Molecular Photochemistry: A General Method for Localizing Conical Intersections Using the Phase-Change Rule

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Abstract: A photochemical reaction in which a conical intersection is involved is shown to lead to several different products. In particular, thermally allowed products are produced in many cases in addition to photochemically allowed ones. This is a consequence of the electronic wave-function phase-change rule [H. C. Longuet-Higgins, *Proc. R. Soc. London Ser. A.* **1975**, *344*, 147], which is a necessary condition for the existence of conical intersections. The rule is used to define the two coordinates along which the conical intersection is formed, and hence its approximate geometry. These two coordinates are defined by the use of the structures of three chemical species on the ground-state surface, termed anchors. Two of the anchors can be chosen as the reactant and the desired product; the third is another possible product. The phase-change rule requires that either one or all the transition states between the three anchors must be phase-inverting, for instance antiaromatic. When only one of the transition states is phase-inverting, a "thermally allowed" product is always involved. The well-known importance of antiaromatic transition states in photochemical pericyclic reactions is explained by their essential role in forming conical intersections. The model provides a rationalization for the properties of many of the recently calculated conical intersections. The phase-change rule provides a simple, chemically oriented method for both the prediction of the course and stereoselectivity of photochemical reactions. It can also be used to reject structures proposed for conical intersections by showing that the conditions necessary for its presence are not fulfilled.

Keywords: conical intersections · photochemistry · reaction mechanisms · rearrangements

Introduction

An ideal photochemical transformation would convert a given reactant (A) quantitatively to a desired product (B). It is well known that in practice, other products often appear. In this paper we show that, in many cases, a single product cannot be formed *in principle* whenever a conical intersection is involved in the reaction. Since all photochemical reactions begin and end on the ground-state potential surface of the system, they necessarily involve a nonradiative crossing from an excited state to the ground state. The crossing from the excited state to the ground state is considered to be efficient whenever the two surfaces touch, or nearly touch.[1, 2] As shown by Teller,[3] the touching of two electronic states is likely to occur, even if they belong to the same symmetry group, by a conical intersection. It has been recognized in the last few years that many conical intersections are possible in most polyatomic systems; this accounts for the high rate at which electronically excited states often decay nonradiatively. Indeed, very rapid excited-state depletion rates (of the order of 10^{13} s^{-1} or higher), have been deduced from the low fluorescence quantum yield measured or from direct ultra-fast measurements for many photo-reactive systems. Such high rates, commonly observed in polyatomic molecules, are believed to involve conical intersections. Recent advances in computational chemistry led to some very successful efforts in locating conical intersections, elucidating their structures, and accounting for the experimentally observed product distributions and stereochemical trends.[4–8] The role of conical intersections in photochemical reactions has been compared with that of transition states in thermal reactions.[4, 9] In spite of their apparent ubiquitous presence, and of the many successful computational efforts, no systematic way of enumerating and localizing the different possible conical intersections is yet available. In the present paper (restricted to singlet-state reactions) we propose a method that may be developed into achieve that goal. The two coordinates defining the conical intersections are shown to lead to a pair of products (B and C), and selection rules determining which pairs are allowed are derived.

Several models outlining qualitatively the conditions required for the presence of a photochemical reaction have

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been offered, all of which involve (sometimes implicitly) the nonradiative coupling of electronically excited states with the ground state. These include the Woodward–Hoffmann orbital symmetry rules,[10] Oosterhoff's valence-bond-based model,[11] the Evans–Dewar–Zimmerman rules,[12, 13–15] the two-electron two-orbital four-state model,[2, 16–18] state correlation models,[18] in which the role of biradicals or biradicaloids is emphasized, and the two diabatic states VB model of Bernardi and Robb,[19–21] which focussed on the conditions required to obtain a conical intersection. These models have been very useful in advancing the understanding of photochemical mechanisms, particularly for accounting for the observed product distribution and stereoselectivity. They have often succeeded to explain the high selectivity observed in some photochemical reactions.[22] However, many ambiguities remain, hampering the interpretation of ultra-fast and resonance Raman measurements,[23] and of quantum chemical calculations.[4, 24] The present approach extends the ideas incorporated in these models by considering the role of conical intersections and by dealing explicitly with two coordinates rather than a single one. As will be shown, the previous models concentrate on one of the two coordinates, and, therefore, provide a partial view of the properties of photochemical reactions (product distribution, stereochemical selectivity).

The dichotomy between thermal and photochemical reactions has been discussed in all models. The Woodward–Hoffmann rules discriminate between "thermally allowed" and "photochemically allowed" reactions, based on frontier orbital symmetry. However, thermally allowed products are known to be formed, often along with photochemically allowed ones, in many light-induced reactions. The four-state model presents what appears to be an "extraordinarily puzzling feature":[17] a biradical intermediate can be formed both from the electronically excited state of the reactant *and* from the ground state of the product. A crossing between different electronic states is evidently implied, and one-dimensional correlation diagrams[1, 18, 25] have been developed to account for the apparent contradiction. As pointed out by Teller,[3] conical intersections (i.e., two-dimensional surface crossings) are required in general and, as we shall see, the one-dimensional ones may be viewed as cuts through them.

Longuet-Higgins[26] has shown that a conical intersection necessarily arises within a region enclosed by a loop along which the electronic wave function changes sign (phase-change rule). The case of a nonlinear triatomic molecule has been analyzed by Herzberg and Longuet-Higgins,[26b] who stated the general phase rule (ref [26b], p. 78) although a proof was published only twelve years later.[26a, 26c] This was later shown by Berry[27] to be a special case of a phase change due to the partition of a quantum mechanical system into parts (the Born–Oppenheimer approximation in the present case). The change in sign in the *electronic* wave function evidently requires a compensating sign change in the *nuclear* wave function; this is known as the geometric phase effect.[28] This effect has been extensively discussed in relation to the dynamics of systems near conical intersections,[5–8, 28, 29] mostly for triatomic systems.

To our knowledge, the application of the phase-change rule for the photochemistry of larger polyatomic molecules was very limited. The 1975 paper seems to have had relatively little impact on organic molecular photochemistry, although the phase-change rule can be used to systemize the search for conical intersection. The example chosen by Longuet-Higgins in the paper involves not one, but three sign changes around the loop. This situation, which is interesting in its own right, appeared to be of little attraction to most practicing photochemists. The case in which the sign changes only once, which appears to be of equal importance, was not explicity considered. The purpose of the present paper is to show that the phase-change rule can be applied to predict the photochemical routes of reactions involving conical intersections in many systems of practical interest. We show that the rule, which leads to a simple recipe for locating conical intersections, can be applied to a variety of photochemical systems. A large number of different photochemical isomerizations and rearrangements can be rationalized using this approach, and the computational search for conical intersections can be greatly helped by eliminating irrelevant structures. Moreover, we shown that the appearance of "thermally allowed" products in some photochemical reactions is not a rare occurrence, but rather a necessary outcome of the involvement of conical intersections.

