

Chapter 16

New insights from a bonding evolution theory based on the topological analysis of the electron localization function

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16.1 Introduction

From a general perspective, any chemical process can be rationalized in terms of the intimate interplay featuring nuclei and electron density reorganizations [1–7]. A deeper understanding of the nature of chemical bonding will imply the proper characterization of global, local, and nonlocal responses associated with the reacting system. Orbital-based tools [8–10], reactivity descriptors strategies [11,12], and topologically-dependent frameworks [7,13–15] are available for such a goal, i.e., trying to reveal details concerning electron density changes driven each stage and steps featuring a given reaction mechanism.

In this chapter, we will focus our attention on a specific application that belongs to the idea of characterizing the gradient field (i.e., the topological analysis) of local quantum-mechanical functions [16–20]. In these cases, the topological analysis enables us to partition the molecular space into basins of attractors (maxima) of a suitable scalar function, which can be related to chemically meaningful information and concepts. This type of analysis provides a powerful interpretative strategy connecting our familiar chemical concepts and the results from quantum mechanics via a model formally supported by the rigorous mathematical terminology arising from the topological theory of dynamical systems [21,22]. Such analysis provides topologically derived *structures* defined in terms of the associated critical points (CPs) and their interconnections via gradient paths. Within such a framework featuring the concept of *gradient vector fields*, the analysis and characterization of the gradient field of the *electron den-*

sity itself, i.e., the quantum theory of atoms in molecules QTAIM [18,23] and the *electron localization function* ELF [19,20,24], constitute fundamental valuable methodological approaches for the interpretation of chemical bonding and reactivity nowadays [25–27]. Of course, several other local well-behaved functions, e.g., the Laplacian of density [28,29], the nuclear potential [30], the electrostatic potential [31], the virial field [32], the magnetically induced molecular current distribution [33], and even the spin density [34], can also be exploited in such a context. Further, a description of changes in the topologically defined structures as a response to the variation of *control parameters* can be addressed via the theory of elementary catastrophes [35,36], as it has been mainly evidenced within the QTAIM [18] and ELF [19,20,24] perspectives. Here we are particularly interested in the ELF framework just because the topology of the electron pairing is straightforwardly provided by this function, enabling a direct-space rationalization or *interpretation* of the evolution of the critical chemical concept of bonding in terms of Lewis-like patterns [37–40]. Such a correlation is not an energetical one, formally speaking, but only *topological*, i.e., related to the form/structure of the extension of electron (de)localization. Further, it should always be emphasized that any picture of regions with localized electrons is just a practical model for chemistry-oriented applications [41]. As electrons ‘move’ through space with their Fermi hole, localization arises due to Pauli repulsion [18]. Within the so-called *bonding evolution theory* (BET) framework [42], changes in the topology of the ELF [19,20,24] are followed along a chosen reaction path (e.g., the intrinsic reaction coordinate IRC [43]). These changes are further rationalized using the unfoldings associated with the elementary Thom’s catastrophes [3,4,21,35–37,39,40,44]. In this context, the sequence of different bonding states become naturally associated with specific structural stability domains (SSDs) separated by catastrophe bifurcations [21,35,36,44]. BET has provided meaningful insights on an ever-increasing number of reactive processes related to problems in almost all fields of chemistry [39,40], including, for example, critical questions on bonding and reactivity associated with the activation of C–H bonds [45], proton/hydrogen transfer reactions [46], [4+2] cycloadditions [15,47], [3+2] cycloadditions [48], [1,3] dipolar cycloadditions [15,49], the process of fixation of CO₂ by metal complexes [50], decarbonylation of unsaturated cyclic ketones [51], the nature of phase transitions for group IV elements [52], the formation of hemiaminals [53], Cope [15,54], and Claisen [55] rearrangements, the thermal decomposition of α -ketoesters [56], hydrometallation of acetylene [57], oxidative additions of ammonia to pincer complexes [58], the Curtis rearrangement [59], the catalytic Noyori hydrogenation [60], and the Wittig reaction [3].

