381$ a.u. at $\mathbf{R}^e(X^2A')$. Experimental values from Ref. 31 given parenthetically. 1.09(± 0.01) indicates average of 1.10 and 1.08.

cm^{-1} ,²¹ while $T_v(5^2A) = 46\,984\text{ cm}^{-1}$ is consistent with the reported excitation to a $3p$ state at $48\,780\text{ cm}^{-1}$.²⁰ These comparisons support the viability of the SOMRCI description in this region.

C. Three state conical intersections: Convergence

Table II provides the key numerical result of this work. There the efficient convergence of the Newton–Raphson procedure to a point, $\mathbf{R}^{x,345}$, on the seam is demonstrated. The initial geometry was a partially optimized structure on the ground state potential energy surface. The algorithm achieves degeneracy of $<1\text{ cm}^{-1}$ in only six iterations. Given the relatively small initial separation of the states 4 and 5 (60 cm^{-1})—definitely not a prerequisite for convergence—this degree of precision is necessary in order to distinguish between avoided and conical intersections. However it must be noted that a numerical procedure can never give exactly degenerate energies. To confirm that $\mathbf{R}^{x,345}$ is a point of conical intersection of three states it is sufficient to demonstrate that the five vectors in Eqs. (3a) and (3b) are linearly independent. The linear independence of these five vectors was considered by first normalizing the vectors and then computing the eigenvalues of their overlap matrix. The absence of a (near) zero eigenvalue established the requisite linear independence.

Since the focus here is the location of a point on the three state conical intersection seam in these calculations

TABLE II. Convergence to a three state conical intersection point using SOMRCI wave functions.

Iteration	ΔE_{43}	ΔE_{45}	$R(\text{C}^3-\text{C}^2)$	$\angle \text{HC}^2\text{H}$	E_3	$ \mathbf{L}' $
0	2226.5	-59.399	3.162	94.4	67273	0.625(0)
1	682.88	-302.72	2.6997	90.3	60840	0.425(0)
2	46.501	-24.939	2.5999	95.1	63293	0.180(0)
3	43.609	-2.2016	2.5823	101.5	57597	0.122(0)
4	9.413	-1.7654	2.5679	104.3	55214	0.821(-1)
5	1.651	-0.360	2.5556	106.1	53978	0.618(-1)
6	0.814	-0.431	2.5474	107.5	53226	0.497(-1)
8	0.180	-0.414	2.5424	109.6	52443	0.353(-1)

^aDistances in a_0 , angles in degrees, and energies in cm^{-1} relative to $E_1 = -78.896381$ a.u. at $\mathbf{R}^e(X^2A')$. For $|\mathbf{L}'|$ characteristic base 10 is given parenthetically.

L^{RR} , which is costly to determine since divided differencing is required, was approximated by a unit matrix. As in the two state conical intersection case, this approximation does not compromise the location of a point on the seam but does limit the efficiency of the energy minimization. This is reflected in the slow change in $|L'|$ after a point on the seam is located. Compare in Table II iterations 1–5 and 6–8. Efficient (approximate) methods for constructing L^{RR} will be discussed in a subsequent work.²⁵

D. Three state conical intersections: Significance

Table I compares the geometry and state energies at $\mathbf{R}^e(X^2A')$ with those at \mathbf{R}^x .^{34,5} The key difference between the two structures is the large change in $R(C^3-C^2)$. However at \mathbf{R}^x ,^{34,5} the molecule is still clearly a distorted ethyl radical, that is, we are *not* dealing with an asymptotic structure in which the molecule has been broken apart to achieve the degeneracy. On the other hand, the three state conical intersections in this region have energies (based on extrapolation of the data in Table II) $\sim 5000\text{ cm}^{-1}$ above the vertical excitation energy to the highest $3p$ Rydberg state. This is probably too high to play a role in photodissociation experiments noted in the Introduction. In future work it will be important to determine the factors that govern the energy of three state conical intersections relative to the vertical excitation energy, including how this energy difference is changed by the introduction of substituents.

Finally it should be emphasized that the seam of conical intersection is a $N^{\text{int}} - 5 = 10$ dimensional surface rather than the single point reported here. In this regard once a single point on the seam is determined, as described in detail previously,³² the use of Lagrange multipliers to incorporate the geometric constraints allows additional points on a seam of conical intersection to be determined relatively quickly by providing a good “guess” for the location of a seam point in the neighborhood of an existing point.

IV. CONCLUSIONS AND FUTURE DIRECTIONS

In this work we have introduced an efficient algorithm for locating points on a seam of conical intersection of three states which is not required by symmetry. The algorithm represents an extension of the algorithm we currently use to locate conical intersections of two electronic states²² and derives considerable efficiency from the use of an analytic gradient, and Lagrange multiplier, techniques. We showed, using wave functions comprised of over 1.2 million configuration state functions, that changes in the molecular framework can cause the $3p$ Rydberg states of ethyl radical to become degenerate.

In future work we will consider how the energy of these three state conical intersections relative to the vertical excitation energy, changes with substituent substitution. It will be particularly interesting to consider the $3p$ Rydberg manifold in molecules including hydroxymethyl for which the splitting of the $3p$ manifold at the ground state equilibrium geometry is much larger than that of ethyl.³³ We will also consider

lower excited states. In preliminary calculations using this algorithm three state intersections of the $2-4^2A$ states of the ethyl radical have been found. These three state intersections involve states of Rydberg and “excited valence” character.²⁵

Finally we hope this study will serve to motivate studies of nuclear dynamics in the vicinity of representative three state conical intersections. These studies should be particularly interesting since when compared with the two state double cones here the branchings available to a wave packet exiting the “cone” are more robust since now there are electronic as well as geometric options available.

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