Results

Extension of the phase-change rule to large polyatomic systems: Conical intersections are defined as the intersection of two different potential-energy surfaces when plotted along two coordinates. It has been shown that while intersections of potential surfaces belonging to two electronic states of the same symmetry are rare in the case of diatomic molecules, they are quite common in polyatomic molecules.[3–8, 26–28] An alternative statement of Longuet-Higgins' phase-change rule is that whenever an electronic wave function changes phase upon a complete loop along a trajectory on the plane defined by these two coordinates, a conical intersection *must* be present inside that loop. We propose a simple, chemically oriented, method for determining the required two coordinates.

We limit the discussion to the experimentally important cases in which the lower surface is the ground state one. On this surface, all structures exchangeable by a thermal reaction can be viewed as being adiabatically connected by the same wave function. In the immediate neighborhood (but not at the exact location) of a conical intersection, the Born–Oppenheimer approximation holds, and the separation of nuclear and electronic wave functions is valid. We shall therefore assume that the electronic wave function is well defined and continuous throughout the region of interest, and also that its phase is continuous. The principle of orbital phase continuity in chemical reactions, discussed by Goddard,[30] is closely related to this work, which focuses on the phase of the *total* electronic wave function.

We need to construct a loop on the ground-state surface, such that the phase changes of the total electronic wave function between different points along the loop will be known. The smallest possible loop on a given surface traverses three points, forming a triangle. For the problem at hand, a natural choice for two of them is the reactant and desired product. *However, the phase-change rule requires an additional, third structure in order to locate a conical intersection.* This structure must be chosen in such a way, that the total electronic wave function will undergo a phase change upon traversing the complete loop. The fact that these structures are lying on the ground-state surface makes it easy to choose appropriate points, as it is known that for thermally allowed reactions the transition state is phase-preserving, while for thermally forbidden ones it is phase-inverting. A well-known example for the latter are antiaromatic transition states (see section on anchors and transition states below).

A graphic representation is given in Figure 1. Suppose a phase-inverting route is found from A to B, as shown by the line marked by I in Figure 1a. One can also find a route leading from A to B via C (namely, traversing the trajectory A→C→B). By the phase-change rule, this route must be phase-preserving for a conical intersection to be found inside the loop. This is possible only if the A→C and C→B transformations are both phase-preserving (P) or both phase-inverting (I).

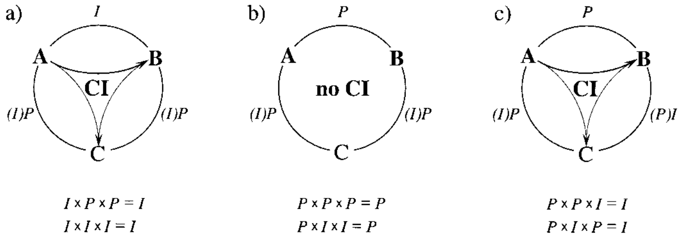
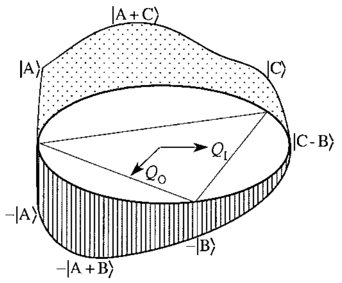


Figure 1. A schematic representation of the ground-state part of a conical intersection involved in the photochemical transformation of A to B. The condition for a conical intersection to lie within a loop is that the total electronic wave function will undergo phase inversion upon being transported around the complete loop. a) Here the transition state between A and B is assumed to be phase-inverting (I). A third structure, C, is required to complete the loop so that a conical intersection will be located inside it. The transition states between A and C, and between B and C, *must both be either phase-preserving (P) or phase-inverting.* b) Here the transition state between A and B is assumed to be phase-preserving. If the transition states between A and C, and between B and C, are both either phase-preserving or phase-inverting—no conical intersection inside the loop is possible. c) Here the transition state between A and B is assumed to be phase-preserving again. In order to have a conical intersection inside the ABC loop, of the two other transition states one must be phase-inverting and the other phase-preserving.

If the route from A to B is phase-preserving (Figure 1b), and the A→C→B trajectory is phase-preserving—no conical intersection can be found inside the loop. This provides a simple selection rule for discarding improper routes. The situation is changed if the A→C→B route is phase-inverting, as shown in Figure 1c. In the following, we use the term anchors for the three molecular structures that define the loop. Clearly, the presence of a conical intersection inside a given loop depends on the nature of the anchors, but the nature of the transition states connecting them is also important. In particular, two given anchors may be connected by both a phase-preserving and a phase-inverting loop. (An example is the conrotatory and disrotatory closure of butadiene to cyclobutene). These two routes cannot be incorporated in the same loop. Figure 1 shows that a phase-inverting arm is essential for the existence of a conical intersection inside the loop. Each of the three anchors is visited once in a given loop. As a corollary, the phase must change either once (i.e., between two anchors only) or thrice (i.e., between each pair of anchors). If the change occurs twice (i.e., between two pairs of points) or not at all, no conical intersection will be found.

The conical intersection coordinates: With the aid of the three anchors, we can define the two coordinates forming the conical intersection. Let the position vectors of the three molecular structures A, B, and C, be $\mathbf{r}_A$, $\mathbf{r}_B$, and $\mathbf{r}_C$, respectively, (each of which is determined by the coordinates of the atoms forming the molecules). The wave functions of these structures are denoted as $\pm|A\rangle$, $\pm|B\rangle$ and $\pm|C\rangle$, in which the plus and minus signs indicate a positive or negative phase, respectively, of the total electronic wave function. The adiabatic transformation of one structure to another can take place either with or without a phase change. As an example, let the phase change between B and C, and remain put between A and B and between A and C (Scheme 1). By its assumed continuity, the wave function $|B,C\rangle$ anywhere between B and C may be written as the out-of-phase combination [Eq. (1)], that is, it is parametrically dependent