We have recently demonstrated the need to recast some details concerning the bonding evolution theory methodology [1,2,61,62]. We evidence that the analysis of sequences of molecular graphs exclusively based on single changes in the number and type of critical points (as exemplified in most available BET applications) is still an imprecise procedure yielding improper identification

of bifurcation catastrophes [1]. For both ground and excited states' processes [1,2,61,62], we have emphasized that the only consideration of ELF maxima is incorrect. The proper treatment in such a context should also consider analyzing the *behavior of the determinant of the Hessian matrix* and the *associated mobility of complete sets of ELF critical points* along the reaction path [1,2].

16.2 General remarks concerning the BET formalism

For the sake of completeness, we briefly review in this section some basics concerning the BET framework, i.e., the topological analysis of ELF and catastrophe theory. Becke and Edgecombe proposed the ELF on the consideration of the same-spin conditional pair electron density, and later generalized by Savin for any density-independent of spin in terms of local kinetic energy densities, namely, $\eta(\mathbf{r}; \mathbf{R}) = [1 + [\tau_P(\mathbf{r}; \mathbf{R})/\tau_h(\mathbf{r}; \mathbf{R})]^2]^{-1}$; where $\tau_P(\mathbf{r}; \mathbf{R}) = \sum_i^N |\nabla \psi_i(\mathbf{r}; \mathbf{R})|^2 - (1/8) |\nabla \rho(\mathbf{r}; \mathbf{R})|^2 / \rho(\mathbf{r}; \mathbf{R})$, and $\tau_h(\mathbf{r}; \mathbf{R}) = (3/5) (6\pi^2)^{2/3} \rho(\mathbf{r}; \mathbf{R})^{5/3}$ are the positive-definite local Pauli and Thomas–Fermi kinetic energy densities, respectively [19,63]. Electron pairing arises thus because of the Pauli exclusion principle. The electron density distribution is written as $\rho(\mathbf{r}; \mathbf{R}) = \sum_i^N n_i |\psi_i(\mathbf{r}; \mathbf{R})|^2$, where $\psi_i(\mathbf{r}; \mathbf{R})$ are molecular orbitals, and n_i occupation numbers. The notation $(\mathbf{r}; \mathbf{R})$ stands for solutions concerning the space coordinate for electrons $\mathbf{r}$ at fixed nuclei space coordinates $\mathbf{R}$. The ELF function $\eta(\mathbf{r}; \mathbf{R})$ takes values in the range [0, 1], the highest values are associated with the spatial positions $\mathbf{r}$ with higher electron localization (compared to the arbitrarily chosen uniform electron gas reference) [19,63]. Both single-determinantal and correlated wave functions can be analyzed using extended formulations [64].

The analysis of the gradient vector field of ELF, $\nabla_{\mathbf{r}} \eta(\mathbf{r}; \mathbf{R})$, provides a division of the molecular space of $\rho(\mathbf{r}; \mathbf{R})$ into *basins of attractors* that are, empirically, associated with chemically meaningful concepts such as atomic cores, valence bonds, lone pairs, and other elements of chemical bonding [26,65]. The critical points (CPs) of $\eta(\mathbf{r}; \mathbf{R})$ and their connectivity determines the *ELF molecular graph* for the system, providing a powerful interpretative model to explore essential and valuable information about bonding and reactivity in chemical processes [19,20,24]. In such a picture of bonding, the valence basin densities are delocalized throughout those associated with core basins' inner atomic shell densities [19,20,24]. The valence basins are characterized by their synaptic order [26]. Valence monosynaptic basins can be associated, for instance, with electron lone pairs, whereas disynaptic basins are related to typical two-center bonds. This concept provides a helpful way to represent multicenter bonds within a topological framework of rationalizing chemistry [26]. The mathematical framework is well-known and universal, i.e., the CPs (i.e., those at which the gradient of the ELF vanishes) determine the complete topological characteristics of the scalar function. The full characterization of each CP is

obtained using the stability matrix or Hessian (i.e., the second derivatives), in terms of the signs of its eigenvalues.

