Conical intersections in molecular photochemistry – the role of phase change

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Abstract

Conical intersections are now known to be involved in a large variety of photochemical transformations. In this paper, we present a simple method for determining the existence of a conical intersection for a given chemical reaction. The method, based on the phase change theorem, is easy to apply, does not require quantum chemical calculations, and uses ground state surface properties only. The method can be used to analyze all kinds of photochemical reactions, including isomerizations, rearrangements and dissociations. It is shown that if the system passes through a conical intersection on its return to the ground state surface, at least two different products are necessarily formed (in addition, the system may return to the reactant by internal conversion). © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

A photochemical reaction is often the most efficient means for converting an available molecule A to a desired product B. Products that are difficult to prepare by thermal reactions (‘thermally forbidden reactions’) may be easily obtained photochemically [1]. In this paper, we consider photoreactions that yield ground state products – such reactions are of great practical interest, for instance in preparative organic chemistry. In this class of reactions, a non-radiative transition between the excited and ground state potential surfaces necessarily takes place. This non-radiative transition, which is an essential part of the photochemical process, is the subject of this work. The molecular configuration through which the transition from the upper state to the ground state takes place has been termed a funnel [1–4]. ¹ One of the most efficient funnels is a conical intersection, a location at which the excited state is degenerate with the ground state [5–12]. In this paper, we propose that if the return to the ground state takes place through a conical intersection funnel, the reaction has the following characteristics:

1. The desired product B is necessarily accompanied by at least another one, C. In other words, a photochemical reaction must produce, in principle, more than one product.
2. Selection rules, determining which pairs of products can be formed, and which are forbidden, can be formulated.

¹ The concept of funnels was introduced by Zimmerman [2,3] and Michl [4]. Funnels as discussed in these pioneering papers included both real degeneracies (conical intersections) and crossing between potential surfaces without touching.

4. The stereochemistry of the photoproducts can be predicted.

The role of conical intersections in photochemical conversions was suggested over 60 years ago [14], but interest in their role has grown in recent years, since their general occurrence in a large variety of photochemical reactions has been amply demonstrated in the last few years [6–12]. The characteristics enumerated above are of general applicability. In particular, the fact that at least two products are formed, is an important limitation on the usefulness of photochemistry. As briefly discussed in Section 4, this restriction may sometimes be alleviated due to special circumstances.

A conical intersection is defined as the touching of two electronic potential surfaces when plotted along two coordinates. Teller [14,15] has shown that such touchings are always possible in polyatomic molecules, even if the two states to which the potential surfaces belong are of the same symmetry. We base our model and analysis on the phase change theorem formulated by Longuet-Higgins [16]. The theorem states that a conical intersection necessarily arises within a region enclosed by a loop, provided the total electronic wave function changes phase when transported along a complete circle around the loop. If the electronic wave function is real, the phase change is expressed as a sign change. The electronic wave function is constructed within the Born–Oppenheimer (BO) approximation, which obviously breaks down at the conical intersection. It is valid, however, around the conical intersection. Appendix A briefly presents the phase change rule.

The sign change of molecular orbitals along the path of a photochemical reactions has been suggested and extensively discussed by Zimmerman (see Ref. [17] and references therein). The Zimmerman model considers Hückel and Möbius systems (see Section 2.2 for definition of these terms) and provides a rationalization for the difference between thermal and photochemical products. The Zimmerman model, as well as the Woodward–Hoffmann approach are thus based on one electron molecular orbital considerations. The present approach, following Longuet-Higgins’ 1975 paper [16] (which was not available when Ref. [17] appeared), is based on the phase properties of the total electronic wave function.

The model can be used to analyze a large variety of photochemical reactions. It provides a simple way to consider all possible photochemical reaction routes, without resorting to computations. At the same time, the model may help to guide high level calculations, by predicting, for instance, where a conical intersection cannot be found, and when it is present, which two coordinates lead to it. An important advantage is that the analysis is based solely on properties of the ground state surface. Orbital symmetry selection rules, such as applied to electrocyclic reactions [13], are a natural consequence of the model.

