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

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ABSTRACT: A method to locate conical intersections between the ground-state potential surface and the first electronically excited states of polyatomic molecules is described. It is an extension of the Longuet-Higgins sign-change theorem and uses reaction coordinates of elementary reactions as the starting point of the analysis. It is shown that the complete molecular landscape [1] can be partitioned into 2-D domains, each bordered by a Longuet-Higgins loop formed from reaction coordinates of elementary reactions. A domain may contain a conical intersection and if it does, it contains only one (the uniqueness theorem), whose energy is higher than the neighboring minima or transition states. The method can be helped by symmetry, but applies also to systems having no symmetry elements. It is demonstrated for some simple cases. The presence of a conical intersection is manifested by the nature of ground-state thermal reactions, as shown for instance by the fact that the transition state in the ring opening of the cyclopropyl radical is nonsymmetric. © 2005 Wiley Periodicals, Inc. Int J Quantum Chem 102: 961–970, 2005

Key words: conical intersection; photochemistry; reaction coordinate; sign change theorem

Introduction

This article presents 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. In general, these singularities are expected to lie at higher energies than stable species positioned at local minima on the ground-state potential. Therefore, it is natural to search for them at positions far away from the minima. Several methods have been developed to
search for these degeneracies [2–5] commonly known as conical intersections, after Teller’s original proposal [6]. We present a model based on the concept of a chemical reaction as a two-state system [7–9] that appears to be uniquely appropriate for this purpose, especially for large polyatomic systems, in which several degeneracies are common. In view of the importance of conical intersections in photochemistry, our principal motivation is the elucidation of photochemical reactions. Consequently, it is natural to base the analysis on chemical concepts, in particular the concept of a chemical bond based on the spin-pairing of two electrons. In the spirit of this approach, valence bond (VB) structures will be used to represent the molecules and transition states; the considerable progress made recently in the application of VB theory to the properties of transition states [10, 11] makes this choice a natural one. Nonetheless, computational implementation is usually done by the CI-MO method. The model considered deals only with intersections between states of the same multiplicity, and in view of the fact that most organic molecules have a single excited state they are usually S1/S0 intersec-
tions.

The Two-State Spin-Pairing Model

Consider an ensemble consisting of all possible chemically bound species (local minima on the ground-state potential surface). We have recently shown that transition states, twofold and threefold degeneracies, can be located by a simple, straightforward procedure, starting at minima on the ground-state potential surface [12].

In the model two species, P and R, are considered as different chemical species if and only if they differ only by their spin-pairing schemes (we termed such species anchors [9, 13]). Within the Born–Oppenheimer (BO) approximation, the corresponding total ground-state electronic wave functions (EWF) are |P⟩ and |R⟩, respectively. |P⟩ and |R⟩ are different but not orthogonal to each other—for the chemical reaction to take place there must be a finite interaction between them. At certain nuclear configurations—QP and QR, respectively—they occupy local minima on the ground-state potential surface. A basic assumption of the model is that each spin-pairing scheme (anchor) is related to a stable minimum on the ground-state potential surface in one of two ways: (1) the anchor represents one and only one structural isomer occupying a minimum on the ground-state potential*; (2) the EWF of a stable species is represented by a superposition of two anchors.

A chemical reaction is conceived as a spin re-pairing process followed by attainment of an energy minimum at a different nuclear geometry. If motion along the coordinate connecting the two species (the reaction coordinate) involves a single local maximum, then the reaction P → R is an elementary one. The EWF of the system along the reaction coordinate Q may be written as one of the linear combination [8, 9, 14]

\[
|\phi_{\text{reaction}}(Q)\rangle = k_P(Q)|P\rangle + k_R(Q)|R\rangle, \quad (1a)
\]

\[
|\phi_{\text{reaction}}(Q)\rangle = k_P(Q)|P\rangle - k_R(Q)|R\rangle. \quad (1b)
\]

The nonnegative coefficients kP(Q) and kR(Q) depend parametrically on Q such that kP = 1 and kR = 0 at QP, whereas kP = 0 and kR = 1 at QR. As the system moves along the reaction coordinate, kP(Q) varies smoothly from unity to zero, and kR(Q), from zero to unity. At a certain point QPR along the coordinate, kP = kR, and the potential surfaces of P and R cross. The interaction between the two states lifts the degeneracy [15]: two adiabatic potential surfaces are formed, a ground state and an excited state. In this standard quantum mechanical problem the wave functions of the adiabatic states are formed by linear combinations of the original wave functions; one is the in-phase combination |P⟩ + |R⟩, and the other, the out-of-phase one |P⟩ − |R⟩.

