J. Phys. Chem. A **1997,** *101,* 7277−7282

Characterization of Elementary Chemical Processes by Catastrophe Theory

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Received: March 27, 1997; In Final Form: July 7, 1997⊗

The topological analysis of the electron localization function (ELF) provides a convenient theoretical framework to characterize chemical bonds. This method does not rely on the particular approximations that are made in actual quantum chemical calculations of the electronic structure. In principle, it can be applied to exact wave functions as well as to experimental electron densities. Introduction of a control space, such as a set of reaction pathways, allows extension of the analysis to chemical reactions. The study of the bifurcations occurring during such processes is of particular interest for their classification and their qualitative description. This is achieved with the help of René Thom's catastrophe theory. The following examples are discussed: the ammonia inversion, the breaking of the ethane C−C bond, and the breaking of the dative bond in NH_3BH_3. The types of catastrophe and their unfolding have been determined for each of these processes. As by-products, nonempirical definitions of covalent and dative bonds are proposed.

1. Introduction

The theory of chemical reactivity mostly relies on an approach related to the energetics and to the dynamics of the reaction. One of the main objectives is the prediction and understanding of the kinetics from the analysis of the energy hypersurfaces, functions of the nuclear coordinates, related to the channels connecting the reactants to the products.[1−5] The kinetic and thermodynamical constants of the reaction are evaluated by a statistical treatment. In this framework, the qualitative pieces of information are provided by the set of nuclear coordinates, which defines a given point of a hypersurface, and by the electronic state that labels the energy hypersurface. In this way, it is possible to get some insight into the reaction mechanism. From a purely qualitative point of view, a chemical reaction can be defined as the changes in the chemical bonds of a system of atoms occurring upon a change in the nuclear configuration. It is difficult to work from this definition, as the chemical bond is not an observable to which a numerical value can be assigned. This concept belongs to a system of representation settled by chemists on the basis of experience. A nonempirical qualitative study of a reaction, from the previously mentioned standpoint, requires a mathematical model that associates a collection of mathematical objects, such as numbers or single points, to the chemical representation of the system. Topological theories of the chemical bond[6,7] provide such mathematical structures. These theories are based on the topological analysis of the gradient field of well-defined local functions (which can be in principle evaluated either from experiments or from exact quantum mechanics), which depend upon a set of external parameters, such as the nuclear coordinates, defining the control space.

The bonding evolution theory (BET) outlined in this paper intends to provide the conceptual tools necessary to perform a precise and close description of chemical reactions within the topological framework. Most of the basic ideas have been originally developed by Richard Bader and co-workers in their study of the electron density properties. As it will be shown, the choice of the electron localization function (ELF), rather than the electron density to study chemical properties, allows one to overcome the limitations encountered in the approach based on the electron density distribution. Particularly, it provides a clear demarcation between chemical and nonchemical processes.

The topological description of the chemical bonding is rather a new point of view in chemistry which is not yet widespread in the community. For this reason it is necessary to avoid any misunderstanding and, more particularly, any confusion between the concepts of the topological approach and those of the standard ones. In this respect, the role of the vocabulary is predominant. To name the objects emerging out of our theory, we use mathematical (topological) terminology for nouns and chemical words for adjectives provided they do not introduce any ambiguity.

We are aware that this new vocabulary represents an additional difficulty for the reader. For this reason we have devoted two paragraphs to introduce and define the mathematical words used in the topological theory of dynamical systems which is the mathematical foundation of the topological description of the chemical bonding and reactions.

2. Theory

2.1. Topological Concepts. Consider a system (Σ) and let M be the *manifold* of its *internal states*. $y_j(t;x \in \mathrm{R}^N;\, c_\alpha \in W) \in M$ are the *state variables* of (Σ), which are solutions of a system of n equations defined over a space R^N, the elements of which are $x = (x_1, x_2, ..., x_N)$. The general expression of these equations is

$$F_i\left(y_i;c_\alpha;t;\,\frac{\partial y_j}{\partial t},\,\frac{\partial^2 y_j}{\partial t^2},\,...;\,x_l;\,\frac{\partial y_j}{\partial x_l},\,\frac{\partial^2 y_j}{\partial x_l x_m},\,...;\,\int \mathrm{d}x_1,\,...\right) = 0 \tag{1}$$

$$1 \le i, \quad j \le n$$

$$1 \le l, \quad m \le N$$

$$1 \le \alpha \le k$$

in which c_α denotes the *control parameters* which are the elements of the set W referred to as the *control space* of dimension k. In the case of applications related to physics or chemistry such parameters may be related to external constraints

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⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1997.