As $\eta(\mathbf{r}; \mathbf{R})$ is a real-valued smooth function on $\mathbb{R}^3$, we have only four types of CPs, i.e., $(3, -3)$ are ELF maxima of index 0; $(3, -1)$ are ELF saddles of index 1; $(3, +1)$ are ELF saddles of index 2; and $(3, +3)$ are ELF minima of index 3. The index of a CP is taken here as the number of positive Hessian eigenvalues [66], and we have used the standard notation ‘(rank, signature)’. The number of nonzero Hessian eigenvalues evaluated at each CP is named the rank, while the sum of the corresponding signs defines its signature [16,18,42]. In the analysis of the dynamics for $\dot{\mathbf{r}} = -\nabla_{\mathbf{r}}\eta(\mathbf{r}; \mathbf{R})$, considered as the subjacent model for the physical reality we are dealing with, the characterization of equilibria $\nabla_{\mathbf{r}}\eta(\mathbf{r}; \mathbf{R}) = 0$ will represent the critical conceptual step. Hence, the equilibrium states of the dynamical system can be unambiguously determined, and phase space portraits built [22]. Considering specific conditions, trajectories of gradient paths connecting different critical points are simply obtained as parametrized integral curves [18,23]. We recall at this point that only nine different types of gradient paths are possible: four of them have a maximum as terminus (i.e., $(3, -1) \rightarrow (3, -3)$ (interpair path), $(3, +1) \rightarrow (3, -3)$ (ring surface), $(3, +3) \rightarrow (3, -3)$, $\infty \rightarrow (3, -3)$ (ELF basin)); three more terminate at a saddle of index 1 (i.e., $(3, +1) \rightarrow (3, -1)$, $(3, +3) \rightarrow (3, -1)$, $\infty \rightarrow (3, -1)$ (interbasin surface)); and the remaining ones terminate at a saddle of index 2 (i.e., $(3, +3) \rightarrow (3, +1)$, and $\infty \rightarrow (3, +1)$ (ring line)) [28]. Also, it is convenient to recall here that the gradient will always point in the direction of the greatest increase (or steepest ascent) in η , i.e., $\nabla_{\mathbf{r}}\eta(\mathbf{r}; \mathbf{R})$ is everywhere perpendicular to a surface of constant η . The infinite collection of gradient paths determines the gradient vector field of the ELF, and hence, its complete topological properties. The critical points of $\eta(\mathbf{r}; \mathbf{R})$, and their connectivity determines the ELF ‘molecular graph’ for any system, enabling a powerful interpretative model for chemical bonding and reactivity. For example, Fig. 16.1 shows the molecular graph for the Diels–Alder reaction between butadiene and ethylene when the separation between both fragments (through terminal C centers) is 2.88Å. Note that the local maxima associated with the double CC bonds in each component become connected via $(3, -1) \rightarrow (3, -3)$ gradient paths. In the BET methodology proposed by Silvi et al., the mathematical results of Thom’s catastrophe theory are applied to the evolution of the resulting phase portraits along the intrinsic reaction coordinate (IRC) by assuming that a subset of nuclei space coordinates $\mathbf{R}$ can be considered the ‘external’ control parameters. The bonding state is then studied in function of continuous variation of the external parameters.

The evolution of the stationary state of CPs at a given fixed $\mathbf{R}$ is examined through the determinant of the Hessian (or stability) matrix, $H_{ij} = \partial^2\eta(\mathbf{r}; \mathbf{R})/\partial r_i \partial r_j$. It allows differentiating between degenerate or nonhyperbolic CPs and Morse-type or hyperbolic ones [21,35,36,44]. The set of configurations of the control space for which the Hessian matrix is nonzero defines a

