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Letter

A criterion for the confluence of two seams of conical intersection in triatomic molecules

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Abstract. It is shown that the cross product $\mathbf{t}^{IJ}(\mathbf{R}_x) \equiv \mathbf{g}^{IJ}(\mathbf{R}_x) \times \mathbf{h}^{IJ}(\mathbf{R}_x)$, where $g_\tau^{IJ}(\mathbf{R}) = (\mathbf{c}^I(\mathbf{R}_x) - \mathbf{c}^J(\mathbf{R}_x))^\dagger \frac{\partial \boldsymbol{H}(\mathbf{R})}{\partial \tau}(\mathbf{c}^I(\mathbf{R}_x) + \mathbf{c}^J(\mathbf{R}_x))$, $h_\tau^{IJ}(\mathbf{R}) = \mathbf{c}^I(\mathbf{R}_x)^\dagger \frac{\partial \boldsymbol{H}(\mathbf{R})}{\partial \tau} \mathbf{c}^J(\mathbf{R}_x)$, τ is an internal nuclear coordinate, the $\mathbf{c}^I(\mathbf{R})$ satisfy $[\boldsymbol{H}(\mathbf{R}) - E_I(\mathbf{R})]\mathbf{c}^I(\mathbf{R}) = \mathbf{0}$ and $\boldsymbol{H}(\mathbf{R})$ is the electronic Hamiltonian matrix, is a unique property of a conical intersection at $\mathbf{R}_x$. $\mathbf{t}^{IJ}(\mathbf{R}_x) = 0$ when $\mathbf{R}_x$ is located at the intersection of two (or more) seams of conical intersection. This criterion for an intersection of two seams of conical intersection has important implications for algorithms that seek to locate such points. Here it is used to analyze the trifurcation of a generic $C_{2v}{}^{2S+1}A - {}^{2S+1}B$ seam of conical intersection, analogous to those recently found in AlH_2 and CH_2.

Key words: Conical intersection – Noncrossing rule – Accidental intersections – Geometric phase effect – Seams of intersection

1 Introduction

For two states of the same spin-multiplicity in molecules of the type AB_2 accidental conical intersections are usually [1, 2] thought to occur for states of distinct spatial symmetry at C_{2v} (and $C_{\infty v}$) nuclear configurations. Expressed in terms of standard Jacobi coordinates $\mathbf{R} = (R, r, \gamma)$, Fig.1, such a seam of conical intersection could be parameterized as $\mathbf{R}_x(\beta) = (R(\beta), r(\beta), \gamma_x)$ where $\gamma_x = 90°$ for C_{2v} and (0°,180°) for $C_{\infty v}$ geometries. Deviations from these "high symmetry" geometries would then result in avoided intersections [1, 2]. This conventional wisdom is, however known to be overly simplistic [3] since in triatomic or larger molecules according to the noncrossing rule [4–6] potential energy surfaces corresponding to states of the same symmetry are allowed (but not required) to intersect. While the location of such "same symmetry" intersections is far from a trivial matter, recent computational advances have made the determination of such intersections relatively routine [7, 8].

Recently a much less common consequence of the noncrossing rule has been encountered for the $1^2A'$–$2^2A'$ seam of conical intersection in AlH_2 [9], and the $2^3A''$–$3^3A''$ seam of conical intersection in CH_2 [10]. For these molecules it was found that the C_{2v} seam of conical intersection trifurcates: the seam of conical intersection has exclusively C_{2v} symmetry for $\beta < \beta_d$, while at $\beta = \beta_d$ two symmetry equivalent branches of a C_s seam of conical intersection emerge and the C_{2v} seam continues. Equivalently at $\mathbf{R}_x(\beta_d)$ the C_{2v} seam of conical intersection intersects a C_s seam of conical intersection. This situation is illustrated in Fig. 2 which is modeled after the $2^3A''$–$3^3A''$ seam of conical intersection in CH_2 as presented in Fig. 5 of Ref. [10]. Previously a similar situation was identified for the $1^1A'$–$2^1A'$ seam of conical intersection in ozone [11]. Berry and Wilkinson have referred to points of conical intersection, denoted by $\mathbf{R}_x$ when the parameter β can be suppressed, as diabolical points [12]. With this in mind, points at the intersection of two seams of conical intersection will be referred to as doubly (or in general, multiply) diabolical points and denoted $\mathbf{R}_{dd}$.