The nuclear configuration at the avoided crossing, QPR, has a stationary point (local maximum or minimum) on the ground-state surface [8, 16]. Reactions for which the wave function |φreaction(Q)⟩ is the in-phase combination [Eq. 1(a)] are labeled as sign-preserving reactions (p type), and those for which |φreaction(Q)⟩ is the out-of-phase combination [Eq. 1(b)], sign-inverting reactions (I type). The opposite combination lies on the excited-state potential, and has a minimum along Q at QPR. The interaction between the original species is defined along a single coordinates—this is a 1D problem. The distinction between the two parity types is straightforward when a symmetry element is added at the transition state (TS); the EWF of a sign preserving TS in this case will transform as the totally symmetric irreducible representation (irrep) of the new

*In the definition of anchors we include all conformers that have the same spin-pairing scheme, even if they occupy different minima.
point group, and if the TS is sign inverting, as one of the non-totally symmetric irreps.

A similar construct may be extended to higher dimensions [12]; with three basis functions $|P\rangle, |R\rangle,$ and $|S\rangle$, a point $Q_{PRS}$ can be found such that the energies of the three anchors are equal, and also the three coupling elements $(x|H|y) (x, y = P, R, S)$ are equal to each other. Diagonalization of the secular matrix at this point yields two eigenvalues, one of which is doubly degenerate and the other nondegenerate. The energy ordering of the states can be determined using the Longuet-Higgins sign-change theorem [17, 18]: if all reactions connecting $P, R,$ and $S$ are sign-inverting (an $i^3$ loop), then the degeneracy is on the electronic ground state. This is also the case if two reactions are sign-preserving and one is sign-inverting (an $i^2 p$ loop [9, 19]). The nondegenerate state is a higher-lying electronic state. However, if all reactions are sign-preserving (a $p^3$ loop) or if two are sign-inverting and one is sign-preserving (an $i^3 p$ loop), the loop encircles a single-valued point, and the EWF maintains its sign. Under these conditions, the ground-state potential surface at $Q_{PRS}$ is a saddle point (second-order transition state): motion away from this point leads smoothly to all three anchors at their respective minima without encountering a barrier. The doubly degenerate state is an electronically excited state.

This process can be repeated for four basis functions, yielding a threefold electronic degeneracy, which will not be further treated here. However, extension to even higher dimension is impossible; as in a 3-D space, it is impossible to find a point at which the energies of five different anchors are equal, and at the point all coupling matrix elements are also equal to each other [12].

The last statement is equivalent to a well-known theorem of graph theory (the embedding theorem) [20]: a finite graph of any dimension can be embedded in a Euclidean 3-D space. In other words, every graph can be drawn without crossings in 3-D space.

The local minima of the different spin-pairing schemes (anchors) can be connected by reaction coordinates defined (for elementary reactions) as the minimum energy path between two minima. In the present context we shall consider as proper minima only those that differ in their spin-pairing schemes. Other minima, such as those occupied by conformers, will be included in a single anchor [9, 13]. As a consequence of the two-state model, two anchors may be connected by one or two reaction coordinates, but not by more [12]. Clearly, not any two minima are necessarily connected by an elementary reaction but there are always ways to connect all minima by elementary reactions, so that the space occupied by the whole ensemble is a connected one. This can be shown, for instance, by constructing all possible chemical species using diatomic units as building blocks.

Figure 1 presents a schematic plot of the total reaction landscape. As a consequence of the above model, the whole ensemble (defined by the number of nuclei and electrons in the system) can be divided into domains (containing in general two or three minima*), that encircle sign-inverting or sign-preserving loops. Consider any sign-inverting loop formed by two or three minima that are connected by elementary reactions: the energies of the stationary points and of the conical intersection can be plotted as a function of the two coordinates that span the plane containing the three minima. One of them is sign-preserving, the other sign-inverting [9]. In such a plot the energy of a transition state is by construction higher than that of the two minima it connects, and the energy of the conical intersection (CI) is higher than any of the TSs.