S1089-5639(97)01150-X CCC: $14.00

TABLE 1: Nomenclature Used for Hyperbolic Critical Points in R^3: The Rank Is the Number of Nonzero Characteristic Exponents, the Signature the Difference between the Numbers of Positive and Negative Ones

type	index $I(\mathrm{R}^3,\mathbf{r}^{(s)})$	(rank, signature)
local maximum (attractor)	0	(3, −3)
saddle point	1	(3, −1)
saddle point	2	(3, +1)
local minimum (repellor)	3	(3, +3)

(i.e. electric or magnetic field, external pressure, temperature). x and t may conveniently be regarded as space and time coordinates.

When eq 1 involves neither integrals, space derivatives, nor space dependence, it can be written as

$$F_i\left(y_j;c_\alpha;t;\frac{\partial y_j}{\partial t},\frac{\partial^2 y_j}{\partial t^2},\ldots\right)=0 \tag{2}$$

Moreover if only first derivatives $\partial y_i/\partial t$ appear in eq 2, it can be written as

$$\frac{\partial y_i}{\partial t}=f_i(y_j;c_\alpha;t) \tag{3}$$

This special system of equations is called the *dynamical system*. The right-hand side of eq 3 may be alternatively interpreted as a vector field $X(M,W,t)$ while an analogy with a velocity field in M can be done for the left-hand side. Therefore, eq 3 appears to be a kind of motion law in the space of the internal states of (Σ). Integration of eq 3 with a given set of initial conditions yields a unique solution $y(c_\alpha,t)$ which is a *trajectory* in M. Any trajectory begins and ends in the neighborhood of points of M for which $X(y^{(s)}\in M)=0$. These points are the *critical points*,[8] also called *singular points* or *equilibrium points*. The eigenvalues of the matrix $H_{ij}(y^{(s)})=(\partial f_i/\partial y_j)_{y=y^{(s)}}$ are the *characteristic exponents* of X at $y^{(s)}$. A critical point is called *hyperbolic* or *elementary* if none of its characteristic exponents has zero real part; it is characterized by its *index*, $I(X,y^{(s)})$, which is the number of positive eigenvalues (counting multiplicities) of its H_{ij} matrix defined above. The Poincaré−Hopf theorem states that if M is compact and X has only isolated hyperbolic critical points, then they fulfill the following relation:

$$\sum(-1)^{I(X,y^{(s)})}=\chi(M) \tag{4}$$

In eq 4, the sum runs over all critical points of X, and $\chi(M)$ is the *Euler characteristic* of M. A critical point is either a local maximum, a local minimum, or a saddle point. Table 1 reports the type of hyperbolic critical points in the case of a real function $f(\mathbf{r})$: $\mathrm{R}^3 \rightarrow \mathrm{R}$. For a given point $y_0 \in M$ the limit sets of $y_0(c_\alpha,t)$ for $t \rightarrow -\infty$ and $t \rightarrow +\infty$ are referred to as α-*limit* and ω-*limit*, respectively. A critical point with $I(X,y^{(s)})=0$ is also called an *attractor*, attractors are only ω-limits. The set of points having a given attractor as ω-limit is called the *basin* of this attractor. The set of trajectories that have a given critical point as a α-limit is called the *unstable manifold* of this critical point, whereas the *stable manifold* is defined as the set of trajectories for which it is the ω-limit. In the R^q the dimension of the stable manifold is equal to the index $I(X,y^{(s)})$; the dimension of the unstable manifold is $q - I(X,y^{(s)})$.