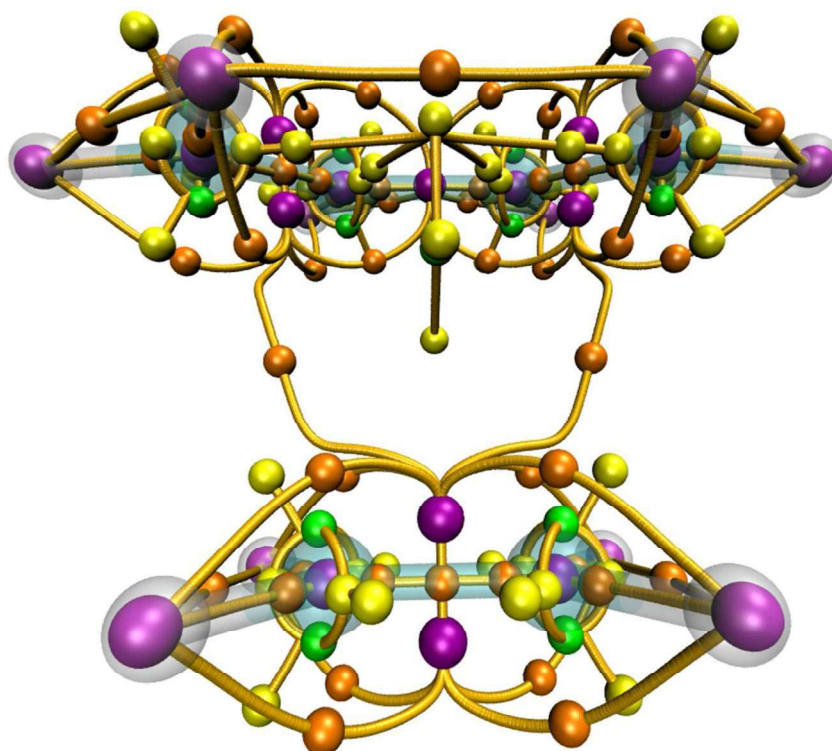


FIGURE 16.1 The molecular graph for the $C_4H_6 + C_2H_4$ reacting system reveals all types of CPs of $\eta(\mathbf{r}; \mathbf{R})$, i.e., $(3, -3)$: attractors or maxima of index 0, represented in purple (dark gray in print version) color; $(3, -1)$ saddles of index 1, depicted in orange (mid gray in print version) color; $(3, +1)$ saddles of index 2, represented in yellow (light gray in print version) color; and $(3, +1)$ or minima of index 3, illustrated in green (gray in print version) color. Gradient paths connecting $(3, -3)$ and $(3, -1)$, as well as $(3, +3)$ and $(3, +1)$, are also included for convenience.

domain of structural stability (SSD) where all CPs are hyperbolic. The system evolves from one domain of stability to another upon small changes in the control parameters $\mathbf{R}$. Each SSD is associated with a particular system's bonding state. The Poincaré–Hopf theorem [67] should always be satisfied [18,67] if only Morse CPs are involved, namely $n_{(3,-3)} - n_{(3,-1)} + n_{(3,+1)} - n_{(3,+3)} = 1$, where n_i is the number of CPs of each type. Catastrophes, i.e., a change in the topographic map induced by splitting a nonhyperbolic CP into a finite collection of isolated hyperbolic CPs, separate different SSDs. This fact assumes the validity of Thom's conjecture [21,35,36,44], which determines the change of the potential function upon slight variations of the control parameters. Thom's theory predicts that, under suitable conditions [21,35,36,44], the local character of potentials in the neighborhood of a degenerate CP can be explored through canonical polynomial forms in 1 or 2 state variables, i.e., the so-called elementary catastrophes, i.e., fold, cusp, swallowtail, hyperbolic umbilic, elliptic

umbilic, butterfly, and parabolic umbilic [21,35,36,44]. Thom's theorem applies for potentials depending on less than five control variables, pointing out essentially that (under suitable conditions) there are only seven specific categories for structure-related variations [21,22,36,44].