2. Phase changes in chemical reactions

2.1. The phase change theorem

A Longuet-Higgins loop (Appendix A) can be formed on either the ground state or the excited state surface. As ground state potential surfaces are usually better characterized than excited state ones, both experimentally and computationally, it is convenient to base the discussion on loops formed on the ground state surface. This turns out to be one of the major advantages of the method – photochemical consequences can be derived from ground state properties. We propose that a loop can be constructed simply by using chemical species familiar to chemists – stable molecules, ions and radicals, represented by Lewis structures. A general method to construct loops by these structures is discussed in Section 2.2.

The loop is formed as the basis of a cone, and thus in general, three points on the potential surface are necessary and sufficient to define it. More than three are in fact redundant. The simplest ‘points’ that suggest themselves in considering photochemical reactions are minima (stable molecules or reactive intermediates) on the potential surface: Thus, reactant A and the desired product
B are chosen to represent two of the points, provided they are connected by an elementary reaction. This means that a single barrier exists between them, without any intermediate. The third point is also chosen to be a stable molecule, C, but must not be equivalent to the others in terms of spin pairing. This requirement is satisfied if elementary reactions connect C with both A and B. Thus, we propose that the characteristics of the system can be represented by three minima on the ground state surface.

Spin-paired structures are commonly used by chemists to represent chemical reactions. They are the basis of the valence bond treatment of chemical bonding. As noted by Kauzmann [18], the attractiveness of valence bond theory to chemists is the simple connection it makes with the notion of a chemical bond. Following Pauling [19], we therefore use Lewis structures to represent molecules involved in the loop. This is conveniently done by employing VB theory.

Since the phase of the electronic orbital wave function is an essential ingredient of the model, it is necessary to consider regions around the minima chosen, in which the total electronic wave function maintains its phase. We used the term 'anchors' to define these regions [20,21]. Different anchors are characterized by their distinct electron spin pairing – as long as the spin pairing does not change, the system remains within the same anchor. (This statement is correct for Hückel-type reactions, the case of Möbius-type ones may be different, see the discussion of ammonia in Section 3.) Thus, conformational isomers lie within the same anchor; likewise, a singlet pair of radicals formed upon bond cleavage lies within the same anchor as the stable molecule from which they originate.

An elementary chemical reaction on the ground state surface that involves spin re-pairing, transports the system from one anchor to another (spin re-pairing is the exchange of spin partners). The loop is therefore formed by combining three elementary reaction coordinates: those leading from A to B, from B to C and from C to A. During this process, the phase of the total electronic wave function is either retained or changed. In the present approach, the overall phase change is derived from the combination of the phase changes of the three individual steps. Thus, the model is intimately connected with the concept of the phase change in an elementary chemical reaction. This concept was frequently discussed; for example, in pericyclic reactions, the phase change can be determined by checking whether the transition state is aromatic (phase retaining) or anti-aromatic (phase inverting) [22–25].

Fig. 1 shows schematically the phase changes incurred by transporting the total electronic wave function around a loop, leading to an overall sign

![Diagram](image-url)
change. Fig. 1a shows the case of a single phase-change loop, i.e. the case where the phase changes once as the wave function is transported around the loop, and Fig. 1b, of a triple phase-change. Each of the anchors A, B and C appearing in the figure is a distinct spin-paired molecular structure. (Intra-anchor reactions, which transform for instance one conformer to another, are obviously spin retaining. In the discussion of photochemical reactions involving conical intersections, conformers are equivalent and may be formed simultaneously. In practice, steric effects may lead to the preferred formation of one of them.) Since we are interested in final stable products, the anchors will be represented by one of them. Thus, the trajectory leading from one anchor to another is simply the usual reaction coordinate. We term each of these three trajectories a leg of the loop.

In order to establish whether a conical intersection is possibly involved in a reaction leading from a given reactant A to a desired product B, it is needed to check all loops containing A and B. If a third molecule C can be found such that the loop $A \rightarrow B \rightarrow C \rightarrow A$ is phase inverting, a conical intersection exists and may be involved in the photochemical reaction $A \rightarrow B$. Fig. 2 shows schematically some different possibilities. Either one or all three of the three reaction pathways in the loop must be phase inverting in order for a conical intersection to be present inside the loop. If none or two legs of the loop are phase inverting, a conical intersection is not enclosed by the loop. An important corollary of this discussion is that the if a conical intersection is involved, the phototransformation of $A$ to $B$ cannot proceed without the formation of another product (C in this case), regardless of the excited state involved! This is a direct consequence of the fact that two coordinates are required to define a conical intersection. This result is in line with the experimental finding that in many photochemical reactions, several products are formed in parallel.