If in eq 3 f_i is time independent, the dynamical system is said to be *autonomous*. Moreover, in this case, f_i locally may be the component of a force derived from the *potential function* $V(y_j;c_\alpha)$. Thus the gradient vector field of a well-defined local function $V(y_j;c_\alpha)$ is called a *gradient dynamical system*.

$$\frac{\partial y_i(c_\alpha;t)}{\partial t}=\frac{\partial V(y_j;c_\alpha)}{\partial y_i} \tag{5}$$

The behavior of a dynamical system is determined by its equilibria

$$\partial y_i(c_\alpha;t)/\partial t=0$$

In the case of a gradient system, these are defined by the equation

$$\partial V(y_j;c_\alpha)/\partial y_i=0$$

2.2. Elementary Catastrophe Theory. Up to now, the quantities c_α have been implicitly considered as constants. *Elementary catastrophe theory* studies how the equilibria $y_i(c_\alpha)$ of a gradient system change as the control parameters c_α change in the special case where $k=\dim(W)\leq 5$. In this context the evolution of the equilibria can be studied by considering the behavior of the *Hessian* matrix $H_{ij}=\partial V(y_k;c_\alpha)/\partial y_i\,\partial y_j$ of $V(y_k;c_\alpha)$. If $H_{ij}(c_\alpha)|_{y=y^{(s)}}\neq 0$, then it is said that the critical point is hyperbolic; in the other case it is called *nonhyperbolic*. The configuration of the control parameters c^*_α for which det $H_{ij}(c^*_\alpha)|_{y=y^{(s)}}=0$ is called the *bifurcation point*. The set of c_α for which the Hessian matrix of a given critical point is nonzero defines the *domain of stability* of the critical point. A small perturbation of $V(y_i^{(s)};c^*_\alpha)$, brings the system (Σ) from a domain of stability to another. If none of the critical points of the system change, then (Σ) is located in a *domain of structural stability*. Thom's theorem[10] states that in the neighborhood of $(y^{(s)};c^*_\alpha)$ after a smooth change of the variables, the potential can be written as[1]

$$V(y;c_\alpha)\doteq u(y_1,\ldots,y_l;c_\alpha)+\sum_{i=l+1}^{n}\lambda_i(c_\alpha)y_i^2 \tag{6}$$

The symbol $\doteq$ means equal after a smooth change of variables. In this equation, $u(y_1,\ldots,y_l;c_\alpha)$ is the *universal unfolding* of the singularity, it is a polynomial function of degree higher than 2 of a "canonical" form depending upon the l variables with zero eigenvalues, l is called the *corank*, and the λ_i's are the $n-l$ nonzero eigenvalues. The unfolding contains all the information about how $V(y;c_\alpha)$ may change as the control parameters change.

Thom has classified these universal unfoldings according to their corank and to the dimension of the control space W called the *codimension*. Thom's classification is reported in Table 2.

2.3. Adaptation to Chemistry. The mathematical concepts outlined above provide a suitable background to every science that studies the evolution of a process located in a system (Σ). To do this, we just need a local, well-defined function $f(y;c_\alpha)$ describing the property involved in the process. This function will play the role of $V(y;c_\alpha)$ seen before.

In this section our method of analysis is outlined, and therefore the function $f(y;c_\alpha)$ will be considered as given and always well-behaved. As already mentioned, the aim of this study is to provide information about elementary chemical processes and the change in the bonding they involve. As we consider the bonding as a local property of the matter, the potential function should be a direct space function, and therefore the y_j state variables considered in the previous sections are the real space coordinates $\mathbf{r}$, whereas the c_α are the set of nuclear coordinates $\mathbf{R}$. The critical points, those points for which $\nabla_{\mathbf{r}}f(\mathbf{r},\mathbf{R})=0$, and their connectivity will determine a molecular graph which will be discussed in a further section. Upon variation of the nuclear coordinates, the molecular

TABLE 2: Thom's Nomenclature of Elementary Catastrophes

name	codimension	corank	universal unfolding
fold	1	1	$x^3 + ux$
cusp	2	1	$x^4 + ux^2 + vx$
swallow tail	3	1	$x^5 + ux^3 + vx^2 + wx$
hyperbolic umbilic	3	2	$x^3 + y^3 + uxy + vx + wy$
elliptic umbilic	3	2	$x^3 - xy^2 + u(x^2 + y^2) + vx + wy$
butterfly	4	1	$x^6 + ux^4 + vx^3 + wx^2 + tx$
parabolic umbilic	4	2	$x^2y + y^4 + ux^2 + vy^2 + wx + ty$