Identification of the catastrophe should be achieved by examining the nature of the CPs in the configuration of the nuclei that constitute the bifurcation point $(\mathbf{r}^*, \mathbf{R}^*)$. So far, and within the BET perspective, only three types of elementary catastrophes (i.e., cusp, fold, and elliptic umbilic) have been claimed to be found as fingerprints associated with the elementary processes driving a chemical transformation. The subject remains indeed open to further research. We here stress that only precise monitoring of the evolution of the CPs of $\eta(\mathbf{r}; \mathbf{R})$ along a reaction path, i.e., following changes in the number and type of all CPs and hence, the determination of the exact form of the universal unfolding [21,35,36,44], will enable the proper association of bifurcation catastrophes to the key breaking/forming chemical bonding events. The unfoldings are simply parametric polynomials of degree equal or greater than 3 in which it is possible to approximate the function $\eta(\mathbf{r}; \mathbf{R})$ in the locality of a topological bifurcation, after fulfillment of specific requirements [22,68]. The set of external parameters splits the nonhyperbolic CP into a new set of Morse CPs, i.e., a collection of finite and isolated nondegenerate CPs. As a result, degeneracy is overcome. Therefore, we stress that following the evolution of the determinant of the Hessian matrix for CPs of the $\eta(\mathbf{r}; \mathbf{R})$ along a reaction path will always provide a suitable and robust tool for identifying when a CP will become nonhyperbolic or degenerate. Considering both the universal unfolding and the strict fulfillment of the Poincaré–Hopf theorem, it is easy to probe [21,35,36,44] for local functions on $\mathbb{R}^3$ that the simplest type of Thom's bifurcations (i.e., the fold one) implies the creation/annihilation of a pair of Morse critical points from/into a wandering point (wp), i.e., $wp \leftrightarrow (3, -3) + (3, -1)$; $wp \leftrightarrow (3, -3) + (3, +3)$; $wp \leftrightarrow (3, -1) + (3, +1)$; and $wp \leftrightarrow (3, +1) + (3, +3)$. Similarly, a cusp catastrophe implies 24 possibilities, given that such a bifurcation separates one Morse critical point on one side from three critical points on the other side, e.g., $(3, -3) \leftrightarrow (3, -3) + (3, -3) + (3, -1)$; $(3, -3) \leftrightarrow (3, -3) + (3, -3) + (3, +3)$; and so on. A note of caution should be, however, always kept in mind behind the consideration of the basic model of gradient systems, i.e., saddle connections cannot affect the local function [22,68].

16.2.1 A warning on identifying elementary catastrophes

It should be recalled at this point that degenerate critical points lead to catastrophes if specific conditions are satisfied [21,35,36,44]. Catastrophe theory provides the mathematical framework for describing or predicting discontinuous transitions between the possible alternative stable states of a system [21,35,36,44]. However, as emphasized in the present work, proper application of catastrophe theory will demand the capacity of identifying the control

parameters as the associated underlying relationships. Very recently, we have evidenced that the analysis of sequences of molecular graphs based on single changes in the number and type of CPs, as exemplified in most insofar applications [12–14,37,38,40,47], constitutes indeed an imprecise procedure that might yield an improper characterization of the bifurcation catastrophes. Moreover, we should emphasize that the assignment of the type of catastrophe performed on the exclusive consideration of the appearance/disappearance of (3, −3) CPs is simply incorrect. Such a process should be complementized by examining additional properties of the Morse critical points in the neighborhood of the catastrophe. Proper knowledge and characterization of the nature of catastrophes will require considering all implied critical points (i.e., maxima, saddles, and minima) [42]. Therefore, we emphasize that a significant formal analysis based on the BET formalism will require examining the *behavior of the determinant of the Hessian matrix* and the *associated mobility of complete sets of CPs* of ELF along the reaction path [1,2,62].

16.3 The case of [4+2] and [2+2] pericyclic cycloadditions

The suitability of the characterization of the local character of the ELF function provides a way to the proper identification of the associated *elementary catastrophes*, i.e., the analysis of how the equilibria of ELF change as the control parameters change. And this is precisely the attractive simplification (i.e., oriented to correctly identifying the control parameters) underlying any effort concerning applying the elementary catastrophe theory [21,35,36,44]. We focus on two simple applications recently developed in our group. We hope these results can further stimulate the discussion of research [1,2,61,62] concerning the detailed identification, characterization, and analysis of chemical processes and reactivity within the methodological framework that offers bonding evolution theory approach [42] based on the combined use of topological analysis of ELF and the catastrophe theory.