The existence of these doubly diabolical points is significant from both conceptual and practical perspectives. Their existence significantly alters our intuition concerning the nature of conical intersections in AB_2 type molecules. They can also be expected to have important implications for nonadiabatic dynamics. In this work these doubly diabolical points in triatomic molecules are considered. A criterion that can be useful computationally for locating such points is introduced and explained using model Hamiltonians and a form of degenerate perturbation theory for conical intersections [13, 14]. The ideas presented in this work are illustrated using a model for the $I^{2S+1}A$–$J^{2S+1}A$ seam of conical intersection encountered in AlH_2 and CH_2. Finally a numerical application is briefly discussed.

2 Intersecting seams of conical intersection

In view of the comparatively novel nature of this phenomenon it is useful to begin this section with simple

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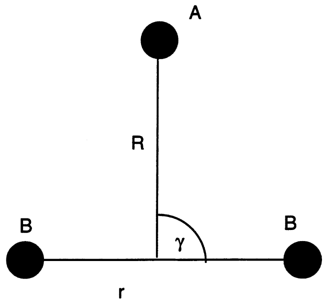

Fig. 1. Jacobi coordinates for an AB_2 molecule

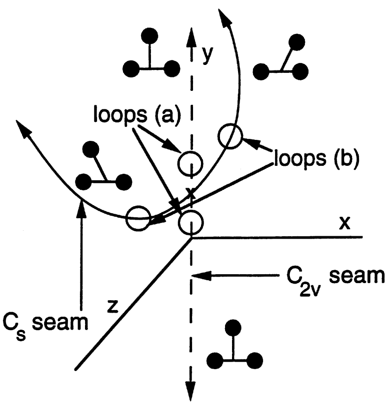

Fig. 2. Trifurcation of the C_{2v} seam of conical intersection based on the model Hamiltonian in Eq. (12). The seam labelled C_{2v} seam [C_s seam] here is also denoted as the seam 1 [seam 2] in the text. *Loops* (*a*) are in planes parallel to the (*x*,*z*) plane. *Loops* (*b*) are in planes perpendicular to the tangent to seam (2). At the doubly diabolical point, labelled **x**, *loop* (*b*) is in the (*x*,*y*) plane

model Hamiltonians that exhibit intersecting seams of conical intersection.

2.1 Model Hamiltonians

Consider the electronic Hamiltonian:

$$\mathbf{H}^i(\mathbf{R}) = \begin{pmatrix} S(\mathbf{R}) + G(\mathbf{R}) & V_i(\mathbf{R}) \\ V_i(\mathbf{R}) & S(\mathbf{R}) - G(\mathbf{R}) \end{pmatrix} \equiv S(\mathbf{R})\boldsymbol{I} + G(\mathbf{R})\boldsymbol{\sigma}_z + V_i(\mathbf{R})\boldsymbol{\sigma}_x \quad (1)$$

for $i = 1$–2, where $\boldsymbol{\sigma}_j$ are the Pauli matrices, and $\mathbf{R} = (x, y, z)$ denotes the orthogonal internal (here Cartesian) nuclear coordinates. The seam of intersection, $w^i(\beta), w = x, y, z$, assumed here to be conical, is given by the solutions of the equations

$$V_i(\mathbf{R}) = G(\mathbf{R}) = 0 \ . \quad (2)$$

Then at any point $\mathbf{R}_x(\beta)$ on $w^i(\beta)$, $\mathbf{t}^i(\mathbf{R}_x)$ the tangent to $w^i(\beta)$ is given by the cross product

$$\mathbf{t}^i(\mathbf{R}_x) = \nabla G(\mathbf{R}_x) \times \nabla V_i(\mathbf{R}_x) \equiv \mathbf{g}(\mathbf{R}_x) \times \mathbf{h}^i(\mathbf{R}_x) \ . \quad (3)$$