Figure 1(A) shows schematically a partial plot of the ensemble of all stationary points of the system, projected on a plane defined by a given pair or trio of minima. Transition states are marked by short lines perpendicular to the trajectory. All other minima can be reached only along different reaction coordinates and therefore lie on different planes. This is a direct corollary of the two-state model: the wave function of a fourth anchor can be either expressed as a linear combination of the wave functions of two other anchors or not. If it can, it must be either the in-phase or the out-of-phase combination; these species are already included in the graph (as the third anchor or as a transition state) so that it is not in fact an independent species. If it does not, it must lie on a different plane (whose existence is guaranteed by the embedding theorem). Thus, each loop defines a separate 2-D domain in this plot. The domain defined by the two coordinates spanning it includes all points enclosed by the loop, as well as

*The two dimensional domain is spanned by two vectors—we choose two reaction coordinates for this purpose. In terms of anchors, a domain must include three independent ones that may represent three minima (a three-legged domain). A two-legged domain having only two minima is also possible, but it must also include at least three independent spin-paired combinations, otherwise it degenerates to a line. The two minima are obtained from different combinations of the anchors, as shown in some examples in Section IV.
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.

The upshot of this construction is that loops formed by elementary reactions define natural separate domains in the complete landscape. The area bounded by a loop is the inside of the domain, and all other points lie outside the domain. The loop formed by \( m_1', m_2', \) and \( m_3' \) in Figure 1(A) (violet), for instance, is spanned by different coordinates than the loop formed by \( m_1, m_2, \) and \( m_3 \) (blue). Loops may consist of only two minima connected by two different transition states: the green loop is an example of such a loop. Loops of higher dimensions are sometimes required by symmetry [21] but will not be further discussed in this article. Figure 1(B) shows a contour diagram, plotted as a projection on the plane spanned by the reaction coordinates. Figure 1(C) shows schematically the potential energy along one possible trajectory \( T(m_1–m_2) \) connecting anchor \( m_1 \) with \( m_2 \) constructed from reaction coordinates. This trajectory is shown as a red line in Figure 1(A).

If the domain contains a conical intersection, it is always possible to use a pair of coordinates such that one is sign-preserving and the other sign-inverting. It is useful to use combinations of reaction coordinates that lead directly to the conical intersection. This is demonstrated in Figure 2 for a two legged domain. The EWFs of the reactant and the product are combinations of a covalent term (C) (different for the two species) and a polar term (D) common to both:

\[
|\text{Reactant} \rangle = |C_1 \rangle + |D\rangle, \quad (2a) \\
|\text{Product} \rangle = |C_2 \rangle + |D\rangle. \quad (2b)
\]

Two transition states can be formed: the sign-inverting one from the out-of-phase combination (3a) and the sign-preserving one from the in-phase combination (3b)

\[
|\text{TS}_{\text{out}} \rangle = |\text{Reactant} \rangle - |\text{Product} \rangle = |C_1 \rangle - |C_2 \rangle, \quad (3a) \\
|\text{TS}_{\text{in}} \rangle = |\text{Reactant} \rangle + |\text{Product} \rangle = 2|D\rangle + |C_1 \rangle - |C_2 \rangle. \quad (3b)
\]

The two coordinates, \( Q_+ \) and \( Q_- \), are defined by the in-phase and out-of-phase combinations, respectively, of the two reaction coordinates:

\[
Q_+ = Q_{\text{React}}(\text{sign-preserving}) + Q_{\text{React}}(\text{sign-inverting}), \quad (4a) \\
Q_- = Q_{\text{React}}(\text{sign-preserving}) - Q_{\text{React}}(\text{sign-inverting}). \quad (4b)
\]

They intersect at the conical intersection. A similar construct can be developed for a three-legged domain, for which at least one reaction is sign-inverting, say \( Q_1 \). The combination of the other two (\( Q_2 \) and \( Q_3 \)) must be sign preserving, so that

\[
Q_+ = Q_1 + (Q_2 + Q_3), \quad (5a) \\
Q_- = Q_1 - (Q_2 + Q_3). \quad (5b)
\]

### The Uniqueness Theorem

The central theorem of this article can be stated as follows: if a loop formed by two or three elementary reactions is sign-inverting, it encircles one and only one conical intersection. The proof is by contradiction using the Longuet-Higgins theorem that guarantees the existence of an odd number of conical intersections, so that it remains to be shown that only one CI exists within the loop. Consider first a domain in which there are two separate minima connected by a sign-inverting loop having two transition states lying on reaction coordinate \( Q_1 \) and \( Q_2 \) (Fig. 3).