**2.2. Change of phase in the electronic wave function during elementary chemical reactions**

In this paper, we restrict the discussion to singlet states only, assuming spin conservation in all reactions. Mathematical details are left out – they have been elaborated by several authors [22–24] and most recently by us [20,25] vis-a-vis a discussion of aromaticity. The wave function $\Psi_R$ of a system undergoing an elementary reaction on the ground state surface, is written as a linear combination of the wave functions of the reactant, $\Psi_A$, and the product, $\Psi_B$:

![Fig. 2. Three possible loops, showing the requirements for a conical intersection to be enclosed inside them, an odd number of phase inverting legs is required.](image)
According to the Born–Oppenheimer approximation, the total wave function \( \Psi \) of a system may be written as the product of two wave functions, the electronic wave function \( \phi \) and the nuclear one \( \chi \). Within the Born–Oppenheimer approximation, the electronic wave function, \( \phi_R \), is well defined, and may be written analogously as

\[
\phi_R = k_A \phi_A \pm k_B \phi_B,
\]

where \( k_A \) is unity in the beginning of the reaction and \( k_B \) is unity at the end \[24\]. Eq. (2) represents two potential energy surfaces, one is the ground state, the other an excited state. If \( k_A \) and \( k_B \) have the same sign (an in-phase combination) on the ground state, the reaction is a phase preserving one, while if they have opposite signs (out-of-phase combination) on the ground state, the reaction is phase inverting. A phase change involves the introduction of a new node (or an odd number of nodes) along the reaction coordinate. This is equivalent to changing the total electronic angular momentum of the system along that coordinate. The role of nodes and nodal parity was discussed extensively for correlated molecular orbitals during a reaction \[17\]. Here we emphasize the properties of the total wave function.

There are two mechanisms by which a phase change on the ground state surface can take place. One was extensively discussed by both MO \[17\] 2 and VB \[28,29\] formulations, and involves the creation of a negative overlap between two adjacent atomic orbitals during the reaction (or an odd number of negative overlaps). A reaction in which this happens is termed Möbius type. A well known example is the conrotatory ring closure in pericyclic reactions. A reaction in which all overlaps between adjacent atomic orbitals along the reaction coordinate are positive (or such that the number of negative overlaps is even) is termed Hückel type. Hückel-type reactions are the only ones possible when only s orbitals are involved.

We refer to this mechanism as the orbital overlap mechanism.

The second mechanism is due to the permutational properties of the electronic wave function, and is therefore referred to as the permutational mechanism. Oosterhoff \[28,29\] assumed that the in-phase combination in Eq. (2) always lies on the ground state potential. This is correct for aromatic Hückel-type reactions, and for antiaromatic Möbius-type ones, as shown specifically for several four electron systems \[22,23\] and more generally by us \[25\]. However, for antiaromatic Hückel-type reactions and for aromatic Möbius-type ones, the out-of-phase combination is the ground state \[25\]. (Aromatic and antiaromatic transition states are terms conventionally used in conjunction with pericyclic reactions. The concept of phase change is more general, it can be applied to any reaction, we will therefore use the terms Hückel and Möbius. See Appendix B for some more details.)

In order to discuss the phase change, it is convenient to introduce the parity of a reaction: a reaction is of odd parity if an odd number \( (1, 3, \ldots) \) of electron pairs exchanges take place in the course of the reaction. (Each exchange involves two spin-paired electron, so that in an odd parity system, an even number of electron pairs exchange spins.) A reaction is of even parity, if an even number \( (0, 2, \ldots) \) of electron pairs exchanges take place in the course of the reaction. In Ref. \[25\], it was shown that for Hückel-type even parity systems, the in-phase combination of Eq. (2) is the ground state, while for odd parity systems, the out-of-phase combination is the ground state. For a Hückel-type system, the phase can change during a reaction only by the permutational mechanism. However, for Möbius-type systems, the total phase change is the combination of the two factors, the geometric overlap and the permutational one. The combined effects lead to the results summarized in Table 1. We proceed to illustrate these general ideas by considering a few examples.