Assume for convenience that the origin is a diabolical point for $i = 1$–2. Construct the composite Hamiltonian:

$$\boldsymbol{H}^{1,2}(\mathbf{R}) = S(\mathbf{R})\boldsymbol{I} + G(\mathbf{R})\boldsymbol{\sigma}_z + V_1(\mathbf{R})V_2(\mathbf{R})\boldsymbol{\sigma}_x \ . \quad (4)$$

The seams of conical intersection for $\boldsymbol{H}^{1,2}$ are given by the solutions to the equations

$$V_1(\mathbf{R})V_2(\mathbf{R}) = G(\mathbf{R}) = 0 \quad (5)$$

which are the union of the above two seams, $w^1(\beta)\mathrm{U}w^2(\beta)$. The tangent to these seams of conical intersection $\mathbf{t}^{1,2}(\mathbf{R}_x)$, is given by the cross product

$$\begin{aligned}\mathbf{t}^{1,2}(\mathbf{R}_x) &= \nabla G(\mathbf{R}_x) \times \nabla V_1(\mathbf{R}_x)V_2(\mathbf{R}_x) \\ &= V_2(\mathbf{R}_x)\mathbf{g}(\mathbf{R}_x) \times \mathbf{h}^1(\mathbf{R}_x) + V_1(\mathbf{R}_x)\mathbf{g}(\mathbf{R}_x) \times \mathbf{h}^2(\mathbf{R}_x) \ .\end{aligned} \quad (6)$$

For points on $w^1, V_1(\mathbf{R}_x) = 0$ so that $\mathbf{t}^{1,2}(\mathbf{R}_x)$ points in the direction of $\mathbf{t}^1(\mathbf{R}_x)$ whereas for points on w^2, $V_2(\mathbf{R}_x) = 0$ so that $\mathbf{t}^{1,2}(\mathbf{R}_x)$ points in the direction of $\mathbf{t}^2(\mathbf{R}_x)$. However, at $\mathbf{R}_{\mathrm{dd}} = (0, 0, 0)$, a doubly diabolical point, $\mathbf{t}^{1,2}(\mathbf{R}_{\mathrm{dd}}) = 0$ although $\lim_{\mathbf{R}_x \to \mathbf{R}_{\mathrm{dd}}} \left(\mathbf{t}^{1,2}(\mathbf{R}_x)/\left|\mathbf{t}^{1,2}(\mathbf{R}_x)\right|\right) \to \pm\, \mathbf{t}^i(\mathbf{R}_x)/|\mathbf{t}^i(\mathbf{R}_x)|$ where $i = 1$ or 2 according to whether the limit is taken along w^1 or w^2. Similar results are obtained using G_i in lieu of V_{i}.

2.2 Perturbation theory

It will be shown that the criterion $\mathbf{t}^{1,2}(\mathbf{R}_{dd}) = 0$ is a necessary condition for a doubly diabolical point. Using degenerate perturbation theory [14] (see also [15]) it has been shown that to first order in displacements from an arbitrary point of conical intersection $\mathbf{R}_x$, the electronic energies of the two adiabatic electronic states, $\Psi_I(\mathbf{r}; \mathbf{R})$ and $\Psi_J(\mathbf{r}; \mathbf{R})$, are rigorously obtained from the Hamiltonian in Eq. (1) with

$$S(\mathbf{R}) = E_I(\mathbf{R}_x) + \left[\mathbf{g}^I(\mathbf{R}_x) + \mathbf{g}^J(\mathbf{R}_x)\right]/2 \cdot \delta\mathbf{R} \quad (7a)$$