Scheme 1. A schematic representation of a closed loop trajectory in which a single phase change takes place. The total electronic wave function has a positive phase (shown dotted) at the beginning of the trajectory ($|A\rangle$), at the transition state $|A+C\rangle$ and at $|C\rangle$. It undergoes a phase inversion at $|C{-}B\rangle$, and has a negative phase (shown hashed) at $|B\rangle$ and $|B+A\rangle$, reaching $|A\rangle$ with a negative phase. The coordinates Q_I and Q_O are defined in Equations (3) and (4): Q_I connects A with C near $|C{-}B\rangle$ (both with positive phase) and Q_O connects C (positive phase) with B (negative phase).

$$|B,C\rangle = b(R)\,|B(R)\rangle - c(R)\,|C(R)\rangle \tag{1}$$

$$|A,B\rangle = a(R)\,|A(R)\rangle + b'(R)\,|B(R)\rangle \tag{2a}$$

$$|A,C\rangle = a(R)\,|A(R)\rangle + c'(R)\,|C(R)\rangle \tag{2b}$$

$$Q_I = 2r_A - r_B - r_C \tag{3}$$

$$Q_O = r_B - r_C \tag{4}$$

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on the nuclear coordinates $R = \{r_A, r_B, r_C\}$. This form ensures the phase change. The structure at which the node is located will be denoted by B–C, and the associated wave function is $|\text{B–C}\rangle$. In a similar fashion, the wave function $|\text{A,B}\rangle$ anywhere between A and B, may be written as the in-phase combinations in Equations (2a) and (2b). For this system, a convenient choice of two coordinates for describing motion on this surface is as follows. The first is the phase-preserving coordinate Q_I (for in-phase), connecting A with B–C, is defined by Equation (3), and the other is Q_O (for out-of-phase), the coordinate connecting B with C, which is a phase-inverting mode [Eq. (4)].

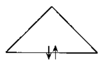
Anchors and transition states in the loops

Properties of anchors: In view of their central role in the model, the nature of the anchors needs to be clarified. A conical intersection is defined by two independent coordinates; These are often chosen, for a given molecule, from among the normal modes, or some simple combination of them. Since our prime interest is in chemical transformations, a more natural choice would be the reaction coordinate connecting the reactant and the product of interest. Although the mathematical expression for such a coordinate in terms of, say, the coordinates of the individual atoms may be complex, such a coordinate necessarily exists for any pair of molecules connected by an elementary reaction. We add the requirement that both will lie on the ground-state surface. The reaction coordinate is defined in the usual manner used in transition-state theory.[31] This determines two anchors. The third anchor is also chosen from among local minima on the ground-state potential, provided an elementary reaction connects it to the other two. The only restriction we impose initially is that the anchor will have a well-defined multiplicity, and for now we restrict the discussion to singlet states. In all cases, the number of electrons changing their spin-coupling scheme in a chemical reaction is limited, and therefore so is the number of spin-pairing possibilities. Each spin-paired structure that lies at a local minimum can serve a an anchor. The transition states arise from a resonance-stabilized combination of the initial and final structures, as suggested by transition state theory.

Some comments are in order:

1) The wave functions of the different spin-paired systems are not necessarily independent. A simple example is the H_4 system: there are three spin pairing possibilities—$H_1H_2 + H_3H_4$, $H_1H_3 + H_2H_4$, and $H_1H_4 + H_2H_3$. Writing out the VB wave function shows that third may be expressed as a linear combination of the first two. *Nevertheless, this is obviously a separate chemical entity, that can be clearly distinguished from the other two.* (This is readily verified by considering, a hypothetical system containing four isotopic H atoms (H, D, T and U). The anchors will be: HD + TU, HT + DU, and HU + DT).
2) While in thermal reactions phase-preserving reaction coordinates are usually dominant, both these and the phase-inverting ones must be considered for conical intersections. In fact, at least one phase-inverting reaction coordinate *must* be included. The other two must be both phase-preserving or phase-inverting. This will lead, in general, to two distinct conical intersections: For instance, in a pericyclic reaction, two different anchor pairs must be assigned for the suprafacial and antarafacial reaction modes.
3) Since we are currently concerned with singlet states only, in terms of spin pairing, a biradical is equivalent to the same molecule in which a bond is formed between the atoms carrying the two electrons. Thus, structure Ia is equivalent to structure Ib.


Ia

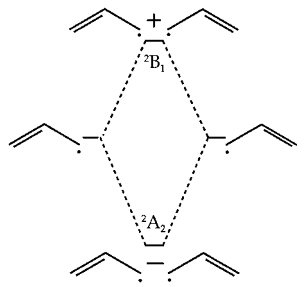

Ib

4) Conformational isomers have the same spin-pairing structure. Thus, a single anchor is assigned to all of them. Since in general all may be formed in the reaction (unless spatial restrictions apply), the proper anchor in this case is the transition state connecting them.

One can, in principle, enumerate all possible structures that may serve as anchors. After doing that, the phase-change rule is used to eliminate the ones that do not lead to a phase change of the total electronic wave function upon a complete loop containing the initial reactant, the product, and the third structure. All remaining structures are legitimate anchors, and may appear as secondary products in a photochemical reaction involving the anchor lying inside the loop.

Phase changes in the course of chemical reactions: In any elementary reaction, the transition state may be constructed as a combination of the wave functions of the reactant and product.[32] There are always two possible combinations: an in-phase one and an out-of-phase one, the latter involving necessarily a phase change. These two combinations lie on two different potential surfaces. In many ground-state reactions the transition state preserves the phase—these are usually the thermally allowed reactions. However, it has been shown that for some reactions the phase must change on the ground-state potential. These reactions are of particular interest in photochemistry, since by the phase-change rule they may be part of a loop that surrounds a conical intersection. Three well known examples are:

1) As shown by Goddard and co-workers,[30, 33] the reaction $H_2 + H \rightarrow H + H_2$ involves a phase change. In a similar way, the allyl radical can be expressed as a resonance hybrid of two VB structures.[33] They can be combined into a stabilized form, which is the out-of-phase combination, and an in-phase antiresonance form, which is destabilized and forms an electronically excited state[33–36] (see Scheme 2). This three-electron system is analogous to the H_3 system, or, as far as phase relations are concerned, to any system in which the transition state involves three electrons.
2) Symmetric antiaromatic structures, that is, cyclic Hückel hydrocarbons with an even number of electron pairs, are ground-state transition states between more distorted structures. They are phase-inverting, being formed by an out-of-phase combination of two VB structures as shown



Scheme 2. A scheme showing the construction of the in-phase and out-of-phase combinations of the two canonical allyl radical structures. The latter is of $^2A_2$ symmetry and is the ground state.

