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Systematic Location of Intersecting Seams of Conical Intersection in Triatomic Molecules: The 1 2A′–2 2A′ Conical Intersections in BH2

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Abstract
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Systematic location of intersecting seams of conical intersection in triatomic molecules: The $1\,^2A'-2\,^2A'$ conical intersections in BH_2

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Points of conical intersection are continuously connected forming seams. Recently a quite unanticipated situation has been found in which two distinct seams of conical intersection—one symmetry-allowed and one same-symmetry—originating from the same two states intersect each other. The identification of these confluences, based on *ab initio* electronic wave functions has been somewhat serendipitous. A systematic approach for locating such confluences, based solely on information obtained on the symmetry-allowed portion of the seam, has been suggested. In this work that approach is applied to identify the point where a C_s seam of conical intersection intersects a symmetry-allowed C_{2v} seam of conical intersection for the $1\,^2A'$ and $2\,^2A'$ states of BH_2, states that correlate with $B(1s^2 2s^2 2p,{}^2P)+H_2$. It is suggested, based on this and previous work, that this unexpected situation, which has fundamental implications for our understanding of nonadiabatic processes, is not at all uncommon. © *1998 American Institute of Physics.*
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I. INTRODUCTION

Conical intersections are of enormous importance in electronically nonadiabatic processes. Points of conical intersection are continuously connected forming seams. In triatomic molecules seams of conical intersection were usually assumed to be isolated features, that is in any plane perpendicular to the seam only avoided intersections are encountered. However recent research has suggested that this conventional wisdom is lacking, as instances of *intersections* of seams of conical intersection have been found for the $1\,^1A'$ and $2\,^1A'$ states of O_3,[1,2] the $2\,^3A''$ and $3\,^3A''$ states of CH_2,[3] and the $1\,^2A'$ and $2\,^2A'$ states of AlH_2 (Ref. 4) based on *ab initio* wave functions. Since points of conical intersection are frequently referred to as diabolical points,[5,6] points at the intersection of two seams will be referred to as doubly diabolical points.[7] The existence of intersecting seams of the conical intersection has important implications for even a qualitative understanding of the dynamics of a nonadiabatic process, since strong nonadiabatic effects will be encountered in unexpected regions of nuclear coordinate space.

Establishing the existence of intersecting seams can be quite tedious. However a numerical procedure[7] has been suggested that permits this feature to be anticipated using only information from the readily determined symmetry-allowed portion of the seam of the conical intersection. This procedure could provide a convenient tool for studying this situation, including the recent suggestion of Ruedenberg and co-workers[2] that the doubly diabolical points in O_3 will have analogs in S_3, S_2O, and SO_2. Above we have referred to a doubly diabolical point as existing on either, a single seam of intersection with intersecting portions, or two intersecting seams. We will not distinguish between these semantic alternatives in this work.

Here the procedure is used to consider the conical intersections of the $1\,^2A'$ and $2\,^2A'$ potential energy surfaces of BH_2. These surfaces govern the reaction of boron with molecular hydrogen

$$B(^2P)+H_2 \rightarrow B\text{–}H_2(1\,^2A_1, 1\,^2B_2) \rightarrow BH_2(X\,^2A_1) \tag{1a}$$

$$\rightarrow BH(X\,^1\Sigma^+)+H. \tag{1b}$$

Reactions (1a) and (1b) are of considerable practical importance, being relevant to the use of B doped cryogenic hydrogen as an energetic material. As explained below, the region of the $1\,^2A'-2\,^2A'$ seam of conical intersection is likely to be important for the stability the van der Waals complex $B\text{–}H_2$ that constitutes the energetic material, since formation of the dihydride $BH_2(X\,^2A_1)$, which has been prepared by laser ablation of boron,[8] could limit the stability of the van der Waals complex. The reason for focusing, initially, on the conical intersections is based on previous work on the AlH_2 system.[4,9] There, as in BH_2,[10,11] the $1\,^2A_1$ section of the $2\,^2A'$ potential energy surface has a high barrier to the formation of the ground $X\,^2A_1$ state of the dihydride.[9] Low energy pathways to the dihydride start on the $^2B_2$ section of the $1\,^2A'$ potential energy surface. The $^2A_1$ portion of the $1\,^2A'$ potential energy surface is reached (for exclusively C_{2v} approach) via the ridge represented by the $^2B_2-{}^2A_1$ seam of conical intersection. The assumption of C_{2v} symmetry is, of course, simplistic. There are *two* directions perpendicular to the ridge one that preserves C_{2v} symmetry, the aforementioned constrained reaction path, and an asymmetric mode that removes the C_{2v} symmetry. It has emerged, however, that in AlH_2, only small displacements along this mode give rise to the true transition state[4] so that the minimum energy crossing point (MECP), the minimum energy point on the $^2B_2-{}^1A_1$ seam of conical intersection, gives approximately the barrier height.[4]

Thus the $1\,^2A'-2\,^2A'$ seam of conical intersections in BH_2 is considered in this work. This is the subject of Sec. II. Section III summarizes and discusses directions for future research.