$$G(\mathbf{R}) = \left[\mathbf{g}^I(\mathbf{R}_x) - \mathbf{g}^J(\mathbf{R}_x)\right]/2 \cdot \delta\mathbf{R} \quad (7b)$$

$$V(\mathbf{R}) = \mathbf{h}^{IJ}(\mathbf{R}_x) \cdot \delta\mathbf{R} \quad (7c)$$

where $\mathbf{R} = \mathbf{R}_x + \delta\mathbf{R}$,

$$\mathbf{g}^I(\mathbf{R}) = \mathbf{c}^I(\mathbf{R}_x)^\dagger(\nabla \boldsymbol{H}(\mathbf{R}))c^I(\mathbf{R}_x) \quad (8a)$$

$$\begin{aligned}\mathbf{g}^{IJ}(\mathbf{R}) &= \mathbf{g}^I(\mathbf{R}) - \mathbf{g}^J(\mathbf{R}) \\ &= \left(\mathbf{c}^I(\mathbf{R}_x) - \mathbf{c}^J(\mathbf{R}_x)\right)^\dagger(\nabla \boldsymbol{H}(\mathbf{R}))\left(\mathbf{c}^I(\mathbf{R}_x) + \mathbf{c}^J(\mathbf{R}_x)\right)\end{aligned} \quad (8b)$$

$$\mathbf{h}^{IJ}(\mathbf{R}) = \mathbf{c}^I(\mathbf{R}_x)^\dagger(\nabla \boldsymbol{H}(\mathbf{R}))\mathbf{c}^J(\mathbf{R}_x) \ , \quad (8c)$$

and

$$\Psi_I(\mathbf{r}; \mathbf{R}) = \sum_\alpha c_\alpha^I(\mathbf{R})\psi_\alpha(\mathbf{r}; \mathbf{R}) \quad (9a)$$

so that the $\mathbf{c}^I(\mathbf{R})$ satisfy

$$[\boldsymbol{H}(\mathbf{R}) - E_I(\mathbf{R})]\mathbf{c}^I(\mathbf{R}) = 0 \ . \quad (9b)$$

Thus $\mathbf{t}^{IJ}(\mathbf{R}_x)$, the tangent to the seam of conical intersection, is given by

$$\mathbf{t}^{IJ}(\mathbf{R}_x) = \mathbf{g}^{IJ}(\mathbf{R}_x)/2 \times \mathbf{h}^{IJ}(\mathbf{R}_x) \ . \quad (10)$$

Since $E_I(\mathbf{R}_x) = E_J(\mathbf{R}_x)$, $\mathbf{c}^I(\mathbf{R}_x)$ and $\mathbf{c}^J(\mathbf{R}_x)$ are defined only up to a one-parameter rotation so that neither $\mathbf{g}^{IJ}(\mathbf{R}_x)$ nor $\mathbf{h}^{IJ}(\mathbf{R}_x)$ is uniquely defined. If the coordinate system is chosen such that the x and y axes are perpendicular to $\mathbf{t}^{IJ}(\mathbf{R}_x)$ then, $\mathbf{g}^{IJ}(\mathbf{R}_x) = (g_x, g_y)$ and $\mathbf{h}^{IJ}(\mathbf{R}_x) = (h_x, h_y)$. From Eqs. (8a–c) if $\mathbf{c}^I(\mathbf{R}_x)$ and $\mathbf{c}^J(\mathbf{R}_x)$ are replaced by $\tilde{\mathbf{c}}^I(\mathbf{R}_x)$ and $\tilde{\mathbf{c}}^J(\mathbf{R}_x)$

$$\begin{pmatrix} \tilde{\mathbf{c}}^I(\mathbf{R}_x) \\ \tilde{\mathbf{c}}^J(\mathbf{R}_x) \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \mathbf{c}^I(\mathbf{R}_x) \\ \mathbf{c}^J(\mathbf{R}_x) \end{pmatrix} \tag{11}$$