16.3.1 The Diels–Alder reaction between butadiene and ethylene

The understanding of the pericyclic processes [10,69] Diels–Alder (DA) reaction mechanism has an impact on all areas of chemistry [8,70]. The nature of ‘concerted’ mechanisms [71] is still the subject of intense debate, at least regarding the local rearrangement of electron density along the single kinetic step [3,5,7,12–14,69,72]. This process has been the focus of renewed attention within the aim of identifying the nature of catastrophe bifurcations [21,35,36,44], as exemplified by the analysis of the prototypical DA reaction between 1,3-butadiene and ethylene (Fig. 16.2) [1,13,14]. Results based on the combination of B3LYP, KMLYP, M06-2X, MPWB1K, and ω B97X-D functionals, and the 6-31G(d), 6-31+G(d,p), and 6-311G(d,p) basis sets, as implemented in the Gaussian 16 package of programs [73], confirm that topological properties are stable enough

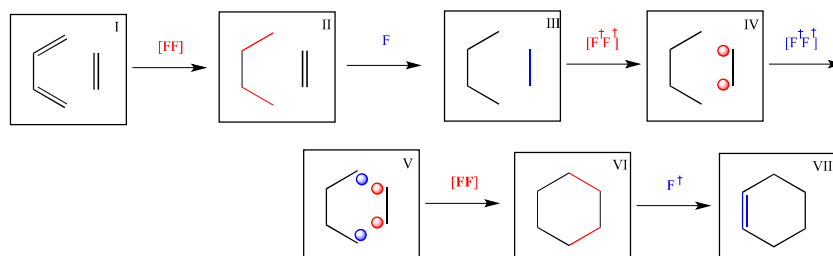


FIGURE 16.2 Simplified Lewis-type formula representation (excluding hydrogen atoms) based on ELF for the sequence of electronic stages implied along the single step of the Diels–Alder reaction between 1,3-butadiene and ethylene to yield cyclohexene. BET analysis reveals that all bifurcations separating the seven structural stability domains I–VII (including those associated with the onset of the formation of the CC bonds) are of fold type [1].

to the choice of the level of the theory, provided the fundamental physics of the system is appropriately being considered. Complete IRC [43] paths connecting the transition structures to reactants and products have been generated with a step size of $0.001 \text{ amu}^{1/2} \text{ bohr}$. The topological analysis of ELF, characterization, and visualization of the associated phase-space portrait at each point incorporating all types of CPs have been performed using the Multiwfn [74] and VMD [75] programs. For each molecular configuration along the path, the fulfillment of the Poincaré–Hopf theorem was strictly verified, ensuring topological consistency.

Based on the performance of the above DFT functionals [76,77], we observe that the ELF topology and its variation along the path are numerically stable, which should always be verified to validate conclusions from the BET analysis further. This fact is essential concerning the process of identification of the elementary catastrophes within a BET framework [21,35,36,44]. The proposed methodological framework (i.e., based on the rigorous analysis of the determinant of the Hessian and the relative mobility of implied critical points along the reaction coordinate) is suitable enough to clarify the nature of each catastrophe unambiguously, allowing an adequate topological characterization that is indeed coherent with all formalities behind the theory [1].

For the DA reaction, we found, as also previously evidenced [13], seven SSDs separated by ten catastrophes as specific signatures for such a single-step reaction mechanism. Note that Fig. 16.1 is a representative molecular graph for SSD-I. However, our analysis reveals that all the implied bifurcations should be categorized as *fold* ones (F and $F^\dagger$) following Thom’s classification [35,36,44] and not as *cusp* for some stages as it was first claimed [13]. For this reaction process, the F and $F^\dagger$ bifurcations belong with no exceptions to the following types: $F : (3, -3) + (3, -1) \rightarrow wp$, and $F^\dagger : wp \rightarrow (3, -3) + (3, -1)$ [1,2]. Surprisingly, no flags for cusp bifurcations have been detected along the intrinsic reaction path, even in those corresponding to the region where the two new CC bonds are formed, i.e., the reaction mechanism (as described through the