II. COMPUTATIONAL APPROACH AND RESULTS

A. Electronic wave functions

The calculations performed here parallel those in our previous treatment of $Al+H_2$ (Ref. 4) where the reader can find more details concerning the level of treatment. Briefly, then the present *ab initio* calculations employ standard state-averaged multiconfigurational self-consistent field (SA-MCSCF)/configuration interaction (CI) techniques[12] so that the electronic wave functions, $\Psi_I(\mathbf{r};\mathbf{R})=\Sigma_{\alpha=1}^{N^{\rm CSF}} c_\alpha^I(\mathbf{R}) \times \psi_\alpha(\mathbf{r};\mathbf{R})$, are eigenstates of the nonrelativistic Born–Oppenheimer Hamiltonian and the $\mathbf{c}^I(\mathbf{R})$ satisfy, $\mathbf{H}(\mathbf{R})\mathbf{c}^I(\mathbf{R})=E_I(\mathbf{R})\mathbf{c}^I(\mathbf{R})$, where $\mathbf{H}(\mathbf{R})$ is the electronic Hamiltonian matrix. The wave functions are described at the second order CI(SOCI) level—all single and double excited electron configurations relative to a five electron, six orbital $(5a',1a'')$ active space, comprising the B$(2s,2p)$ orbitals and the H$(1s)$ orbitals. Contracted Gaussian basis sets B $(8s5p3d)$ and H $(6s3p1d)$ are used to expand the molecular orbitals determined from a SA-MCSCF procedure. Using this basis $N^{\rm CSF}=252\,255$. It is useful to note that this level of treatment predicts a reaction endoergicity of 1.051(1.075) eV for reaction (1b) in excellent agreement with the experimental value[13] given parenthetically.

B. Specification of molecular geometries and seams of conical intersection

Molecular geometries will be specified by the Jacobi coordinates, $\mathbf{R}=(R,r,\gamma)$, where r is the H^1–H^2 distance, $R(H^1$–$H^2)$, R is the distance between B and the center of mass of H_2, and γ is the angle between the line segments corresponding to R and r, such that $\gamma=90°$ for C_{2v} geometries. Points, $\mathbf{R}_x$, on a seam of conical intersection will be parameterized either by r, that is $\mathbf{R}_x(r)\equiv(R(r),r,\gamma(r))$ or by γ, that is $\mathbf{R}_x(\gamma)\equiv(R(r),r(\gamma),\gamma)$.

C. Anticipating the unexpected

The quantity $\mathbf{t}^{IJ}(\mathbf{R}_x)\equiv\mathbf{g}^{IJ}(\mathbf{R}_x)\times\mathbf{h}^{IJ}(\mathbf{R}_x)$, which is the tangent to the seam of conical intersection, vanishes at a point of intersection of two seams,[7] where

$$2g_\tau^{IJ}(\mathbf{R})=(\mathbf{c}^I(\mathbf{R}_x)-\mathbf{c}^J(\mathbf{R}_x))^\dagger \frac{\partial \mathbf{H}(\mathbf{R})}{\partial \tau}(\mathbf{c}^I(\mathbf{R}_x)+\mathbf{c}^J(\mathbf{R}_x)), \tag{2a}$$

$$h_\tau^{IJ}(\mathbf{R})=\mathbf{c}^I(\mathbf{R}_x)^\dagger \frac{\partial \mathbf{H}(\mathbf{R})}{\partial \tau}\mathbf{c}^J(\mathbf{R}_x), \tag{2b}$$

τ is an internal nuclear coordinate. Here $I=1\,^2A'$ and $J=2\,^2A'$. It is important to emphasize here that both $\mathbf{g}^{IJ}$ and $\mathbf{h}^{IJ}$ are readily evaluated for SA-MCSCF/CI wave functions using analytic gradient techniques.[14]

Our algorithm for locating points of the conical intersection requires both $\mathbf{g}^{IJ}(\mathbf{R}_x)$ and $\mathbf{h}^{IJ}(\mathbf{R}_x)$ to be nonvanishing.[15] Thus a doubly diabolical point cannot be located directly using this procedure. However since the C_{2v} seam, $\gamma=90°$, is easy to anticipate and locate, plotting $\mathbf{t}^{IJ}(\mathbf{R}_x)$ for $\mathbf{R}_x$ on the C_{2v} seam should enable the presence (or absence) of a doubly diabolical point to be established.