then $\mathbf{g}^{IJ}$ is replaced by $\tilde{\mathbf{g}}^{IJ} = (g_x \cos 2\theta + \; h_x \sin 2\theta,\; g_y \cos 2\theta + h_y \sin 2\theta)$ and $\mathbf{h}^{IJ}$ is replaced by $\tilde{\mathbf{h}}^{IJ} = (-g_x \sin 2\theta \; + h_x \cos 2\theta, -g_y \sin 2\theta + \; h_y \cos 2\theta)$. It is then straightforward to show that $\mathbf{t}^{IJ}(\mathbf{R}_x) = (g_x h_y - g_y h_x)\hat{k} = (\tilde{g}_x \tilde{h}_x - \tilde{g}_y \tilde{h}_x)\hat{k}$ so that $\mathbf{t}^{IJ}(\mathbf{R}_x)$ is independent of this one parameter rotation and thus is a unique property of the diabolical point, $\mathbf{R}_x$.

If $\mathbf{g}^{IJ}(\mathbf{R}_x)$ and $\mathbf{h}^{IJ}(\mathbf{R}_x)$ are nonzero and not parallel then $\mathbf{t}^{IJ}(\mathbf{R}_x)$ is unique. In this case there cannot be two linearly independent tangent vectors at $\mathbf{R}_x$, that is $\mathbf{R}_x$ cannot be a doubly diabolical point. On the other hand if either of these conditions does not occur, so that $\mathbf{t}^{IJ}(\mathbf{R}_x) = \mathbf{0}$, a doubly diabolical point is possible. While the condition $\mathbf{t}^{IJ}(\mathbf{R}_x) = \mathbf{0}$ is necessary, it is not sufficient for the existence of a doubly diabolical point since it occurs at Renner-Teller intersections [16, 17]. In case the perturbation expansion begins at quadratic terms while in the case considered here there is one direction in which the degeneracy is lifted in a linear manner. By judicious choice of V_2 it is also possible to design composite hamiltonians for which the degeneracy is lifted linearly in one direction at intersections that are not doubly diabolical. The situation is not considered here.

2.3 Trifurcation of a C_{2v} *seam of conical intersection in* AB_2

In order to clarify the ideas presented above the trifurcation illustrated in Fig. 2, which served to motivate the present analysis, is considered using model Hamiltonians. We define model Hamiltonians (1) and (2) and the associated surface normals by

$$\mathrm{G}(\mathbf{R}) = \mathrm{x} \qquad \nabla G = \hat{i} \tag{12a}$$

$$V_1(\mathbf{R}) = z \qquad \nabla V_1 = \hat{k} \tag{12b}$$

$$V_2(\mathbf{R}) = y - a - z^2 \qquad \nabla V_2 = \hat{j} - 2z\hat{k} \tag{12c}$$

where the Cartesian coordinates can be thought of as corresponding to $x = r - R, y = r + R$ and $z = \gamma$. Since $\mathbf{t}^1 = -\hat{j}$, Hamiltonian (1) has the y-axis, the dashed line in Fig. 2, as its seam of conical intersection (seam 1 the C_{2v} seam in Fig.2), while the Hamiltonian (2) has the parabola in Fig. 2 (seam 2, the C_s seam in Fig.2) as its seam of conical intersection, with $\mathbf{t}^2 = 2z\hat{j} + \hat{k}$. $\mathbf{R}_{dd} = (0, a, 0)$ is a doubly diabolical point. In the vicinity of $\mathbf{R}_{dd}$ Hamiltonians (1) and (2) have, to lowest order in displacements, the form:

$$\boldsymbol{H}^1(x,z) = x\boldsymbol{\sigma}_z + z\boldsymbol{\sigma}_x, \qquad \boldsymbol{H}^2(x,y) = x\boldsymbol{\sigma}_z + \delta y \boldsymbol{\sigma}_x \ , \tag{13}$$