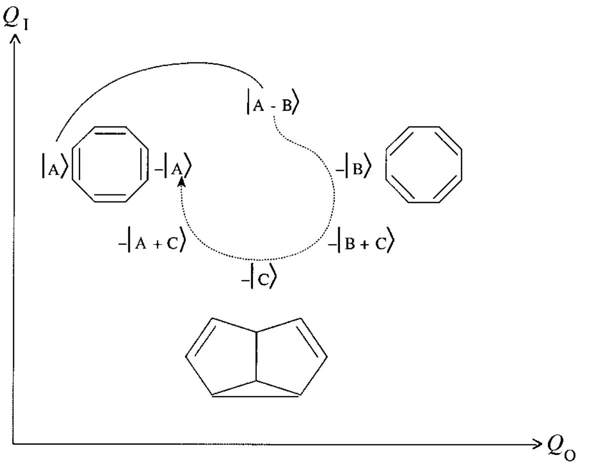
specifically for cyclobutadiene,[37, 38] and planar symmetric cyclooctatetraene,[39] and generally in ref. [40]. In a similar way, Möbius cyclic hydrocarbons with an odd number of electron pairs are phase-inverting.

3) The transition state in the *cis–trans* isomerization of olefins is a perpendicular ethylene structure. As shown by Mulder,[41] this is a four-electron system, in which the out-of-phase combination is the ground state, completely analogous to cyclobutadiene. Therefore, any *cis–trans* isomerization transition state is phase-inverting.

The construction of the potential surface along the reaction coordinate by considering the resonance stabilized hybrids is in the spirit of the VB avoided-crossing model of Shaik et al.[42] The fact that this model points out explicitly when an adiabatic motion on the ground-state surface requires an out-of-phase combination, makes it useful in choosing anchors.

Single phase-change loops: The single phase-change case, shown in Scheme 1, was not discussed by Longuet-Higgins[26a] (this situation is impossible for the three atom case, as long as only s electrons are involved). It turns out that in larger molecular systems, this case is quite common. The electronic properties of such systems must be different from those of the three phase-change case. In the latter, all the transition states from one structure to another necessarily involve the same number of participating electrons. However, if motion along one reaction coordinate leads to a phase change, and motion along another coordinate does not, a different electronic structure is called for. For instance, in a pericyclic reaction, a phase-preserving transition cannot be realized with an even parity Hückel system ($4n$ electrons, or an even number of electron pairs[40]); an odd parity system ($4n$+2 electrons, or an odd number of electron pairs) is required. That means that in these systems, if the phase-inverting $A \rightarrow B$ reaction path involves, say, q electron pairs, one pair must be either added or "frozen" in the $B \rightarrow C$ and the $C \rightarrow A$ paths for a single phase change to take place.

An example is the cyclooctatetraene (COT) → semibullvalene (SB) photo-rearrangement[43] (Scheme 3). Here the three anchors are two Kekulé structures of planar COT, and one SB structure. A change of phase occurs on the transition between the two COT Kekulé structures through an out-of-phase combination of two even parity (8 electrons) structures; this is an even parity Hückel system. The transition from either one to semibullvalene is phase-preserving, since

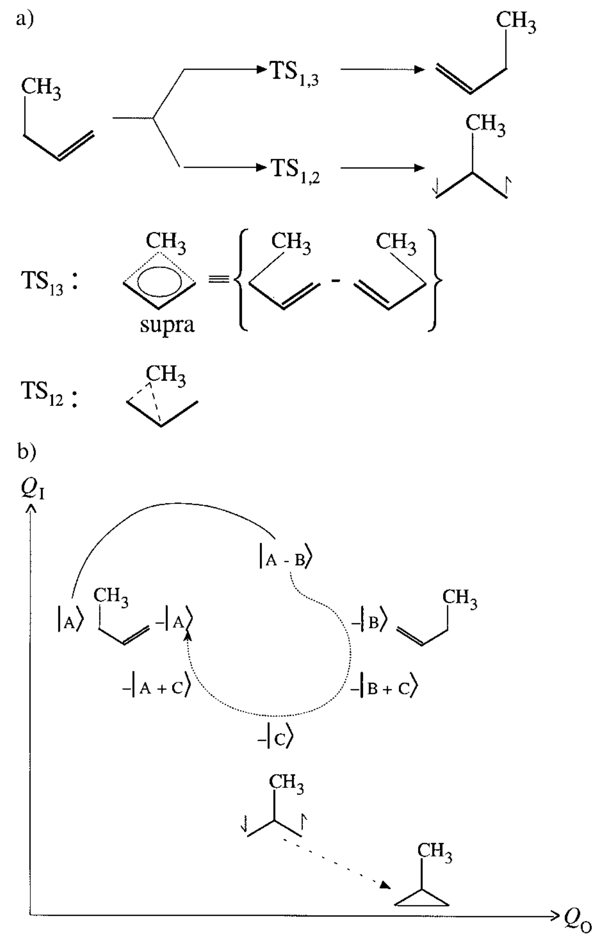


Scheme 3. The COT/semibullvalene rearrangement: A and B are two D_{4h} planar bond-alternating structures of cyclooctatetraene and C is a semibullvalene molecule. The coordinates Q_O and Q_I are defined analogously to those in Scheme 1. The transition between the two cyclooctatetraene structures is via an antiaromatic structure and, therefore, phase-inverting. The transition from either of them to the semibullvalene structures is phase-preserving. The positive-phase part ($|A\rangle \rightarrow |A{-}B\rangle$) of the loop is shown as a solid line, and the negative phase part ($|A{-}B\rangle$ via $-|B\rangle$ and $-|C\rangle$ to $-|A\rangle$) as a dotted line. A conical intersection must therefore be found within the triangle formed by the three structures.

only six electrons are involved in the transition state (an odd-parity Hückel system)—one pair is "frozen" in this reaction.

A more familiar example of pericyclic reactions is the group of photochemical sigmatropic rearrangements, which are very common in olefin photochemistry.[44, 45] We illustrate this group of reactions by discussing the rearrangement of but-1-ene (I), which has been studied extensively both experimentally[46] and theoretically,[47] keeping in mind that the results are of general nature. Orbital-symmetry rules[10] predict that the major photochemical pathway be a [1,3] suprafacial sigmatropic shift that preserves the molecular stereochemistry. It is found experimentally that a [1,3] shift does indeed take place, but in addition, a cyclopropane derivative is obtained (presumably due to a [1,2] shift[46]), and that the [1,3] shift reaction is indeed stereospecific—the methyl group migrates by a *supra* path, with retention of the configuration. No evidence for an *antara* path products was reported.