### 2.2.1. Reactions involving sigma bonds only

We begin by considering the simplest case – that in which only sigma bonds change during the reaction. Among these, dissociation of bonds involving only s type atomic orbitals are necessarily
Hückel type – no orbital phase change can take place along the reaction coordinate. Spin re-pairing requires a minimum of three electrons; it occurs for instance in the H + H₂ exchange reaction (3)

\[ \text{H} + \text{H}_2\text{H}3 \rightarrow \text{H}1\text{H}_2 + \text{H}3 \]  

which has been shown to be phase inverting [5,16]. Atoms H₂ and H₃ are paired in the reactant, while in the product, atoms H₁ and H₂ are paired. The reaction involves a single (odd) exchange of electron spin pairs and is therefore phase inverting.

Another example is the metathesis reaction H₂ + H₂ → H₂ + H₂. As shown in Fig. 3, there are three spin pairing possibilities in this system. In the notation of Appendix B they are \{12,34\}, \{13,24\} and \{14,23\}. The transition between any two is phase inverting as this is also a Hückel type odd parity system [25,30].

As the number of electron pairs is increased, so does the number of spin pairing possibilities. For instance, adding one more pair (leading to a six electron system), the reaction remains of even parity if any two electron pairs are re-paired. However, if three electron pairs are re-paired (achieved by two exchanges), the reaction is of even parity and the phase is preserved (Table 1).

As the example of the H + H₂ system shows, even if one of the electron “pairs” contains only one electron, the nature of the parity is maintained. Thus, a three electron system is phase inverting (as the four electron one), a five electron system is phase preserving just like a six electron one, etc.

Another type of sigma bonds involves a p orbital lying along the reaction coordinate, as for instance in reaction (4) (Scheme 1).

\[ \text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}. \]  

This is an example of a Möbius reaction system – a node along the reaction coordinate is introduced by the placement of a phase-inverting orbital. As in the H + H₂ system, a single spin exchange takes place. Thus, this odd parity reaction is phase preserving, as seen from Table 1. Möbius reaction systems are quite common when p orbitals (or hybrid orbitals containing p orbitals) participate in the reaction, as further discussed in the next subsection.

Upper panel of Scheme 1 shows three electron reactions; in both there are two electron spin re-pairings. In the H + H₂ system, no new node is formed along the reaction coordinate – this is a Hückel-type forbidden reaction. In the H + HCl system, a new node is formed in the reaction – this is a Möbius-type allowed reaction.

Lower panel shows the ring closure reaction of butadiene to cyclobutene – a four electron system.
On the left, the closure is disrotatory, no new node is formed along the reaction coordinate. This is a H/C$_127$uckel-type forbidden reaction. On the right, a conrotatory ring closure leads to a new node, this is a M/C$_127$obius-type allowed reaction.

2.2.2. Reactions involving π bonds

Hückel-type systems (suprafacial reactions) obey the same rules as sigma electron systems. This was shown for instance for reactions involving aromatic and antiaromatic transition states [2,17,22,23]. The rationale for this behavior is clear: As long as the overlap between adjacent π-electron orbitals is positive along the reaction coordinate, only the permutational mechanism can lead to sign inversion. In Möbius-type systems (antarafacial reactions), the system will change phase only if an even number of electron spin-pair exchanges takes place.

Electrocyclic reactions are examples of cases where π-electron bonds transform to sigma ones [17,20,21,28,29]. A prototype is the cyclization of butadiene to cyclobutene (Scheme 1, lower panel). In this four electron (odd parity) system, phase inversion occurs if no new nodes are formed along the reaction coordinate. Therefore, when the ring closure is disrotatory, the system is Hückel type, and the reaction is a phase-inverting one. If however the motion is conrotatory, a new node is formed along the reaction coordinate just as in the HCl + H system. The reaction is now Möbius type, and phase preserving. This result, which is in line with the Woodward–Hoffmann rules and with Zimmerman’s Möbius–Hückel model, was obtained without consideration of nuclear symmetry. This result was obtained previously by Goddard [22,30].

3. Localizing conical intersections

We can now analyze photochemical systems using the phase-change rule. As stated earlier, an important corollary of this rule is that passage through a conical intersection may lead to the formation of a ground state ‘allowed’ (i.e. photochemically ‘forbidden’) product (in the orbital conservation sense). This will happen if the conical intersection lies within a single phase-change loop (Figs. 1 and 2). Triple phase-change loops lead to two photochemically ‘allowed’ products. The very existence of a conical intersection requires at least one ground state phase-inverting reaction in the loop, leading to at least one thermally ‘forbidden’ product. However, as seen from Fig. 2b, photolysis of A can yield two phase preserving products B and C (i.e. thermally ‘allowed’ products), provided the reaction leading from B to C is phase inverting!

