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Our research focuses on the electronic structure aspects of electronically non adiabatic processes relevant to the stability and combustion of high energy density materials (HEDMs) and atmospheric chemistry. Our funded research has focused on two problems the reaction of $B(^2P)$ with H_2 and reaction $O(^3P) + H_2O \rightarrow OH(X^2\Pi) + OH(A^2\Sigma^+)$. Perhaps the most potentially influential aspect of our research is our work on how the connectivity of points conical intersection impacts nonadiabatic events. In each of these systems unanticipated aspects of the loci of these seams of conical intersection has lead to new avenues of research. In the course of our previous AFOSR funded research we demonstrated that $B\text{-}H_2$ exhibits a confluence, an intersection of two branches of same seam of conical intersection, a feature of conical intersections unknown a decade ago. Recently we have shown that confluences can exist not just in tri-atomic molecules but in polyatomic molecules as well and developed an efficient method for locating and characterizing confluences. Our study of the $O(^3P) + H_2O$ reaction suggests the existence of an alternative coalescence, a subspace of nuclear coordinate space in which two distinct seam coalesce. While intersections of three states are well known when there is symmetry they appear to be essentially unknown for general polyatomic systems.

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1. *On the adiabatic to diabatic states transformation near intersections of conical intersections* David R. Yarkony, J. Chem. Phys., 112, 2111-2120 (2000).

2. *Vibronic Energies and the breakdown of the Born-Oppenheimer approximation in diatomic molecules: Adiabatic and Diabatic representations* *David R.* Yarkony, in *Computational Molecular Spectroscopy*; Jensen, P. ;Bunker, P., Eds.; J. Wiley, Chichester, 2000; p. 459-484.

3. The geometric phase effect. Perspective on:*Some Recent Developments in the Theory of Molecular Energy Levels*: by H. C. Longuet-Higgins[Advances in Spectroscopy 2, 429-472 (1961)].
David R. Yarkony, *Theoretical Chemistry Accts*, New century issue, *103*, 242-246 **(2000).**

4. *Conical intersections: The New Conventional Wisdom* – Feature Article, D. R. Yarkony, *J. Phys. Chem. A* **105,** 6277-6293 (2001).

5. Conical Intersections and the Spin-Orbit Interaction, Spiridoula Matsika and David R. Yarkony, in *Intersecting Potential Energy Surfaces,* Michael Baer and Gert. Billing, eds, Wiley, to appear

6. Confluences of Conical intersection seams: their prediction, representation, and affect on local topography
Spiridoula Matsika and David R. Yarkony, J. Phys. Chem. A - to appear

7. On the Reaction : $O(^3P) + H_2O \rightarrow OH(X^2\Pi) + OH(A^2\Sigma^+)$: A mechanism involving conical intersections
Spiridoula Matsika and David R. Yarkony, J. Chem. Phys. - submitted

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

Our research focuses on the electronic structure aspects of electronically non adiabatic processes relevant to the stability and combustion of high energy density materials (HEDMs) and

atmospheric chemistry. Our funded research has focused on two problems the reaction of $B(^2P)$ with H_2 and reaction $O(^3P) + H_2O \rightarrow OH(X^2\Pi) + OH(A^2\Sigma^+)$. Perhaps the most potentially influential aspect of our research is our work on how the connectivity of points conical intersection impacts nonadiabatic events. In each of these systems unanticipated aspects of the loci of these seams of conical intersection has lead to new avenues of research. In the course of our previous AFOSR funded research we demonstrated that $B\text{-}H_2$ exhibits a confluence, an intersection of two branches of same seam of conical intersection, a feature of conical intersections unknown a decade ago. Recently we have shown that confluences can exist not just in tri-atomic molecules but in polyatomic molecules as well and developed an efficient method for locating and characterizing confluences. Our study of the $O(^3P) + H_2O$ reaction suggests the existence of an alternative coalescence, a subspace of nuclear coordinate space in which two distinct seam coalesce. While intersections of three states are well known when there is symmetry they appear to be essentially unknown for general polyatomic systems.