where the replacement $y = a + \delta y$ has been used. As shown by Longuet-Higgins [18], this linear dependence of the matrix elements in Eq. (13) in the (x, z) plane for Hamiltonian (1) and in the (x, y) plane for Hamiltonian (2) gives rise to the geometric phase effect [15, 19, 20–22]. The geometric phase effect, the signature property of a conical intersection, causes $\Psi_I(\mathbf{r};\mathbf{R}) \to -\Psi_I(\mathbf{r};\mathbf{R})$ when $\mathbf{R}$ is transported along a closed loop containing an $\mathbf{R}_x$.

Seam 1 $(x = 0,\ y,\ z = 0)$ and seam 2 $(x = 0,\ y = a + z^2, z)$ are seams of conical intersection of the composite Hamiltonian $\boldsymbol{H}^{1,2} = G\boldsymbol{\sigma}_z + V_1 V_2 \boldsymbol{\sigma}_x$. Here $\mathbf{t}^{1,2} = (a + 3z^2 - y)\hat{j} + z\hat{k}$. Thus on seam 1, $\mathbf{t}^{1,2} = (a - y)\hat{j}$ is parallel to $\mathbf{t}^1 = -\hat{j}$, while on seam 2, $\mathbf{t}^{1,2} = 2z^2\hat{j} + z\hat{k}$ is parallel to $\mathbf{t}^2 = 2z\hat{j} + \hat{k}$, as expected.

We are interested in the properties of $\boldsymbol{H}^{1,2}$ near $\mathbf{R}_{dd}$ in general and the geometric phase effect in particular. In the vicinity of $\mathbf{R}_{dd}$ the composite Hamiltonian becomes:

$$\boldsymbol{H}^{1,2}(\mathbf{R}) = x\boldsymbol{\sigma}_z + z(\delta y - z^2)\boldsymbol{\sigma}_x \ , \tag{14}$$

$\mathbf{t}^{1,2}$ vanishes at $\mathbf{R}_{dd}$, as it must, although $\mathbf{t}^{1,2}/|\mathbf{t}^{1,2}| \to \pm\hat{j}$ along seam 1 and $\mathbf{t}^{1,2}/|\mathbf{t}^{1,2}| \to \pm\hat{k}$ along seam 2. In view of the limiting values of $\mathbf{t}^{1,2}/|\mathbf{t}^{1,2}|$ at $\mathbf{R}_{dd}$ the geometric phase effect should be considered for loops in the (x,z) plane, seam 1, and (x,y) plane, seam 2.

Consider a sequence of closed loops in the (x,z) plane, analogous to the loops denoted *loops* (*a*) in Fig. 2, but with sufficiently large radii so as not to intersect seam 2. For $y < a$ these loops enclose a single diabolical point while for $y > a$ these loops enclose three (an odd number of) diabolical points. For each of these classes of loops the geometric phase effect is obtained [15, 17]. Here the geometric phase effect reflects the behavior of the composite Hamiltonian in the vicinity of seam 1, where for $\delta y \neq 0$ the lowest-order terms are linear in x and z producing the geometric phase effect as noted above. At $\mathbf{R}_{dd}, y = a(\delta y = 0)$, there would appear to be a problem since $V_1 V_2 \approx z^3$ which is not linear in z. However, despite the absence of a linear dependence in $V_1 V_2$ it is straightforward to show that since z is raised to an odd power the geometric phase effect is still obtained. Therefore the geometric phase effect persists for loops, of sufficiently large radius, in the (x,z) plane for all values of y.

Next consider the sequence of closed loops denoted *loops* (*b*) in Fig. 2. These loops contain diabolical points on seam 2. For $\mathbf{R}_{dd}$, $z = 0$ and the loop is in the (x, y) plane. For $|z|$ small the coupling is linear in δy, however, for $z = 0$ the coupling vanishes and there can be no geometric phase effect. Again this would appear to be a problem since the geometric phase exists for loops (b) on either side of $z = 0$ but not at $z = 0$. However, this apparent contradiction is illusory since any loop in the (x,y) plane must intersect two, singular, diabolical points on seam 1.