The formation of the cyclopropane product, though not readily explained by the orbital-symmetry rules, is expected based on the present model, along with the [1,3] shift reaction, if a single phase change is assumed. Scheme 4 shows the model used: the reactant and the [1,3] product are two of the anchors (A and B, respectively), and the third (C) is a singlet biradical, which can easily close to give the cyclopropane derivative (along a different coordinate). Scheme 4, showing the relevant structures and pathways, has the same topology as Scheme 1. The *supra*-type transition between A and B proceeds via a four-electron antiaromatic transition state (TS_{13}), which is an out-of-phase combination of the two bond-alternating structures of the reactant and product.[40, 37] This phase-inverting route is in agreement with the Woodward–Hoffmann and the Evans–Dewar–Zimmerman rules. The transition to the biradical C from either A or B is a phase-preserving process, since two of the electrons do not

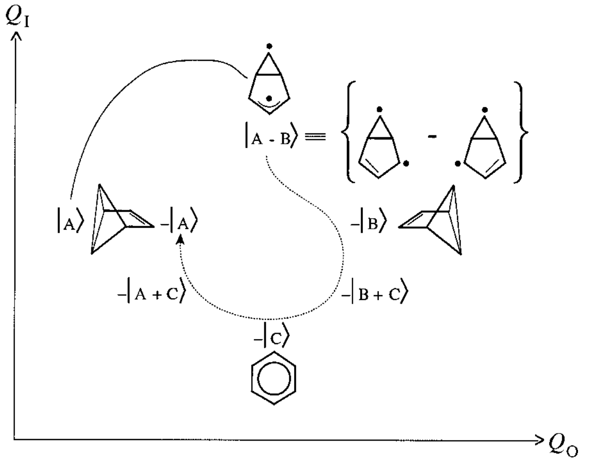


Scheme 4. The photochemical sigmatropic shift reaction of but-1-ene. a) The 1,3- and 1,2-shift products and their assumed transition states. The wave function representing TS$_{13}$ is the *out-of-phase* combination of the two VB structures shown. TS$_{12}$ is represented by a single VB structure. b) The three structures used to locate the conical intersection. A and B are two but-1-ene isomers, the transition state between them (denoted as $|A{-}B\rangle$) is the phase-inverting structure TS$_{13}$. Structure C is a singlet biradical, in which the two electrons are localized. The transition states between it and either A or B are the phase-preserving structures $|A+C\rangle$ and $|B+C\rangle$, provided the methyl group maintains its configuration (phase inversion would result if the configuration were inverted, as can be seen if the group is chiral). A complete loop starting at $|A\rangle$ therefore leads to $-|A\rangle$. The solid and dotted lines are the positive and negative parts of the loop, respectively. The coordinates Q_O and Q_I are defined analogously to those in Scheme 1. [C is calculated to be a local minimum, but under usual experimental conditions will close to the shown cyclopropane derivative, along a third coordinate (dashed arrow)].

participate. Thus, a conical intersection is necessarily found somewhere inside the loop shown in Scheme 4. On the other hand, the *antara*-type process requires that A will transform to B through the in-phase combination of the reactant and product.[11, 40] In this case the phase would be preserved upon a complete loop, *and no conical intersection is possible for this case.* The only way to equalize the energies of the ground and excited states is along a trajectory that increases the separation between atoms in the molecule. Indeed, the two are computed to meet only at infinite interatomic distances, that is, upon dissociation.[47]

As stated in the previous section, a conical intersection may be expected for photochemical reactions involving *cis–trans* isomerization around a double bond. The two isomers are a natural choice for two of the anchors, the third structure will determine whether a single or triple phase change will occur. For the parent ethylene molecule, an example of a phase-preserving structure is the CH_3CH carbene formed by the transfer of one hydrogen atom from one of the carbons to the other. In this case, the *cis–trans* isomerization of ethylene and the H atom transfer will occur from the same conical intersection (funnel) as previously suggested.[1] Another possibility is pyramidalization (ref. [1], p. 363),[48] which leads to a triple phase inversion. Such a conical intersection cannot lead to H atom transfer. The existence of these conical intersections explains the rapid *cis–trans* isomerization of small olefins upon direct photolysis, as well as the appearance of other reaction products. Analysis of the photochemistry of larger polyenes is a bit more complex owing to the existence of several contributing VB structures, and is discussed elsewhere.[60]

The photochemical valence isomerization of benzene to form benzvalene (ref. [25], p. 357) is an example in which allyl radical structures play a central role. The system is shown in Scheme 5. In order to use the topology of the previous examples, we show the two benzvalene isomers as anchors A and B, and benzene as the third. The benzvalene→benzene transformation is phase-preserving. Since the two benzvalene structures are connected via the shown allylic prefulvene structure, which involves a phase change, the phase-change rule predicts the existence of a conical intersection near the region enclosed by these anchors. In a photochemical experiment, irradiation of benzene leads to S_1, which connects to the ground-state surface through the conical intersection. The much more stable benzene is expected to be recovered preferentially, but the prefulvene structure which transforms



Scheme 5. The valence isomerization of benzene to benzvalene. On the ground-state potential surface, benzene is connected through phase-preserving transitions to two isomers of benzvalene, A and B, which are connected among themselves via a biradical structure A–B that contains an allyl-type transition state. This structure is an out-of-phase combination of two resonance structures (see inset), making the A→B transition a phase-inverting one. The solid and dotted lines are the positive and negative parts of the loop, respectively. The coordinates Q_O and Q_I are defined analogously to those in Scheme 1.

to benzvalene is also formed. Another possible route from the prefulvene, along a different coordinate, will lead to fulvene after hydrogen-atom transfer from one of the carbon atoms to another. This scenario was obtained computationally by Palmer et al.[49]

Loops involving three phase changes: The $H+H_2$ problem, discussed by Herzberg and Longuet-Higgins[26b] is an example of this case. There are three equivalent stable structures in this system as shown in Figure 2a. They are connected via linear transition-state structures, each of which is phase-inverting. The three anchors are assigned as $A=H_1+H_2H_3$, $B=H_2+H_1H_3$, and $C=H_3+H_1H_2$. As seen from Figure 2b, a complete loop starting at, for example, $|A\rangle$ with a positive phase, changes phase and reaches structure A with a negative phase (cf. Figure 1 in ref. [26b]). The coordinates shown, chosen so as to simplify the location of the conical intersection, were defined in Equations (3) and (4). They are of course equivalent to those used in previous treatments of this system (see, for example, ref. [32]), and can be constructed from them by linear combinations. A schematic illustration of the phase changes of the total electronic wave function around the loop is shown in Figure 2c. The A, B, and C anchors are located at the vertices of the triangle shown. The phase is taken as positive above the plane of the triangle (dotted area), and as negative below it (dashed area). By symmetry, in this case the conical intersection is located at the intersection point of the heights of the isosceles triangle defined by the loci of the anchors A, B, and C, and has a triangular structure (Figure 2a).