A pertinent question is how many different conical intersections exist that are involved in a given A → B photochemical reaction. This can be answered by finding all possible third anchors C, that form phase inverting loops A → B → C, → A. Their number is finite for any finite system, and the analysis can be systematically performed. The method is to consider all possible, energy accessible, independent spin-pairing structures. We illustrate the technique by considering two prototype systems, ammonia and ethylene (for further examples, see Ref. [20,21]).

3.1. Photolysis of ammonia

There are eight valence electrons in ammonia. Restricting the discussion to neutral species only (ionic ones require high energy, and are not important in the 170–220 nm UV range, where
ammonia absorbs strongly), there are two low energy reaction channels to ground state products:

\[
\text{NH}_3 \rightarrow \text{NH}_2(X^2B_1) + \text{H}(^2S)
\]

\[
\text{dissociation to ground state atomic hydrogen}
\]

(5)

\[
\text{NH}_3 \rightarrow \text{NH}(a^1\Delta) + \text{H}_2
\]

\[
\text{dissociation to molecular hydrogen}
\]

(6)

Several loops containing conical intersections can be constructed for this system; two are shown in Fig. 4. The non-bonding electrons of the nitrogen atom are important in determining spin re-pairing, and hence the conical intersections. This is the origin of the topicity concept developed by Salem and coworkers [1,31,32].

Two possible spin pairing schemes forming the ammonia molecule are shown; they represent the two umbrella isomers of ammonia, which are two different anchors, as are two tetrahedral enantiomers. The hybridization scheme in both is sp\(^3\) and they differ by the electrons that are paired with the hydrogen electrons. In the transition state, symmetry requires that the lone electron pair occupies a non-bonding p orbital that changes phase along the reaction coordinate – the reaction is a phase inverting one. This umbrella inversion process may be viewed as either a Hückel four electron reaction, or a Möbius two electron one (in which the p orbital changes sign in the transition state and all electrons in the NH bonds maintain their spin partners). In either case it turns out to be a phase-inverting reaction. In Fig. 4, it forms one leg of the Longuet-Higgins loop shared by two loops. The upper loop has H\(_2^1\Sigma^+_g\) + NH\(^{a^1\Delta}\) as the third anchor while in the lower one the NH\(_2^2\Pi\) + H\(^2S\) pair is the third anchor. In both, the transformation from NH\(_3\) involves four electrons (indicated as by dots in Fig. 4), making these odd parity Hückel-type reactions phase inverting. Both loops are thus triple phase-change ones and a conical intersection exists inside them. A third loop may be constructed from one ammonia isomer and the other two anchors; it is also a triple phase change one. Note that the H atom dissociation channel requires planarization en route to the conical intersection. This expectation was verified computationally [33].

3.2. The photochemistry of ethylene

Ethylene has six atoms and 12 valence electrons. The number of possible singlet reactions involving neutral species is much larger than in the case of ammonia. Using the enthalpy of reaction as a guide, we limit the discussion of UV-induced transformations to reactions whose \(\Delta H\) is less than 120 kcal/mol. These reactions are
cis–trans isomerization, \( \Delta H = 0 \) (7)

\[
\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 \text{ (acetylene)} + \text{H}_2, \quad \Delta H = 38 \text{ kcal/mol}
\] (8)

\[
\text{C}_2\text{H}_4 \rightarrow \text{H}_2\text{CC}(\text{H}), \quad \Delta H = 87 \text{ kcal/mol}
\] (9)

\[
\text{C}_2\text{H}_4 \rightarrow \text{H}_2\text{C}_2 + \text{H}_2, \quad \Delta H = 92 \text{ kcal/mol}
\] (10)

\[
\text{C}_2\text{H}_4 \rightarrow ^*\text{C}_2\text{H}_3 + \text{H}^*, \quad \Delta H = 111 \text{ kcal/mol}
\] (11)

The first step is to establish the phase retention properties of these reactions. Reactions 7–10 involve each the single spin re-pairing of two electron pairs; they are of odd parity. All are thus phase inverting if the reactions are Hückel type. Cis–trans isomerization is a four electron process, as shown by Mulder [34], and easily verified when considering the fact that both \( \pi \) and sigma electrons of the double bond are involved (Appendix B). As shown in Scheme 2, different sets of four electrons are re-paired in reactions (8) and (10). The hydrogen migration reaction (9) also re-pairs two electron pairs and is phase inverting if it takes place suprafacially. Note that two of the electrons re-paired in this reaction are common to those re-paired in the cis–trans isomerization. The simple C–H bond fission reaction (11) is phase preserving (it belongs to the same anchor as ethylene).