TABLE OF CONTENTS

REPORT DEFINITION

GRANT:	F49620-99-1-0198
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SUMMARY

This grant period was one of considerable excitement and discovery. We are particularly excited about the potential impact of two classes of intersections of conical intersection seams. We have determined two pathways for the nonadiabatic reaction $H_2O + O(^3P) \rightarrow OH(X^2\Pi) + OH(A^2\Sigma^+)$. One pathway involves two distinct seams of conical intersection, the $1^3A'$-$2^3A'$ seam and the $2^3A'$ - $3^3A'$ seam. What is a particularly exciting about these seams is that they exist in the same region of nuclear coordinate space. We believe that *it will be possible to locate points where two seams coalesce.* While intersection of three *interacting* states (Σ - Π intersections, and the like, are excluded since one of the components of the Π state does not interact with either of the other states) are well known when there is symmetry they appear to be essentially unknown for general polyatomic systems. This completely unexpected finding suggests a more robust mechanism than previously suspected for this reaction and will serve to motivate us to develop a general algorithm to locate this feature. Our work on our other focus system $B(^2P) + H_2$ has lead to a new, more general approach, for locating this second class of intersections of intersection, confluences, in which two branches of the same seam of conical intersection intersect.

TECHNICAL REPORT

Our research program focuses on aspects of nonadiabatic chemistry that are relevant to the combustion of potential high energy density materials (HEDMs) and the reactions in the upper atmosphere. During the current grant we have focused on two problems; the forward and reverse directions of the reaction $H_2O + O(^3P) \rightarrow OH(X^2\Pi) + OH(A^2\Sigma^+)$, relevant to the uV emission from the engines of vehicles in low earth orbit ; and the potential energy, and derivative coupling, surfaces for the reaction of $B(^2P)$ with H_2, relevant to the combustion of boron doped cryogenic hydrogen. As part of the former study we have located a nonadiabatic pathway in which successive nonadiabatic transitions occur in the same region nuclear coordinate space. This result strongly

suggests theh existence of a subspace in which two distinct seams of conical intersection colasce a situation not, to our knowledge, previously reported except when facilitated by symmetry. As part of the later study we have, for the first time, obtained a piecewise analytic representation of a seam of conical intersection that includes a confluence, an intersection of two branches of the same seam. This representation will be of considerable interest owing to our recent demonstration of the existence of this class of intersections of intersections in general polyatomic systems.

ACCOMPLISHMENTS/NEW FINDINGS

A: Confluences of Conical Intersections and Energetics Materials

(i) The potential energy surfaces for $B(^2P) + H_2 \rightarrow BH_2 \rightarrow BH + H$

The captioned reaction is relevant to the combustion of boron doped cryogenic H_2. Our initial work on this system established the existence of a novel seam of conical intersection separating the van der Waals complex B—H_2 from the molecular region BH_2 and hence from the possible products of combustion BH + H. The seam is composed of a C_{2v} (T-shaped) branch, a symmetry-allowed $^2A_1 - {}^2B_2$ seam of conical intersection and a C_s branch $1^2A'$-$2^2A'$ conical intersection seam of two states of the same symmetry, that intersects the C_{2v} seam near R(H-H) ~ 3.12 a_0.[1] This intersection of two branches of a seam is referred to as a confluence.

The goal of this research program was to provide high quality *ab initio* potential energy, and derivative coupling, surfaces to be used by David Weeks in studies of the dynamics of the captioned reaction. Indeed we are currently putting the finishing touches on a grid representation of the potential energy and derivative coupling, surfaces.[2] However the unique aspect of the electronic structure problem was the need for a functional representation of the energies and derivative couplings in the vicinity of a seam with intersecting branches. This problem has been solved by using perturbation theory to construct a piecewise linear representation of the seam including its confluence. The details of this representation can be found in Refs. [3,4].

The impact of a confluence on the intersecting potential energy surfaces is demonstrated in the following two figures. In these figures the energy of the two potential energy surfaces is plotted against two internal coordinates, one coordinate in the branching space where the degeneracy is lifted in a linear manner, and one seam coordinate along which the degeneracy is preserved. Fig. 1 illustrates the double wedge topography of a typical conical intersection. For further discussion of this figure see Ref. [4].