By construction, the loop passes through two minima (A and B) differing in their spin-pairing arrangements. No other minima are present in the domain. In Figure 3 we plot the diagram as a function of two coordinates, \( Q_+ \) and \( Q_- \), defined in Eqs. (4a) and (4b).

For a sign-inverting loop, the EWF’s sign is preserved for motion along \( Q_+ \) and inverted for motion along \( Q_- \). In Figure 3, \( Q_+ \) connects the reactant and the product and \( Q_- \) connects the two transition states. The conical intersection CI\(_a\) lies at the origin of this plot. Assume that in addition to it there are two more conical intersections, which must be symmetrically positioned along the y axis. Consider, for instance, CI\(_b\): it may be part of the previously defined conical intersection, even if it differs in spatial symmetry. Assuming it is distinct from CI\(_a\) there must be a stationary point on the trajectory connecting CI\(_a\) and CI\(_b\), which can only be either a minimum or a transition state (marked in the figure as
Because the presence of an additional minimum within the domain is ruled out by the basic assumption, \( \text{TS}_{0-1} \) must be a transition state. Within the two-state model, all EWFs lying on the positive side of the \( y \) axis are represented by an in-phase combination of the EWFs of |A\rangle and |B\rangle. This means that a sign-preserving loop A-TS\(_1\)-B-TS\(_{0-1}\) encloses the point represented by CI\(_2\), which therefore cannot be a conical intersection. The contradiction shows that the assumption that there is more than

\[ \text{TS}_{0-1} \].

FIGURE 1. A scheme showing the division of the whole reaction space into domains using the reaction coordinates of elementary reactions. A. An overview of the multidimensional hyperspace spanned by reaction coordinates. Small circles represent species lying at a local minimum, short sticks denote transition states. The lines connecting them are drawn along reaction coordinates, namely along a minimum energy path on the ground state potential surface. Two three-legged loops and one two-legged loop are designated by the anchors forming them: \((m_1, m_2, m_3), (m_1', m_2', m_3'), (m_1'', m_2'').\) Each domain is spanned by the two independent reaction coordinates \( Q_i \) and \( Q_j \), whose construction is described in the text. In order to avoid congestion in the figure, only the coordinates \( Q_1 \) (the reaction coordinate connecting \( m_1 \) and \( m_2 \)) and \( Q_2 \) (the reaction coordinate connecting \( m_2 \) and \( m_3 \)) are explicitly shown. Strictly speaking, each domain spans a different plane, and a multidimensional plot is required to represent the complete hyperspace. The loops shown are further discussed in the text. B. A schematic energy diagram (shown as contour plots) of the ground state in the vicinity of the domain spanned by the triad \((m_1, m_2, m_3)\). C. A schematic energy profile along a combined reaction trajectory from \( m_1 \) to \( m_1' \) passing through \( m_2 \) and \( m_1'' \), showing local minima and maxima (energies of the transition states) along the way.

FIGURE 2. An example of two-legged sign-inverting domain. CI is a conical intersection; TS is a transition state.

FIGURE 3. Checking the possible existence of more than one conical intersection inside a domain bounded by reaction coordinates. A and B are minima, 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 \( Q_1 \) and \( Q_2 \) axes. Any other conical intersection must be off the \( Q_1 + 0 \) axis, as it must have a contribution from both an in-phase combination of |A\rangle and |B\rangle (the area marked green) and also the out-of-phase combination (area marked red).
independent coordinates are required to construct it.

In any given problem, we shall be interested in the possible products of a photochemical reaction starting with one of the stable minima (the reactant). The number of possible elementary reactions that a single system can undergo is in general small, considering the usual range of energies available (usually not exceeding ~100 kcal/mol). In practice this usually limits the number of bonds that are simultaneously exchanged in an elementary reaction to two or three. Conical intersections are sought by checking the parity of each loop, using the Longuet-Higgins theorem.