Some Longuet-Higgins loops, constructed from these anchors are depicted in Fig. 5. Only two loops pertaining to the cis–trans isomerization reactions are shown, others can be constructed in a similar fashion. An important result of this discussion is that if conical intersections are involved, a photo-induced, cis–trans isomerization cannot proceed without the formation of other products! The fact that cis–trans isomerization is almost always accompanied by other reactions (notably H atom migration) has indeed been noted for many years [12,35]. Analysis shows also that 1,2 \( \text{H}_2 \) elimination to form acetylene cannot accompany cis–trans isomerization in a common loop; it is a phase preserving \( P \times I \times I \) loop, Fig. 2. 1,1 \( \text{H}_2 \) elimination, leading to \( \text{H}_2 \) and a vinylidene biradical, on the other hand, is a phase-inverting reaction that can take place from both the cis and the trans isomer. The loop formed by these three anchors is phase inverting, so that a conical intersection lies within it. Isotopic substitution studies [36] revealed that acetylene is indeed formed primarily by the 1,1 elimination route,
followed by ground state isomerization of the vinylidene biradical to acetylene.

4. Discussion

The purpose of this paper is to show that the concept of phase change of the total electronic wave function is of general interest to the practicing photochemist. Using VB structures, the model can be cast into a simple working tool that facilitates the prediction of the course of photocatalytic reactions and their stereochemical properties [20,21].

The practical application of the model to a desired reaction (converting A to B by a photon whose energy is \( E = \hbar \omega \), which is absorbed by A), can be implemented using spin-paired structures, as is the usual practice in VB theory. The procedure is as follows:

1. Check whether A and B have the same spin pairing; if so, they belong to the same anchor and the model does not apply. If the spin pairing is changed, check whether the reaction is phase preserving or inverting using the rules of Table 1.
2. Check all other spin pairing possibilities for the atoms contained in A. This involves all reaction channels leading to a third product C: dissociations, isomerizations, rearrangements, etc.
3. Determine the phase properties of the reactions \( A \rightarrow C \) and \( B \rightarrow C \) for all conversions selected in step 2.
4. Construct Longuet-Higgins loops (\( A \rightarrow B \rightarrow C \rightarrow A \)) for each triad (ABC) and check whether the total electronic wave function changes sign upon being transported around the loop.
5. All loops for which step 4 yielded a positive result contain a conical intersection and irradiation of A by the photon \( \hbar \omega \) is expected to lead to products B and C.

The present approach is in the spirit of the Wigner–Whitmer rules [37], which have been extended to larger molecular systems [38,39]: symmetry rules are sought that determine the outcome of a chemical reaction. In that sense our model is related to other symmetry rules, such as those proposed by Fukui [40] and by Woodward and Hoffmann [13], that considered molecular orbital correlations. Correlation diagrams using the total electronic wave functions were developed by several authors [1–4,17,31,32,41,42]. However, in all of them only electrocyclic reactions were considered, and nuclear symmetry considerations were a major part of the argument.

This model differs from most previous ones by requiring the consideration of two reaction channels in the analysis of chemical systems. Thus, it is a two-dimensional model, whereas most previous ones [1–4,13,31,32,41–44], based on correlation diagrams, or a sequence of reactions, are one-dimensional ones.

The frequent observation of the simultaneous formation of several photoproducts is readily explained in this model. Exceptions exist, due in part to low quantum yields of some products. It can be shown that if an anchor lies above the conical intersection, only one product will be formed, if two such anchors exist, rapid internal conversion will follow, and no new products are formed. A possible example is the rapid internal conversion in azulene [45]. The practical implementation of the model, namely, selection of the most probable conical intersection, will depend on energetic and dynamic factors. The computational search for conical intersection is actively and successfully pursued by many groups. It is often quite tedious due to the large dimensionality of the problem. The present approach can provide general guidelines helping in selecting the coordinates most likely to lead to a conical intersection.