At $\mathbf{R}_{dd}$ the two $\mathbf{t}^{1,2}$ are perpendicular. This need not be the case as can be seen by taking $G = x, V_1 = y$, and $V_2 = y - z$. In this case the two seams intersect at a 45° angle – seam 1 is the z-axis and seam 2 is the line $y = z$ in the $x = 0$ plane. At $\mathbf{R}_{dd} = (0, 0, 0)$ the Hamiltonian matrix for displacements in the plane perpendicular to seam 1, in the (x,y) plane, has the form $\boldsymbol{H}^{1,2} = x\boldsymbol{\sigma}_z + y^2\boldsymbol{\sigma}_x$ which clearly has a quadratic off-diagonal coupling matrix element.

These examples illustrate that a variety of power-law dependencies for the matrix elements of $\boldsymbol{H}^{1,2}$ in the vicinity of $\mathbf{R}_{dd}$ are possible suggesting the lack of a more general result for doubly diabolical points than the criterion presented here.

2.4 Computational implications

Previously we have developed a highly efficient algorithm to locate general points of conical intersection in which the Newton-Raphson equations

$$\begin{pmatrix} \boldsymbol{Q}^{IJ}(\mathbf{R},\boldsymbol{\xi},\boldsymbol{\lambda}) & \mathbf{g}^{IJ}(\mathbf{R}) & \mathbf{h}^{IJ}(\mathbf{R}) & \mathbf{k}^{IJ}(\mathbf{R}) \\ \mathbf{g}^{IJ}(\mathbf{R})^{\dagger} & 0 & 0 & \mathbf{0} \\ \mathbf{h}^{IJ}(\mathbf{R})^{\dagger} & 0 & 0 & \mathbf{0} \\ \mathbf{k}^{IJ}(\mathbf{R})^{\dagger} & \mathbf{0}^{\dagger} & \mathbf{0}^{\dagger} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \delta\mathbf{R} \\ \delta\xi_1 \\ \delta\xi_2 \\ \delta\boldsymbol{\lambda} \end{pmatrix} = -\begin{pmatrix} \mathbf{g}^{I}(\mathbf{R}) + \xi_1\mathbf{g}^{IJ}(\mathbf{R}) + \xi_2\mathbf{h}^{IJ}(\mathbf{R}) + \sum_i \lambda_i \mathbf{k}^{i}(\mathbf{R}) \\ E_I(\mathbf{R}) - E_J(\mathbf{R}) \\ 0 \\ \mathbf{K}(\mathbf{R}) \end{pmatrix} \quad (15)$$

are solved [8]. Here $\boldsymbol{\lambda}, \boldsymbol{\xi}$ are Lagrange mulipliers, $\delta\boldsymbol{\lambda} = \boldsymbol{\lambda}' - \boldsymbol{\lambda}, \delta\boldsymbol{\xi} = \boldsymbol{\xi}' - \boldsymbol{\xi}, k^i_{\tau}(\mathbf{R}) = \frac{\partial K_i(\mathbf{R})}{\partial \tau}, K_i(\mathbf{R}) = 0$ are con-straint equations, and $\boldsymbol{Q}^{IJ}(\mathbf{R})$ is a second derivative matrix [17]. The existence of nonvanishing $\mathbf{g}^{IJ}$ and $\mathbf{h}^{IJ}$, Eq. (8), is essential to this algorithm. Thus on the basis of the above analysis the determination of diabolical points using this algorithm becomes problematic in the vicinity of a doubly diabolical point. However, one can turn this apparent limitation to advantage. By monitoring $|\mathbf{t}^{IJ}(\mathbf{R}_x)|$ and $\mathbf{t}^{IJ}(\mathbf{R}_x)|/|\mathbf{t}^{IJ}(\mathbf{R}_x)|$ one can anticipate the (possible) existence of a doubly diabolical point. The search can be extended to look for the additional seam of conical intersection. Then the two seams can be extrapolated into the region of the doubly diabolical point to find its location. Note that attempts to understand the situation by monitoring $\mathbf{g}^{IJ}$ or $\mathbf{h}^{IJ}$ individually would be futile.