IRC) should imply a *sequence of fold catastrophes*: $C_4H_6 + C_2H_4$: $7-[FF]F[F^\ddagger F^\ddagger][F^\ddagger F^\ddagger][FF]F^\ddagger-0$: C_6H_{10} , where eight of these bifurcations occur concurrently (represented in squared brackets) [14]. The catastrophes associated with forming the two single CC bonds are indicated in bold font and appear after the transition structure is overpassed. Remarkably, all forming/breaking processes of the chemical bond along this cornerstone reaction mechanism can be associated with the simplest unfolding within the framework of elementary catastrophe theory [21,35,36,44]. How can we expressly understand the DA reaction described in a topological framework? Results tell us that we can always choose only one ‘external’ parameter (related to the reaction coordinate space) to describe each bonding change event throughout the process. It is crucial in this point to note that the ELF maxima in the terminal C centers in the butadiene fragment are responsible for the formation of the disynaptic basin associated with the new CC bonds, just after the collision and annihilation of the ELF maxima centered on the C centers in the ethylene fragment and the saddle $(3, -1)$ CP already present in the CC bonding region [1,2]. Furthermore, and based on the above observations, it seems that the main changes in the DA bonding processes, as represented by the topology of ELF, should be related to the fold catastrophes *given the inherent asymmetry of the electron distribution in the implied fragments* [1,2]. Furthermore, it can be expected that cusp catastrophes (or even higher-dimensional ones) will be entirely associated with highly symmetry conditions, such as exemplified in any homolytic bond rupture/formation implying completely equivalent fragments (e.g., the homolytic CC bond breaking in ethane features a cusp catastrophe of the type $C : (3, -3) \rightarrow (3, -3) + (3, -1) + (3, -3)$) [42]. This subjacent hypothesis merits further systematic work to test its validity. The way the catastrophe signatures vary in function of the electronic nature of the reactants is a subject open to further research [3–7,25,57,78].

The single control parameter can always be chosen as the interatomic distance between the implied carbon centers, allowing us to adequately describe all the catastrophic bifurcations in the phase space associated with chemically significant bond formation/bond rupture events. On the other hand, cusp catastrophes require two control parameters, one of which can be taken as the distance between two atoms; however, the other is not always easily identified, obscuring the application of the BET analysis in the examination of chemical reactions. In light of these findings, available BET results implying cusp or elliptic umbilics [12–14,37,38,40,47,78] might require some careful reexamination.

16.3.2 The photochemically induced addition of two ethylenes

By considering next the case of concerted 2+2 cycloaddition of two ethylenes [8], a prototypical model described as a ground-state forbidden/excited-state allowed process within the classical Woodward–Hoffmann rules [9], we can explore the performance of the methodology in systems implying a crossing

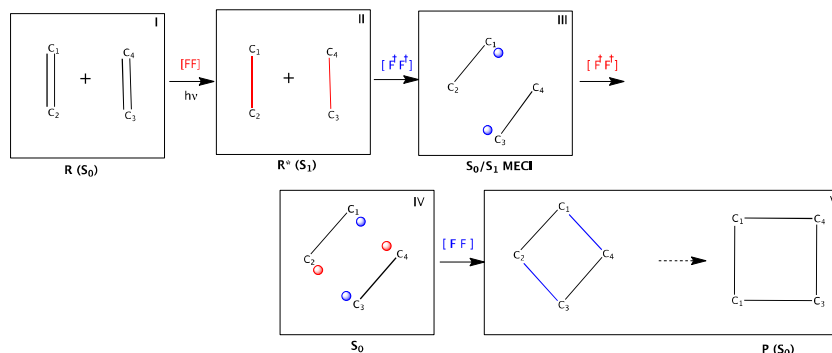


FIGURE 16.3 ELF-based Lewis-like representations along the lowest $2s+2s$ photoinduced cycloaddition path in terms of the sequence of structural stability domains I-V [1,3,4,7,11,12,14,15,28]. The excitation process separates the SSD-I reactant ground state $R(S_0)$ and the SSD-II featuring the reactant excited state $R^*(S_1)$ which yields the evolution of the system along the first singlet excited electronic state S_1 . SSD-III corresponds to the conical intersection MECI point neighborhood, whereas SSD-IV and SSD-V belong to the S_0 ground state [2].