Figure 1

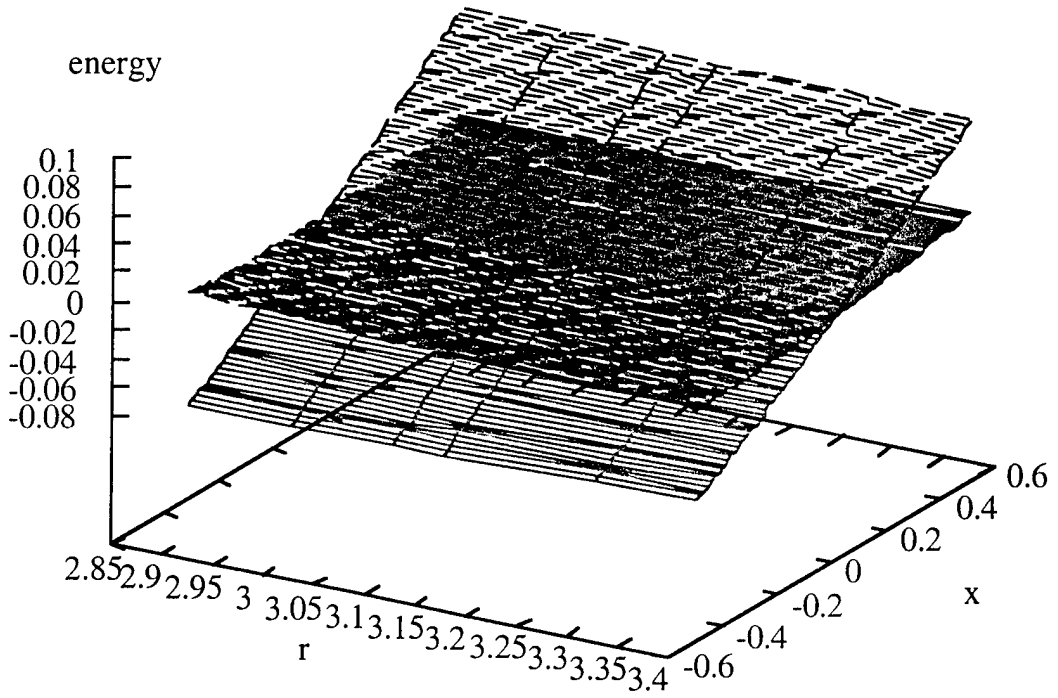
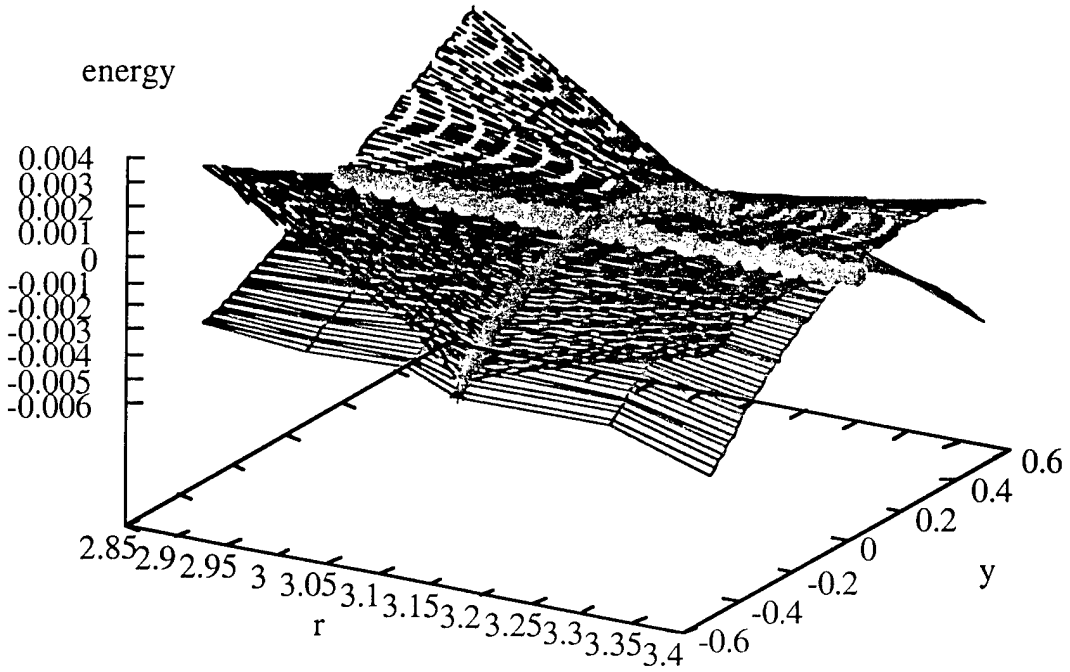


Figure 2 below, from Ref. [4], illustrates the dramatic effect on the energy landscape produced by a confluence. This plot was made possible by the functional representation of the seam noted above.