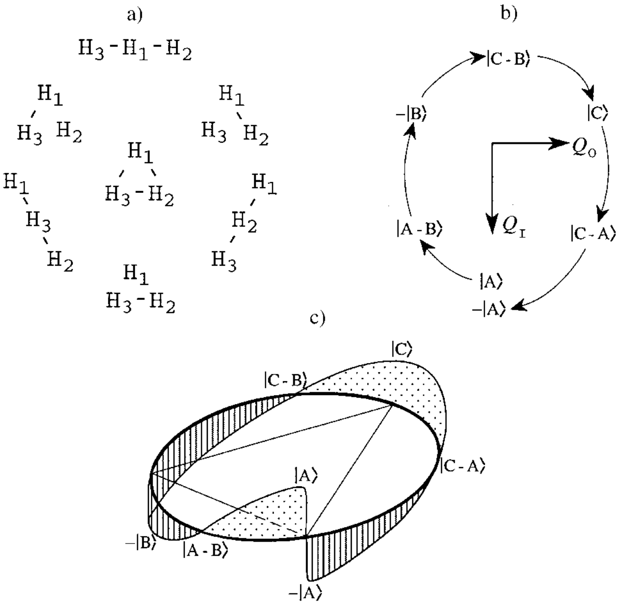
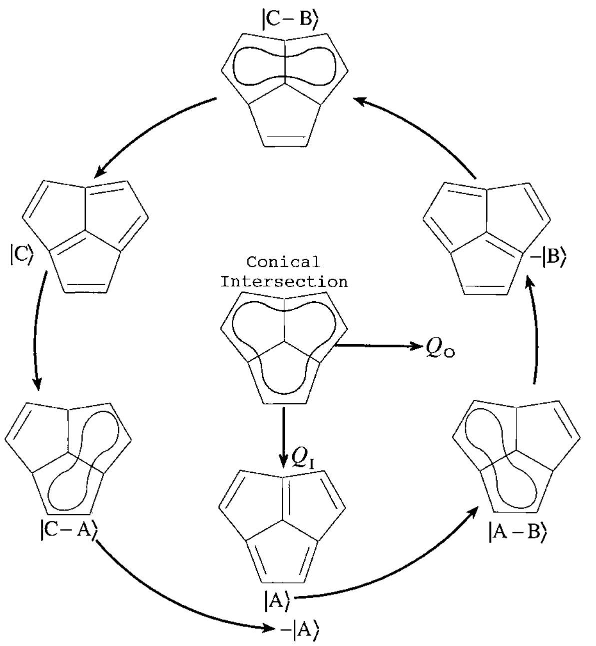


Figure 2. The symmetric three atom system, represented by the $H_2+H\rightarrow H+H_2$ reaction. a) The three equivalent structures $A=H_1+H_2H_3$, $B=H_2+H_1H_3$ and $C=H_3+H_1H_2$, connected via linear HHH phase-changing structures. The symmetric triangular structure in the center is that of the conical intersection. b) The definition of the two coordinates that determine the conical intersection: $Q_I(=2r_A-(r_B+r_C))$ is the in-phase (phase-preserving) coordinate and $Q_O(=r_A-r_B)$ is the out-of-phase (phase-inverting) one. c) A schematic representation of the phase changes taking place on transporting the system from an initial structure A (with a positive phase) through the loop shown in a). Dotted regions represent a positive phase, negative phase ones are hashed.

If we relax the requirement that the three atoms be identical, we still have the same topological structure with three phase changes, except that the location of the conical intersection is now not at the geometrical center of the triangle.[26b]

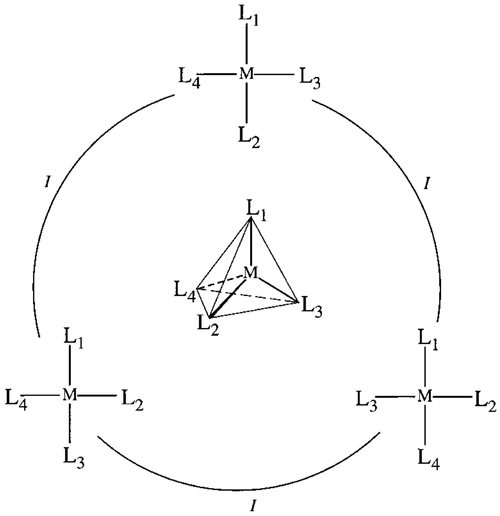
The threefold phase change case is not limited to atomic systems only. A molecular example is the isomerization of the antiaromatic molecule acepentalene (Scheme 6). In this molecule (whose isolation is still to be realized), the bond lengths alternate, as shown by quantum chemical calculations.[50] The anchors are chosen to be the three possible isomers shown in Scheme 6, the transition from one to the other being via the antiaromatic structures A–B, B–C, and C–A, in which the pentalene part is symmetric, (i.e., has equal bond lengths). It has been shown that the symmetric pentalene ground-state structure is formed by the out-of-phase combination of the two Kekulé structures.[40] Thus, the electronic wave function undergoes a phase change. A calculation shows that the conical intersection has a C_{3v} structure, which lies at the geometrical center of the three isomers.[51] Three phase-change loops are encountered in many other systems, for instance in the photochemistry of polyenes, as discussed in a recent publication.[60]



Scheme 6. A schematic representation of the of the acepentalene isomerization. A, B, and C are the three bond-alternating isomers. A closed loop that changes phase three times is shown, leading from $|A\rangle$ to $-|A\rangle$. The structures A–B, C–B and C–A are antiaromatic transition states. The conical intersection lies in the center of the triangle formed by r_A, r_B, and r_C. The coordinates Q_I and Q_O are defined in Equations (3) and (4).

The role of conical intersections in photochemistry is not limited to organic systems only. The *cis–trans* isomerization of a planar square of a d^8 transition metal complex (for instance of Pt^{2+}) is known to be photochemically allowed and thermally forbidden.[52] It was found experimentally[53] to be an intramolecular process, namely, to proceed without any bond-breaking step. Calculations show that the ground state and the excited state touch along the reaction coordinate (see Figure 12 in ref. [54]). Although conical intersections were not mentioned in these papers, the present model appears to apply to these systems.