5. Summary

Assuming that conical intersections play a central role in many photochemical reactions, a simple method for finding the products formed from them is presented. It is based on the analysis of the phase change of the electronic wave function occurring during ground state (thermal) reactions. Thermal reactions may be classified as either phase inverting or phase preserving, depending on whether the electronic wave function changes sign during the reaction or not. This in turn makes it possible to establish, based on ground state
properties only, whether a conical intersection can be involved in the transformation of A to B. The model can be applied systematically to find all possible conical intersections; it also provides a simple explanation for the fact that in many photochemical processes more than one product is formed. Selection rules predicting the formation of certain product pairs can be derived. However, the relative importance of different conical intersections in a given reaction cannot be determined from the model. For this purpose, the detailed structure of the potential surfaces near the different conical intersections must be known.

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Appendix A. A short presentation of a Longuet-Higgins loop and its relation to the phase change of the electronic wave function

The purpose of this appendix is to briefly summarize the phase change rule, and to introduce the idea of phase change in chemical reactions.

The complete wave function, ψ, of the system is written as a function of the coordinates of the electrons, q, and of the nuclei, Q, as follows:

\[ \psi = \phi(q, Q) \chi(Q), \]

where \( \phi(q, Q) \) is the electronic wave function that depends parametrically on Q. This partition into \( \phi \) and \( \chi \) introduces an ambiguity to the definition of both \( \phi \) and \( \chi \); suppose that at a certain set of nuclei coordinates \( \{Q_0\} \), the electronic wave function is non-degenerate. As the nuclei move away from this configuration, \( \phi(q, Q) \) will in general vary smoothly and continuously (we assume \( \phi(q, Q) \) to be real, for simplicity). Let us choose a closed loop, by which the nuclei move away from \( \{Q_0\} \) to some configuration \( \{Q_1\} \) and return to \( \{Q_0\} \) without retracing. \( \phi(q, Q) \) will return to its original value, but not necessarily with the same sign. It may have changed sign on returning to the original point \( \chi(Q) \) will naturally also change sign, so that \( \psi \) is uniquely defined, as required). The sign change represents a change in the phase of the total electronic wave function. We term a loop that maintains the phase (i.e. preserves the sign) as a phase preserving one, and a loop that inverts the sign as a phase inverting route. Longuet-Higgins [16] showed that if the loop encloses the nuclear configuration \( \{Q_{CI}\} \) of a conical intersection (i.e. a degeneracy of the total electronic wave function), \( \phi(q, Q) \) necessarily changes sign.

Appendix B. Spin pairing, anchors, the parity of a reaction and the aromaticity of transition states

This appendix summarizes the properties of aromatic and antiaromatic transition states. Aromatic transition states have been discussed extensively in the literature [47–49], and the concept is used in text books of photochemistry [50] and organic chemistry [46, p. 644]. For the purpose of this paper, it is convenient to base it on the VB theory of aromaticity and antiaromaticity, in particular, with relation to the phase of the electronic wave function in the context of the Born–Oppenheimer approximation. In the VB approach, valence bond structures are constructed by forming electron pairs; a bond is formed by pairing the spin of two electrons originally situated in two different atomic orbitals. The concept of the aromaticity of the transition state in Hückel-type reactions may be introduced by an example.

The cis–trans isomerization of ethylene shown in Scheme 3 involves the change in spin pairing from \{12,34\} to \{13,24\}. The notation \{12,34\} means that the electron occupying orbital #1 of carbon atom 1 is spin coupled to the electron occupying orbital #2 of carbon atom 2, and the electron occupying orbital #4 of carbon atom 1 is spin coupled to the electron occupying orbital #3 of carbon atom 2. This notation is in line with the common notion of chemical bonding being due a pair of shared electrons. Pauli’s principle requires that the wave function will be antisymmetric with respect to the exchange of any two electrons.
In addition, electrons are indistinguishable. It is required that the two paired electrons will have opposite signs. The presentation of the wave function determinant form ensures the fulfillment of Pauli’s principle:

$$\phi = \frac{\phi_1(1)\phi_2(1)\phi_3(3)\phi_4(4)}{\phi_1(2)\phi_2(2)\phi_3(3)\phi_4(4)} = \frac{\phi_3(1)\phi_2(2)\phi_3(3)\phi_4(4)}{\phi_4(1)\phi_2(2)\phi_3(3)\phi_4(4)}.$$