Figure 2



Comparing Figs. (1) and (2) shows that the dynamics near a confluence will differ dramatically from that near a standard conical intersection. However, confluences, in general, would be of limited importance if they were restricted to triatomic molecules. Using the ideas developed in this project,we have recently shown that confluences are likely in a general polyatomic molecule that has a symmetry-allowed seam of conical intersection.[5] Since symmetry-allowed conical intersections are perhaps the most commonly studied type of intersection we believe that methods and insights gained through this aspect of our research program will have wide ranging significance in nonadiabatic chemistry.

As part of our future research we will study the dynamics near confluences of conical intersections using the time dependent wave packet techniques we have developed.[6]

B. Nonadiabatic Processes in Atmospheric Chemistry

(i) $H_2O + O(^3P) <\!\!-\!\!> OH(A^2\Sigma^+) + OH(X^2\Pi)$ (1)

The captioned reaction is relevant to the interaction of spacecrafts in low earth orbit with their environment.[7-9] As a first step in predicting the rate of this reaction an assessment of the reaction mechanism, the key regions of the relevant potential energy surfaces, is desirable. This is by no means a straightforward task. The captioned reaction is electronically nonadiabatic. Two of the three degenerate states in the reactant channel must correlate with the 5th and 6th states of the products. Since the captioned reaction is energetically uphill, it is convenient to study it in reverse:

$OH(A)+OH(X) \rightarrow (\ OH(X)+OH(X)\ )$ or $(H_2O + O(^3P))$ (2)

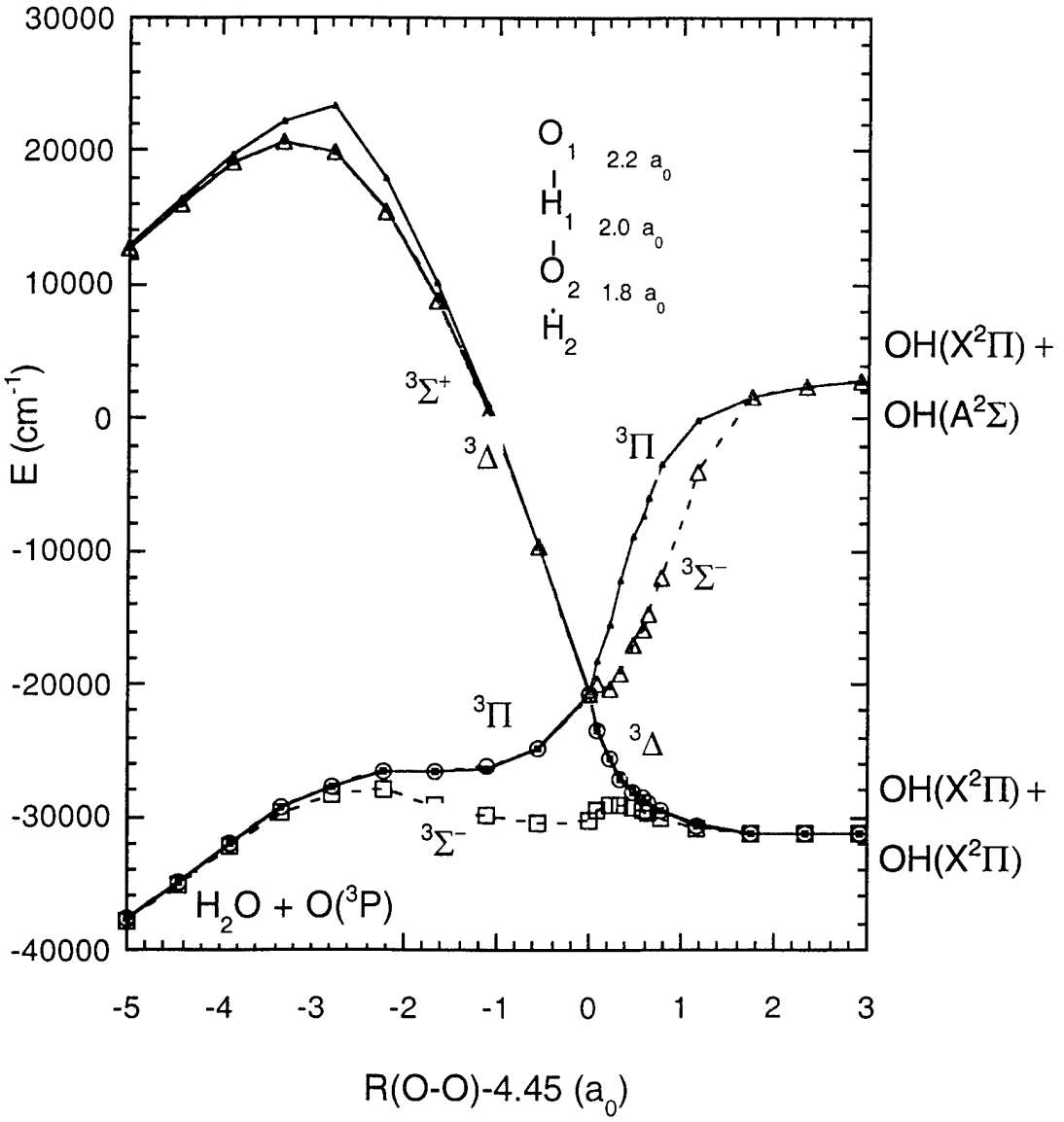
The analysis of the reverse reaction will directly complement experimental work on the OH-OH system by M. Lester's group at the University of Pennsylvannia. In the backward direction two channels - non reactive- producing OH(X)+OH(X), and reactive - producing $H_2O + O(^3P)$, quenching - must be considered. Below we describe the connections between the product channel, and the reactant channel states. Both symmetry and serendipity play key roles in facilitating the requisite non adiabatic transitions.