Consider a metal M bound to four ligands, L_1–L_4, lying at the corners of a square around the metal. Three anchors can be written for this system, as shown in Scheme 7. They consist of all three possible geometrical permutations of pairs of ligands lying across the metal ion. Transition states between each pair are phase-inverting (thermally forbidden, ref. [52]). The conical intersection in this case is a tetrahedron, shown schematically in the center of the scheme. In fact, there are two different (though energetically equivalent) conical intersections—the tetrahedral structure can exist in two enantiomeric forms. A possible way to distinguish between them is by the use of a chiral molecule as one of the ligands, so that the two conical intersections become diastereomers rather than enantiomers.



Scheme 7. A proposed scheme for the intramolecular ligand-exchange reaction of a planar complex of a metal ion M with four different ligands. The same system applies to the *cis–trans* photo-isomerization of an MA_2B_2 complex. The transition states between the three possible anchors shown are phase-inverting, making this a three phase-change system. Irradiation of any one of the anchors will lead to an excited state, and the decay back to the ground state through the conical intersection will result in intramolecular isomerization.

These conical intersections allow the photo-isomerization to proceed without breaking a single bond. In the ground state, a bond-breaking–bond-recombination mechanism is often energetically more favorable. An experimental example for such a system is provided by the photo-isomerization of $[Pt(gly)_2Cl_2]$.[53]

Discussion

The present work stresses the central role of the phase of the total electronic wave function in determining the location of conical intersection. Following the theorem of Longuet-Higgins, the importance of three anchor structures on the ground-state potential surface as the key ones that define the conical intersection region. These structures, in turn, are used to define the two coordinates, one phase-preserving and one phase-inverting as the ones leading to the conical intersection. A natural choice of two of the anchor structures is the reactant and the product. *However, no discussion of a conical intersection, and hence a photochemical reaction, is complete without considering a third structure.* The third structure can be another possible product, or any other stationary point on the ground-state surface. It can be found systematically, though tediously, by considering all possible chemical structures. An intuitive guess is a faster way, and the phase-change test can be readily used to discard structures not leading to a conical intersection. *In any case, a photochemical reaction involving conical intersections invariably leads to at least two reaction products.* The second product can be an isomer that is not readily distinguishable from the first product unless special tagging methods, such as isotopic substitution, are used.

Attention was focussed on the ground-state part of the conical intersection. The important work of Bernardi, Robb, and their associates[4, 19–21, 47] has revealed that when several conical intersections are found, the trajectory on the upper state will determine the outcome of the reaction—the system will develop along the steepest descent. The present model complements their work by showing that a systematic search for possible conical intersections in the region of chemical interest is possible. This should be the first step in the analysis. Regardless of the nature of the upper state, *the presence or absence of a conical intersection can be determined by the properties of the lower part only.* This can be done simply by checking whether the phase of the total electronic wave function inverts or not upon being transported around the assumed conical intersection in a complete loop.

The required phase change between at least two anchors in the loop implies the consideration of ground-state transition states that are often *not* encountered in thermal (ground state) reactions. These must be phase-inverting ones such as resonance stabilized out-of-phase combinations of two VB structures. Examples are any allylic or antiaromatic transition states,[33–35] perpendicular ethylenes,[41] and Möbius type aromatic transition states.

An important new feature is the introduction of single phase-change loops. In a three phase-change systems, both products are the standard photochemically allowed ones. *In contrast, in a single phase change system, one of the products is necessarily a ground state allowed product.* Therefore, the sharp dichotomy occasionally made between photochemically allowed and thermally allowed reactions holds strictly only for a restricted class of light-induced reactions. The single phase-change systems, which appear to be quite common in organic chemistry, always lead also to a thermally allowed product. The branching ratio between the two possible products will be determined by the details of the potential surfaces—one of them may have a small yield as a result of kinetic or dynamic constraints. An important result of the model is that certain product pairs are predicted to be simultaneously formed. A more detailed discussion of the expected ones in polyene photochemistry was recently published.[60]

As emphasized in the Introduction, this treatment applies to photochemical processes involving a conical intersection, as is expected to be the case when no minimum is found on the excited-state potential. If a local minimum is found, as revealed for instance by fluorescence, the transition from the excited state to the ground state may be slower, and involve different selection rules.

Comparison with other models: Several workers pointed out the importance of the sign change of molecular orbitals involved in pericyclic photochemical reactions, and correctly analyzed the equivalence of Möbius aromatic structures and Hückel antiaromatic ones in cyclic transition states.[11, 13, 14, 22, 55] Oosterhoff and co-workers used VB language, while Heilbronner and Zimmerman have formulated the difference between Hückel and Möbius structures by considering molecular orbitals: Hückel structures have zero or an even number of sign inversions, whereas Möbius ones have an odd number. The present model is an extension of these views; conical intersections were not specifically mentioned, and the phase-change rule, which was clearly stated by Longuet-Higgins a bit later, was not presented as the physical basis for the central role of these structures in photochemical reactions. The calculations presented by Lugt and Oosterhoff[11b] show the presence of a structure with an energy maximum in the ground-state potential and a minimum in the excited-state one (erroneously labeled as having the same symmetry). This situation can now be understood as a cut in the double cone that avoids the apex (Figure 3). Had they considered the other coordinate, the real conical intersection would probably have been found by them. Oosterhoff's treatment may therefore be taken as a special case of the more general one discussed here. It is noted that the closely related case of the noncyclic allylic structures, which are equivalent to the above-mentioned cyclic ones according to the phase-change rule, appears to have been overlooked in their work.

Phase changes are central for the derivation the Dewar–Evans–Zimmerman rules. They were used to predict the stereochemical characteristics of thermal and photochemical sigmatropic [*i,j*] shifts. A succinct summary is given in Table 7.4 of ref. [1]. They are now seen to be a special case of a more general scenario.

Zimmerman developed a model[22] that regards photochemical reactions as a succession of elementary steps in which intermediates such as biradicals are present, analogous to thermal reaction mechanisms. In the present approach, the role of an intermediate is replaced by that of a conical intersection, which in principle cannot be isolated, and can lead to two (or more) final products. It is an experimental fact, that the assumed intermediates were notoriously difficult to observe (see e.g., the discussion of the Zimmerman di-π-methane rearrangement in ref. [25], p. 246). Likewise, such intermediates were not found in an extensive ab initio calculation;[56] instead, a conical intersection was revealed.