The $$\phi_i$$s without a bar stand for spin 1/2 (α) and the barred ones for spin –1/2 (β). In shorthand notation, we represent this determinant by its diagonal $$\phi_1(1)\phi_2(2)\phi_3(3)\phi_4(4)$$ which is simplified to 1234. However, this is only one possible determinant, since here we let $$\phi_1$$ and $$\phi_3$$ carry spin α only, and $$\phi_2$$ and $$\phi_4$$ carry spin β only, in violation of the indistinguishable character of the electrons. Therefore, the complete wave function must be written as the sum of all possible determinants in which the electrons are properly paired [51,52]. In the shorthand notation, the complete wavefunction may be written as

$$\{12, 34\} = (1\bar{2} - 1\bar{2})(3\bar{4} - 3\bar{4}),$$

which is the sum of four determinants (a normalization factor is assumed).

It is seen that the cis–trans isomerization may be represented by the transformation

$$\{12, 34\} \rightarrow \{13, 24\}.$$

This is a four electron problem, which was dealt with by many authors [22,23] and by us in relation to antiaromaticity [25]. For consistency with Eq. (2) (Section 2.2), let us denote $$\{12,34\}$$ by $$\phi_A$$ and $$\{13,24\}$$ by $$\phi_B$$.

Of the two combinations of Eq. (2), one forms the ground state potential, the other, an electronic excited state. In a two electron problem (such as H2) the in-phase (positive) combination is always the ground state, and the out-of-phase one is the excited state. When more than two electrons are involved, two singlet states may be constructed, and the in-phase combination is not necessarily the excited state. As shown in Refs. [20,21], and in Section 2.2, for Hückel-type, even parity systems, the in-phase combination is the ground state, and for Hückel-type, odd parity systems, the out-of-phase combination is the ground state.

When an even number of spin exchanges takes place, an odd number of electron pairs are exchanged in the reaction, and so $$4n + 2$$ ($$n = 0,1,2,\ldots$$) electrons are involved, bringing to mind the Hückel definition of aromaticity. The transition state in this case is the in-phase combination in Eq. (2), justifying the use of the term aromatic transition state for this situation. In general, the transition state of a Hückel-type, even parity reaction is defined as aromatic and the transition state of a Hückel-type, odd parity reaction as antiaromatic. For a phase change to take place by this mechanism, a minimum of three electrons must participate (this allows spin re-pairing as in the H + H2 system which may be presented as $$\{1,23\} \rightarrow \{12,3\}$$, a single electrons acts as half a pair). No permutational phase change can take place in a two electron Hückel system. The crucial parameter is the number of electron pair exchanges, which is odd in the H + H2 system, as in the ethylene isomerization reaction (Scheme 3). One of the pairs may consist of single electron, if it participates in the re-pairing of spins. The concept of antiaromatic transition states is, therefore, generalized to include non-symmetric nuclear systems, just as the concept of aromatic transition states includes non-symmetric nuclear systems, such as the Diels–Alder reaction.

The existence of antiaromatic (phase-inverting) transition states in thermal reactions is rather counter intuitive; this situation is in fact not frequently observed in practice: most thermal reactions involve Hückel-type, aromatic transition states. It may be noted, that a reaction having an out-of-phase (antiaromatic) transition state is
equivalent to a Woodward–Hoffmann forbidden thermal reaction. However, these reactions are of prime importance in photochemical reactions as they are essential for constructing Longuet-Higgins loops. Examples of antiaromatic transition states are the exchange reactions $H_2 + H \rightarrow H + H_2$, $H_2 + H_2 \rightarrow H_2 + H_2$, the cyclization of butadiene to cyclobutene and the addition of two ethylenes to form cyclobutane.

For completeness, we add that in Möbius-type reactions (Section 2.2), an odd parity system (i.e. in which an odd number of electron spin-pairs exchanges take place) is phase preserving, and an even parity system is phase inverting, just opposite to the case of Hückel-type reactions. This arises from the fact that phase inversion here is the combination of the atomic orbital phase change and the permutational phase change.

References