The ground state of the reactants $O(^3P) + H_2O$, in C_s [$C_{\infty v}$] symmetry, gives rise to the $1,2^3A''$, $1^3A'$ [$^3\Pi$, $^3\Sigma^-$] states. The $OH(X^2\Pi)+OH(X^2\Pi)$ and $OH(X^2\Pi)+OH(A^2\Sigma^+)$ states in the product channel give rise to the $1,2^3A''$, $1,2^3A'$ [$^3\Delta$, $^3\Sigma^+$, $^3\Sigma^-$] states and $3^3A''$, $3^3A'$ [$^3\Pi$] states. The later states are the 5th and 6th electronic states. Nuclear motion on $1^3A''$ [$1^3\Sigma^-$] potential energy

surface, which correlates with ground state products, is likely to be adiabatic. Thus, the path to excited state products originates on either the $1^3A'$ or the $2^3A''$ potential energy surfaces. Details concerning the calculations described below, which used configuration interaction expansions as large as 4.8 millions CSFs, can be found in Ref. [10].

The reactant surfaces and product surfaces of $^3A'$ ($^3A''$) symmetry are joined by seams (a seam) of conical intersections. The lowest energy portions of these seams have collinear geometries.

Figure 3



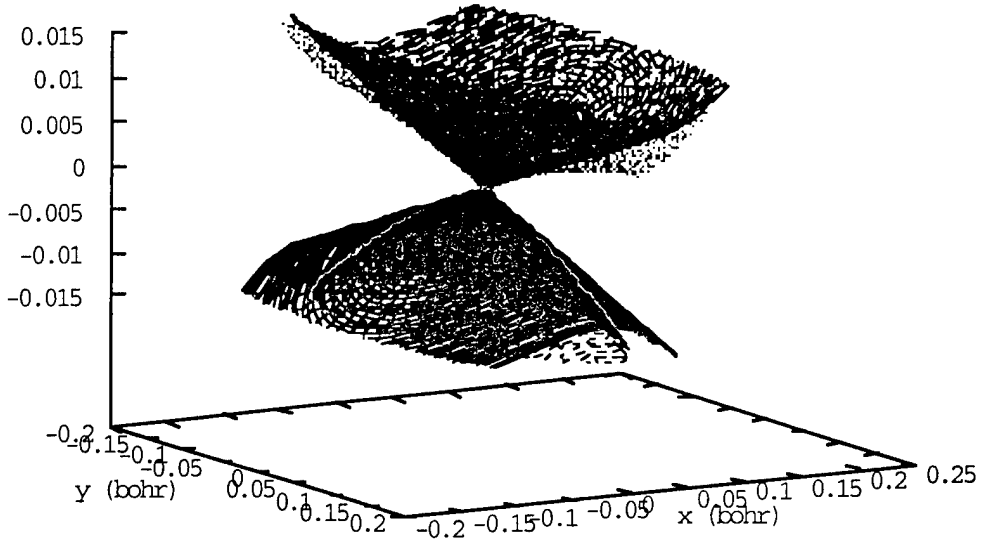
In Fig. 3 it is seen that a $^3\Delta$ - $^3\Pi$ conical intersection seam joins the OH(X)+OH(X) (via a $^3\Delta$ state) and the H_2O + O(^{3}P) (via a $^3\Pi$ state) ground states with excited electronic states. In C_s symmetry notation this seam includes both the (2^3A" - 3^3A") and the (1^3A'- 2^3A') seams of conical intersection. $C_{\infty v}$ symmetry is key here since by requiring these two conical intersections to occur at the same point in nuclear coordinate space, the **3**^{3}A(2^3A") state can become the **5**^{3}A(3^3A") state by passing though a single seam of conical intersection! However in the ^{3}A' manifold this is not the case. An additional the 2^3A'-3^3A' conical intersection is required. If this intersection were to occur in a different region of nuclear coordinate space access might be an issue. However this additional conical intersection which for $C_{\infty v}$ symmetry is a $^3\Sigma^+$- $^3\Pi$ conical intersection occurs, as is evident from Fig.3 in immediate vicinity of the $^3\Delta$ - $^3\Pi$ conical intersection. We anticipate that with the proper algorithms we will be able to locate a coalescence of these two, two-states conical intersections to produce a single three state conical intersection.

A general three state conical intersection is much more complicated that its two state cousin. It has 5 directions in which the degeneracy is lifted linearly and corresponding a seam of dimension N^{int} - 5.[11] Our work on the impact of the spin-orbit interaction in conical intersections in odd electron systems has required us to deal with N^{int} - 3 and N^{int} -5 dimensional seams.[12-15] We will use that expertise to develop an analytic gradient driven algorithm to locate this class of conical intersection seams.