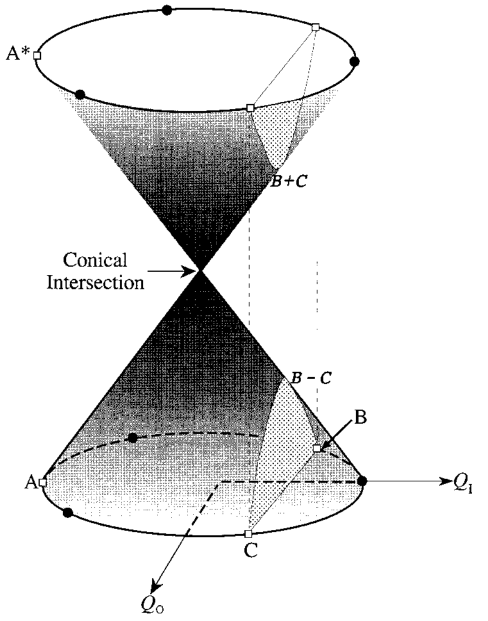


Figure 3. A schematic representation of the potential surface near a conical intersection, plotted as a function of the two coordinates Q_I and Q_O [Eqs. (3) and (4)]. In the ground state, B and C are connected by a phase-inverting transition state (– B + C), while A is connected to both by phase-preserving transition states—this is a single-phase-change system. The relation to the Oosterhoff model is shown by the cut across the two cones that does not contain the apex. It forms a one-dimensional energy-level diagram, in which a given structure will have a maximum in the ground state and a minimum in the excited state. Compare with Figure 1 in ref. [11a]. A Salem correlation diagram is obtained by making the cut pass through the apex, and contain two of the anchors.

The correlation diagrams suggested by Salem,[18, 57] may also be viewed as a two-dimensional cut through the double cone (Figure 3), the intersection point being the apex. In these calculations, the structures of the excited states are explicitly considered. Being one-dimensional plots, they do not carry the complete information provided by the conical intersection. Nonetheless, by a proper choice of the symmetry element, using chemical intuition, this approach quite often leads to the correct result. The complete two-dimensional treatment provides a more systematic way for choosing the necessary coordinates.

The Woodward–Hoffmann model makes the simplification of considering frontier orbitals only. It is attractively simple, and is indeed very helpful in analyzing thermal reactions. Phase-inverting reaction paths are usually avoided in the ground state in thermal reactions, since lower barriers are provided by alternative phase-preserving ones. However, when coming down a conical intersection, the phase-inverting process may dominate. We note that the strict dichotomy predicted by the Woodward–Hoffmann rules is actually expected within the phase-change rule model, *if the phase is inverted upon transition between any pair of anchors.* This condition, however, appears to hold only for a limited group of reactions. In cases in which the phase changes only once, both the thermally allowed and the photochemically allowed products are expected. Their relative yields are determined by dynamic constraints.

The renewed interest in the role of conical intersections in organic photochemistry is owed largely to the extensive work of Olivucci, Bernardi, Robb, and their co-workers[4, 19–21, 24, 47] over the last ten years or so. They showed that these structures are involved in many pericyclic reactions and in nonradiative transitions,[58] and that the experimentally observed stereochemistry of these reactions is predicted by the calculations. In their work, a simple 2×2 VB-based model that includes two molecular structures, the reactant and the product, was introduced. This basically sound model is in the spirit of the Oosterhoff treatment. The condition for a conical intersection was expressed mathematically in terms of the exchange integrals of these structures; a requirement is that the energy difference between the upper and lower states is zero. This is a necessary condition, but is not sufficient, and so cannot by itself determine the location of a conical intersection. Since only one coordinate connects two structures, no a priory guide-lines are given for the location of a conical intersection that requires two coordinates. An example that was noted above is the coordinate found leading to the dissociation of but-1-ene.[47] Our work complements these studies, and should help to systemize the search for these structures. The use of the third anchor structure suggested in this work, and the check for phase inversion, provide the extra necessary condition missing in the 2×2 model. It is hoped that the "chemically inspired" coordinates proposed in the model will help to guide the computational search for all conical intersections.

The two electron (3×3 full configuration interaction) model[1, 2, 16] focuses attention on four states formed by different occupation of two relevant atomic orbitals. The breaking of the sigma bond in H_2 upon bond stretching and of the π bond in ethylene upon twisting the angle between the two CH_2 moieties are treated in this model on a similar basis. According to the present model, they are fundamentally different: the H–H stretching coordinate is symmetric, and cannot lead to phase change. The complete treatment of twisted ethylene, in contrast, is that of a four electron system,[33, 37, 41] and a phase-inverting coordinate connects the two planar structures via the perpendicular one. The latter can be considered as a delocalized biradical, in which the biradical nature cannot be associated with a given atom pair. In contrast, bond-stretching transition states, lead to localized biradicals and are not necessarily involved in a conical intersection.

Nonetheless, the phase-change rule model may be considered as an extension of this model if a third structure is chosen such that the transition states leading to it will have a different parity (of participating electron pairs), for example, by "freezing" one pair. This can be done, for instance, by the formation of a biradical in which only two electrons (rather than four) are not fixed in sigma bonds, as in the but-1-ene rearrangement. Another possibility is the formation of an ion pair by grouping two electrons together on a single atom. This pathway is a key feature in the 3×3 CI description of the two electron two orbital model.[2, 59]

In ref. [4] it was noted that previous models were limited by the fact that the reaction coordinates are *assumed*. A systematic search for the proper ones was called for. The present approach provides a means for guiding systematically the computational search of minimum-energy paths and possible reaction routes towards the relevant parts of the potential energy surface.

Conclusion

The course of many photochemical reactions is determined by conical intersections. The phase-change rule can be used to locate conical intersections and to predict the product distribution and stereochemical properties of many polyatomic systems. It is shown that three molecular structures are essential to determine the location of a conical intersection, and that if a single phase change takes place, the electronic excitation will result in general in *two* products, of which one is photochemically allowed, the other thermally allowed. On the other hand, the dichotomy between thermally allowed and photochemically allowed reactions is expected to hold for systems in which the conical intersection is due to a three phase-change loop.

A recipe proposed for identifying the regions in which conical intersections are to be found (in general more than one conical intersection can be found for any given system) requires consideration of ground state surface properties only. It consists of the following two steps:

1) Choose three ground state structures (anchors), two of which are the reactant and the product. Consider the adiabatic trajectory connecting the reactant with the desired product. If it involves a phase change of the total electronic wave function, the third anchor must be such that its conversion to both of them either preserves or inverts the phase. If the reactant → product trajectory in the ground state preserves the phase, the only way to obtain a conical intersection is by finding a third anchor connected to one of the two by a phase-preserving path, and to other by a phase-inverting one.
2) Determine the two coordinates defined by the three anchors as outlined in Equations (3) and (4). The conical intersection is to be found along these two coordinates, in the region bordered by the three anchors.

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