seam [3,6,10] and conical intersections [10] as the main decay channel connecting singlet electronic states S_1/S_0 for the $2s+2s$ (face-to-face) cycloaddition [1,8,11,12]. It is now well accepted that the most favorable $2s+2s$ path implies a conical intersection (MECI) with a rhomboidal configuration [7,28]. Regarding chemical bonding in excited states [22,23,26,48], the ELF performance has been explored only in a few systems [22,24,49,50]. Exploring changes of electron density or derived quantities involving excited states and conical intersections have been the subject only of more recent applications [20–26]. A simplified representation of such an ‘evolution of the bonding nature’ can be observed in terms of the Lewis-like picture represented in Fig. 16.3 as derived from a BET perspective [1,2]. To properly consider the multiconfigurational nature of the problem at hand, calculations were performed within the MC-SCF theoretical background. The $2s+2s$ reaction path was modeled via the Nudged Elastic Band (NEB) approach [55] at the CASSCF(4,4)/Def2-SVPD level of theory using the Gaussian16 [53] and ORCA v4.2.1 [54] packages of programs. Dynamical correlation effects were further considered at the NEVPT2(4,4)/Def2-TZVPD. The chosen level of theory provides an excellent energetical agreement with the available experimental [59], and already well-known highest level theoretical [16,60] characterizations of the excited state of ethylene and the $2s+2s$ reaction path [1–3,11,12,14]. The minimum energy paths contain thus the evolution of the reacting system in the excited state S_1 towards the MECI, followed by the decay to the ground state S_0 in the direction of the cyclobutane product. The topological analysis of ELF was carried out using the Dgrid v5.2 [56] and Multiwfn v3.7 [57] programs. As in the case already discussed above, the identification of the bond-breaking/bond-formation events along the path was carried out following the analysis of the determinant of the Hessian and the relative

mobility of the critical points [44]. The ELF function was calculated using the natural orbital-based formulation described by Matito et al. [58] using some derivations discussed recently [50].

The results allow us to evidence that electron localization decreases in the unsaturated CC bonding regions of both ethylenes [1,2]. The ELF topology changes observed in the Frank–Condon domain can formally be associated with two simultaneous fold catastrophes [45], each located in the double CC bonding region (associated with the annihilation of a maximum and a saddle in the C=C bonding region). As also emphasized for the Diels–Alder reaction [44], the sudden changes in the ELF topology can be here also precisely associated with the simplest elementary Thom’s universal unfolding [42,43,45]. Therefore, the onset of the evolution of the system along the face-to-face path involving a conical intersection seems naturally associated with the activation of the carbon center regions over the excited surface S_1 as a consequence of the depletion of electron density from the CC double bond region. We have found five additional critical variations of the ELF topology along the entire path connecting the R^* and P configurations. All these bifurcations are associated with fold bifurcations [1,2]. Therefore, the most favorable reaction mode $2s+2s$ (face-to-face) involving a rhomboidal conical intersection S_1/S_0 can be represented through the sequence of SSD configurations that have been fully characterized. Following the standard accepted notation [14], the sequence of catastrophes can be written as: $C_2H_4 + C_2H_4$: $5-[FF][F^\dagger F^\dagger][F^\dagger F^\dagger][FF]-0$: C_4H_4 . The new CC bond formation does not occur in the S_1 excited state, but in the ground state. It is only possible after the systems evolve from the rhombohedral MECI to the electronic state S_0 . This prediction constitutes a challenge for both theoretical [20,22,23,25,26,30,34] and experimental [18,19,61] methodologies.

16.4 Conclusions

This work has revised some basic concepts concerning the bonding evolution theory. After a brief on the fundamental ideas behind the topological analysis of the ELF and the catastrophe theory, we emphasize the need to carefully examine the behavior of the determinant of the Hessian matrix and the associated mobility of ELF critical points along the reaction path to proper identification of catastrophes. Detailed analyses are referred to in the primary literature, as here we have just stressed the general conclusions in each of the two applications discussed. Both in the case of the thermally induced Diels–Alder reaction between 1,3-butadiene and ethylene and the photochemically induced cycloaddition of two ethylenes, our methodology reveals that the different structural stability domains are separated by a sequence of fold elementary catastrophes [1,2]. This fact offers a simple perspective for the rationalization of the CC bond formation in pericyclic reactions in terms of the simplest Thom’s universal unfolding [43–45] for the elementary catastrophe, namely the one-(state) variable, one-(control) parameter function. These results invite us to reexamine the commonly accepted rationalization of both types of reaction mechanisms [61,62].

Further efforts are welcome to determine if the observed features constitute a general signature in the realm of pericyclic reactions [44,50,52].

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