D. The $1\,^2A'-2\,^2A'$ seam of the conical intersection

Figure 1(a) presents $E_{1\,^2A'}(\mathbf{R}_x(r))=E_{2\,^2A'}(\mathbf{R}_x(r))$ and $R(r)$ along seam 1, the C_{2v} portion of the seam of conical intersection of the $1\,^2A'$ and $2\,^2A'$ potential energy surfaces of BH_2. This portion of the seam is parameterized by r. Here and below $E_{\rm ref}$, the zero of energy, is taken as the energy of the $1\,^2A'$ state at the $B(^2P)+H_2$ asymptote, with $R(H^1$–$H^2)=1.4\ \ a_0$, $E_{\rm ref}=E_{1\,^2A'}=-25.770\,181$ a.u. The key result of this work, a plot $\mathbf{t}^{IJ}(\mathbf{R}_x)$ for $\mathbf{R}_x$ on seam 1, is presented in the inset to Fig. 1(a). On the basis of the vanishing of $\mathbf{t}^{IJ}(\mathbf{R}_x)$, this plot establishes the existence of a doubly diabolical point, $\mathbf{R}_{dd}=(2.6,\ 3.11,\ 90°)$. Using this information, non-C_{2v} points on the seam of conical intersection were sought and located. The result, seam 2, parameterized by γ, is reported in Fig. 1(b). Seam 2 has two symmetry equivalent branches, for γ and $180°-\gamma$; only the $\gamma<90°$ branch is shown. It has only C_s symmetry except at $\gamma=90°$, where seam 1 and seam 2 intersect. Figure 1(b) presents $E_{1\,^2A'}(\mathbf{R}_x(\gamma))=E_{2\,^2A'}(\mathbf{R}_x(\gamma))$, $r(\gamma)$, and $R(\gamma)$ along seam 2. The inset to Fig. 1(b) plots $\mathbf{t}^{IJ}(\mathbf{R}_x)$ for $\mathbf{R}_x$ on seam 2. $\mathbf{t}^{IJ}(\mathbf{R}_{dd})=0$ as expected, although this plot is less useful than that in Fig. 1(a) since seam 2 is difficult to anticipate.

The points reported were shown to be true conical intersections rather than narrowly avoided intersections by showing that the circulation of the derivative coupling along a small loop surrounding the point in question is π rather than zero.[3]

When $\mathbf{R}_{dd}$ is compared with the equilibrium structures, of the van der Waals complex $\mathbf{R}_{\rm vdw}$ and, of the dihydride $\mathbf{R}_{\rm eq}$, which are $\mathbf{R}_{\rm vdw}=(6.082,\ 1.405,\ 90°)$, $\mathbf{R}_{\rm eq}=(3.206,\ 4.059,\ 90°)$, it is seen that $\mathbf{R}_{dd}$ is located in the *molecular* region. The confluence is therefore *not* the consequence of an asymptotic degeneracy or a highly compressed, energetically irrelevant, configuration.

E. Implications

$E_{1\,^2A'}(\mathbf{R}_{dd})$ is $\sim$0.6 eV above that at the MECP on seam 1, $\mathbf{R}_{\rm MECP1}$, and $\sim$0.15 eV above that at the MECP on seam 2, $\mathbf{R}_{\rm MECP2}$. Thus for this system $\mathbf{R}_{dd}$ will not contribute to processes dominated by ''threshold'' energetics. $E_{1\,^2A'}(\mathbf{R}_{\rm MECP1})$ is only $\sim$0.6 eV above the $B+H_2$ asymptote. This is over 0.5 eV lower than in the $Al+H_2$ system. It will be important to determine the true transition state for, and the propensity for electronic nonadiabaticity—induced by this seam of conical intersection—in, the formation of $BH_2(X\,^2A_1)$. In this regard determination of potential energy, and derivative coupling, surfaces is currently in progress.

For AlH_2, $\mathbf{R}_{dd}$ was found to be quite close to $\mathbf{R}_{\rm MECP1}$ and $\mathbf{R}_{\rm MECP2}$.[4] Thus for AlH_2 threshold processes should re-