Examples

**E-Z ISOMERIZATION OF THE FORMALDIMINIUM CATION [22]**

The system, which is an example of a two-legged loop of the type shown in Figure 2, is schematically portrayed in Figure 4. As shown in Ref. [22], the EWFs of the reactant and product can be represented by Eqs. (2a) and (2b)—the polar form is common to both species. The covalent transition state is analogous to the biradical perpendicular transition state of olefins: the π bond is broken and the two π-orbitals of the carbon and nitrogen atoms are perpendicular to each other. The ionic form is stabilized due to the electronegativity difference between the nitrogen and carbon atoms. Q+ is in this case torsion around the C==N bond plus stretching of the bond and Q− is primarily pyramidalization of the nitrogen atom. The covalent transition state is of C2v symmetry, but different from that of the reactant and product. Its EWF transforms as one of the non-totally irreps (a2). The polar transition state transforms as the totally symmetric irrep of the C2v point group, as expected from the general theory—its EWF is formed by the in-phase combination of the EWFs of the reactant and product and a new symmetry element was added. As detailed calculations show [22], the ionic transition state and the biradical transition state are of almost equal energy in the gas phase, with the conical intersection slightly higher.

**THE CIS-TRANS ISOMERIZATION 4-CYCLOPENTADIENYLIDENE-1,4-DIHYDROPYRIDINE (CPDHP) [23]**

This molecule (Scheme 1) is much more polar than most olefins because of the considerable contribution of a polar structure stabilized by aromatization. Therefore, the isomerization around the CC double bond in this system can proceed along a reaction coordinate having an ionic TS and is also an example of a two-legged loop, as shown in Figure 5.

The two transition states are of C2v symmetry, with different symmetry elements from those of the reactant and product. Their EWFs transform, as expected from the model, as one of the non-totally irreps (a2).
irreps \((a_2)\) for the covalent TS and as the totally symmetric one for the polar one.

Figure 6 shows the results of a CASSCF\((10,9)/DZV\) calculation for this system, which fully validate the qualitative model: both transition states were found to have a single imaginary frequency, and the conical intersection was found along the coordinates shown in the figure. Its energy is slightly higher than the energy of the ionic TS.

THE RING-OPENING OF THE CYCLOPROPYL RADICAL TO AN ALLYL RADICAL

This system was extensively studied theoretically \([24–27]\) partly as a result of the dilemma raised by Longuet-Higgins and Abrahamson \([24]\): the reaction (whether conrotatory or disrotatory) appears to be allowed both thermally and photochemically in apparent contradiction to the Woodward–Hoffmann rules \([28]\). A conical intersection is predicted by an early calculation of Merlet et al. \([29]\). The conrotatory and disrotatory routes are almost equally probable with a small preference for the disrotatory mode \((57:43)\) according to recent high-level \(ab\) initio direct dynamics quasiclassical trajectory calculations by Mann and Hase \([27]\). Experimental studies of this reaction have not resolved the issue yet, to our knowledge.

In this case both reactant and product have a plane of symmetry, whereas the two transition states have none. As discussed by Olivella et al. \([25]\), the reaction cannot proceed if the two CC bonds are constrained to be of equal length, as the reaction does not preserve symmetry in either the conrotatory mode or the disrotatory one. They found that one of the CC bonds is shorter than the other in the transition state, and concluded that the reaction is not concerted. The connection to the presence of a conical intersection was not made.

According to our analysis, the symmetric species which is avoided in the thermal reaction (two equal CC bond lengths) is the conical intersection, situated in a loop formed by the reactant, product, and two transition states. This is another example of a domain formed by only one reactant and one product (Fig. 1).

The three anchors required to construct the system are in this case found by considering the special properties of the allyl radical. The EWF of the allyl radical is formed by the out-of-phase combination of two VB structures (Scheme 2), so that they are the required spin-paired structures. The third is the EWF of the cyclopropyl radical. Thus, the asymmetric stretch vibration of the allyl radical is the sign-inverting coordinate in this reaction! The reaction coordinate is the combination of this coordinate and the torsional coordinate (disrotatory or conrotatory) is the sign preserving one. The two coordinates that combine to form the reaction coordinate are shown in Figure 7 for the two reaction modes. There are therefore four sign-inverting loops in this system, two each for a given reaction mode; the enclosed CIs are four structural isomers. The coni-
cal intersection manifests itself on the ground-state potential surface by the fact that the transition states are bent and have different CC bond lengths. A demonstration of the presence of the conical intersection, in principle, is possible in this case. The two equivalent conrotatory conical intersections in this system are mirror images (as are the two disrotatory ones). If the allyl radical is promoted to the electronically excited state, and moves on to the conical intersection, it has exactly equal probability of crossing the right- and left-handed conical intersections. Constructive and destructive interferences between the two wave packets may arise, observable in principle by time-dependent intensity fluctuations in the product signal.