The funnel-like topography of the upper cone, see Fig. 4 below, makes the role of the seam of conical intersection in the reverse reaction, the quenching of OH(A) by OH(X), unequivocal. In addition, as demonstrated in Ref. [10] the topography of its branching space facilitates both reactive (production of ground state H_2O + O(^{3}P)) and nonreactive (production of ground state OH+OH) quenching. However the contribution of a seam of conical intersection to the forward reaction requires additional discussion. Conical intersections necessarily create regions of close approach of the potential energy surfaces in question. However their direct participation in a lower state to upper state (LtU) transition -such as reaction (1)- is often ignored since the topography of a standard symmetry-required Jahn-Teller cone, which resembles a 'line of mountain peaks', tends to steer wave packets away from the conical intersection.[6,16] However recently we have used time dependent wave packet theory to demonstrate that conical topographies in which the cone is significantly tilted – see below and Ref. [16] – can lead to efficient LtU transitions.[6] Figure 4 depicts

a representative conical intersection without (red and blue) and with (green and purple) quadratic terms.[10]

Figure 4



For low kinetic energies this cone would tend to steer wave packets away from the point of conical intersection. However as seen from Figure 3 these conical intersections occur well below the product channel asymptote. Thus in these region there is a large excess of kinetic energy that can enable a wave packet to access these conical interesections. In future will study this aspect of the nuclear dynamics using wave packet techniques.

Although we have made considerable progress in elucidating the mechanism of this reaction much work remains to be done. An algorithm to locate conical intersections of three eletronic states must be written and to confirm (or refute) the existence of two seam coalescences. We would also like to carry out wave packet studies to determine the relative efficiency of non adiabatic transitions involving a single three state conical intersection vs two, two state conical intersections. Finally once this data has been used to established effective pathways for non adiabatic transitions we will 'grow' the portions of the potential energy, and derivative coupling surfaces necessary to describe reactions (1) and (2) using the classical trajectory sampling techniques of Michael Collins[17,18] with whom we have an active collaboration in place.

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