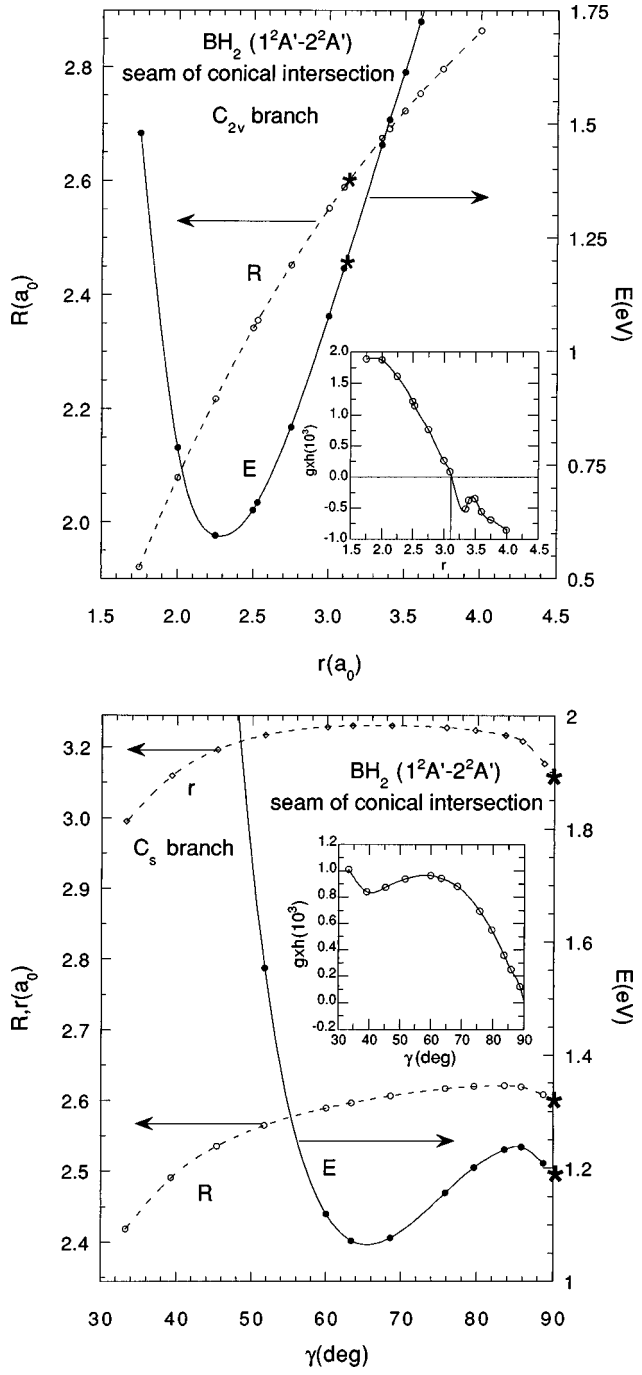

FIG. 1. (a) $R \equiv R(r)$ and $E \equiv E_{1\,^2A'}(\mathbf{R}_x(r)) = E_{2\,^2A'}(\mathbf{R}_x(r))$ as function of the parameter r along seam 1 (the C_{2v} seam). The asterisks (*) indicate the values of these quantities at the doubly diabolical point, $r \sim 3.11$. The inset plots $\mathbf{g} \times \mathbf{h}$ as a function of the seam parameter r on seam 1. Markers indicate the results of actual calculations. Connecting lines are spline fits. (b) $R \equiv R(\gamma)$, $r \equiv r(\gamma)$, and $E \equiv E_{1\,^2A'}(\mathbf{R}_x(\gamma)) = E_{2\,^2A'}(\mathbf{R}_x(\gamma))$ as function of the parameter γ along seam 2 (the C_s seam). The asterisks (*) indicate the values of these quantities at the doubly diabolical point, $\gamma = 90°$. The inset plots $\mathbf{g} \times \mathbf{h}$ as a function of the seam parameter γ on seam 2. Markers indicate the results of actual calculations. Connecting lines are spline fits.

flect the presence of the doubly diabolical point of the conical intersection.

For both BH_2 and AlH_2 the lowest energy conical intersections are found on seam 1, the C_{2v} seam. This is likely a reflection of the fact that the H_2 bond is approximately 1 eV (1.4 eV) stronger than the BH (AlH) bond.[13] This situation is reversed for MeX_2 species, where Me is an alkaline earth atom such as Ca or Ba, and X is a halogen including F, Cl, and Br. In this case the MeX bond is stronger than the XX bond. Thus it will be important to examine these molecules from the present perspective.

III. SUMMARY AND CONCLUSIONS

In this work intersecting seams of conical intersection were established for the $1\,^2A'$ and $2\,^2A'$ states of BH_2. One seam is a conventional C_{2v} symmetry-allowed $^2B_2 - ^2A_1$ seam of conical intersection, while the second occurs for C_s nuclear configurations. The two seams intersect at a point of C_{2v} symmetry. The existence of the C_s seam was anticipated by monitoring the quantity $\mathbf{g}^{IJ} \times \mathbf{h}^{IJ}$ [Eq. (2)] along the readily established C_{2v} seam. The C_s seam provides regions of large nonadiabatic effects that do not possess even approximate C_{2v} symmetry and thus can have profound and unexpected effects on reaction dynamics. This finding, together with similar findings based on *ab initio* wave functions in O_3, CH_2, and AlH_2, and in H_2Cl^+ (Ref. 16) based on diatomic in molecules wave functions, suggests that this situation is not at all uncommon.

For the triatomic systems considered here the $\mathbf{R}_{dd}$ are isolated points. It will be most interesting to study this situation in larger molecules where the locus of such points will be more complicated.

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