To illustrate how this works in practice Fig. 3 plots r and $\mathbf{g}^{IJ} \times \mathbf{h}^{IJ}$ along the C_s portion (the parabola in Fig. 2) of the $2^3A''$–$3^3A''$ seam of conical intersection in CH_2 noted in the introduction. The extended Gaussian basis set based MCSCF/CI treatment, which is described in detail elsewhere [10], comprises 561,114 configuration-state functions [23] [the $\boldsymbol{\psi}(\mathbf{r};\mathbf{R})$ in Eq. (9a)]. The key here is the $\gamma \to 90°$ limit of $\mathbf{g}^{IJ} \times \mathbf{h}^{IJ}$. By explicit computation it is known [10] that this limit will yield a point on the C_{2v} seam of conical intersection for these states, and hence a doubly diabolical point. Thus $\mathbf{g}^{IJ} \times \mathbf{h}^{IJ}$ must approach 0. This is in fact seen to be the case. Further r (and E_I and R which are not shown) can be extrapolated to determine the $\gamma = 90°$ limit.

It has recently been found [24] that the $1^2A'$–$2^2A'$ seam of conical intersection in BH_2, a seam analogous to that reported in AlH_2, exhibits a trifurcation of the type discussed in this work. As part of a forthcoming discussion of the $1,2^2A'$ potential energy surfaces in BH_2 [24] a more detailed analysis of the computational aspects of the ideas developed in this work will be presented.

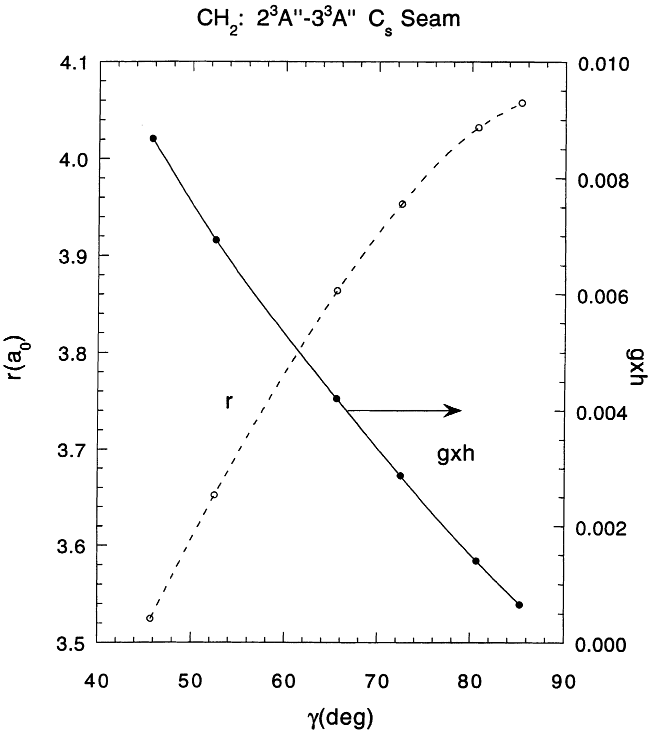

Fig. 3. r and $\mathbf{g}^{IJ} \times \mathbf{h}^{IJ}$ plotted as function of γ along the C_s portion (*parabola* in Fig. 2) of $2^3A''$–$3^3A''$ seam of conical intersection in CH_2 as described in [10]

Acknowledgements. This work has benefitted from a preprint of Ref. [25] provided by K. Ruedenberg which also discusses the issue of doubly diabolical points but from the perspective of approximate diabatic states.

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