Discussion

The scope of the method

The method presented in this article is based on two key assumptions. (1) A chemical compound is defined by the spin-pairing arrangement of its electrons, which may be represented by a VB structure or a combination of such structures. (2) A chemical reaction is properly represented by a two-state model, so that the EWF of a transition state is given by a superposition of the EWFs of the reactant and product [7, 8]. For most molecules it is convenient to categorize the VB ground-state structures as covalent or ionic ones. A single transition state (of covalent nature) results if the covalent form dominates in both the reactant and product. In that case a second combination of the EWFs of the reactant and the product (an in-phase one) often leads to a third minimum on the ground-state potential surface, leading to a three-legged loop [9, 13]. If the contribution of the ionic term is of the same order as the covalent one, two transition states may arise, the ionic one being always the in-phase combination. In this case a 2-D domain (encircled by a two-legged loop) is defined by three anchors: two covalent ones (having different spin-pairing arrangement) and an ionic one. A fourth independent anchor will lead to a 3-D domain [12], which is beyond the scope of this article.

As an illustration of these principles, we may compare our results for the formaldehyde cation and for CPDHP with their parent molecule ethylene. The ionic forms of ethylene have minor importance in the ground state (but are important in some electronically excited states). Therefore, the EWFs of the cis and trans isomers are represented to a very good approximation by pure covalent structures (Fig. 8). Consequently there is only one transition state for this isomerization reaction, the covalent one. An ionic structure similar to that shown in Figure 4 can be drawn [as shown in Fig. 8(a)], but it is not a transition state on the ground-state potential surface, but actually lies on an excited state potential surface. This structure in which one of the carbon atoms is pyramidal can be stabilized by transferring a proton from one carbon atom to the other forming methyl carbene, which is a stable minimum on the ground-state potential surface [Fig. 8(b)]. Thus, the loop encircling the conical intersection (which has a pyramidal structure [30] as expected from the model) in this case is a three-legged one. The two-legged loop of the formaldehyde cation is possible because, as a result of the electronegativity difference between the nitrogen and carbon atoms, the polar VB form becomes much more stable and is found on the ground-state potential surface. Likewise, aromatization stabilizes the polar VB form of CPDHP with similar results.

Comparison with other methods

Several theoretical methods developed for the search of conical intersections do so by simulating the experimental procedure [2, 3, 5]: the system is elevated to an electronically excited state and the minimum energy path (MEP) to the ground state is sought by computing the gradient of the excited-state potential surface or the energy difference between the excited state and the ground state. This “top-down” approach is different from our “bottom-up” method. Whereas our method searches for the conical intersection nearest to the ground state, the top-down method does not necessarily consider electronically excited states which may be high lying in the Franck–Condon region, but may become S1 at other geometries.

Another frequently used method starts with 1-D curve crossing between states of different symmetries and looks for a coupling coordinate that maximizes the interaction between the two states [4]. Symmetry is often of cardinal importance in this case as it determines the character of the second coordinate. However, in a large molecule several modes have the desired symmetry; the specific coordinate is found by calculating the magnitude of the vibronic coupling for all modes and choosing...
the one with largest coupling coefficient. This method correlates directly with ours in the sense that the coupling coordinate turns out to be a component of the reaction coordinate defining the domain in which the conical intersection is found as shown in the example of the allyl radical–cycloproyl radical reaction (Fig. 7).

**Summary**

Reaction coordinates of elementary chemical reactions are shown to be natural coordinates for finding conical intersections connecting the ground-state potential surface and the first excited state. The complete ensemble of molecules composed of a given set of atoms can be partitioned into domains, each of which may contain one and only one conical intersection (or no one). Each domain is bounded by two or three reaction coordinates of elementary reactions. In this coordinate system, the conical intersection is the highest point on the ground-state potential surface within the domain. The search for conical intersections reduces to the search for all possible chemical reactions in the system. It is shown that the presence of a conical intersection is revealed by properties of the transition states of ground-state reactions that have an asymmetric component.

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