structure evolves. Bond paths between atoms are created, others destroyed. Along the reaction path, the system goes from one region of structural stability to another one, and this evolution can be described in terms of bifurcation catastrophes[9] in the sense of René Thom.[10] As a first step toward a more complete theory, we will only consider those chemical processes that occur on a single Born–Oppenheimer energy surface when the set of nuclear coordinates is varied. As already mentioned, a chemical reaction can be viewed as successive structural stability domains, each corresponding to a given bonding state. In each structural stability domain, the critical points are hyperbolic and their number fulfills the Poincaré–Hopf theorem eq 4, in which for finite and periodic chemical systems in R^q, $q \leq 3$, the Euler characteristic is 1 and 0, respectively. The transition from one bonding state to another is achieved by a bifurcation catastrophe at which some of the critical points become nonhyperbolic, in a such way that the Poincaré–Hopf theorem is always fulfilled. The latter assertion is easy to understand if we think that f is always well-behaved and that the manifold of definition of $\nabla_{\mathbf{r}} f(\mathbf{r}, \mathbf{R})$ remains the same, R^q, for any nuclear configuration. The identification of the catastrophe will be done by studying the behavior of the critical points $\mathbf{r}^{(\mathbf{s})}$ involved at the bifurcation point $\mathbf{R^*}$, hereafter referred to as the *bifurcation state*, and by trying to set up the Taylor development of $f(\mathbf{r}, \mathbf{R})$ about $(\mathbf{r}^{(\mathbf{s})}, \mathbf{R^*})$ in one of the "canonical" forms of Table 2. This gives access to the unfolding of the catastrophe, which is a simple parametric expression of the local behavior, and therefore to the dimension of the active control space which is the number of parameters of the unfolding.

As we have to deal with calculations on chemical systems the problem of the choice of the method of calculations and even of the basis set can be raised. For these reasons we introduce the term of *minimal reliable level of calculation* as being the simplest level that gives a good description of the system. In a region of structural stability, the improvement of the wave function induces a weak perturbation of the dynamical system which does not modify its phase portrait. The only effect should be a displacement of the locations of the bifurcation states in the space of the control parameters. A better calculation than the minimal reliable one, therefore, doesn't provide any change in the molecular graphs of the structurally stable states occurring along the reaction path. The method outlined above provides, in its spirit, a local model of reactive processes that is free from any technical assumption made to calculate an approximative wave function. Therefore, the evolution of the molecular graph shape contains the underlying chemical information.

2.3.1. Bader's Theory of Atoms in Molecules. In Bader's theory of atoms in molecules,[6] the local function investigated is the charge density $\rho(\mathbf{r})$. The attractors of the charge density gradient field are generally located on the nuclei. The unstable manifolds of the (3, −1) critical points constitute the bond paths that link the bonded centers to one another. Though this approach provides a nonempirical description of the structure, it has some weaknesses mainly due to the particular behavior of the charge density if one wants to describe a reaction. This theory has been successfully applied on the one hand to unimolecular reactions involving either isomerization or ring breaking (see ref 6 and references therein) and on the other hand to dissociative processes occurring in those systems possessing a non-nuclear attractor.[11−13] In both cases the catastrophe theory provides the convenient mathematical framework to describe the evolution of the system. However in the most general case of a bond dissociation, without a non-nuclear attractor, the study of the density doesn't allow the identification of any change in the structure. Consider for example a diatomic molecule. In this case, the control space parameter is simply the internuclear distance. For any value of the internuclear distance there exists a (3, −1) critical point between the two attractors, and therefore the system is structurally stable over the whole domain of the control parameter. Thus usually nothing happens. An alternative topological approach based on the density has been proposed by Mezey and co-workers,[23−26] who consider the change of the shape of bonding isosurfaces. This enables one to recognize formal species along the path that characterize the steps of the reaction. However, this method relies on properties which are not able to provide a description of the bonding such as is done by the density Laplacian or by ELF.

2.3.2. The Electron Localization Function. Our study is based on the Becke–Edgecombe[14] electron localization function (ELF) defined in eq 7, which is more appropriate to study bonding in molecules.

$$\eta(\mathbf{r}) = \frac{1}{1 + (D(\mathbf{r})/D_h(\mathbf{r}))^2} \qquad (7)$$

For a single-determinantal wave function built from Hartree–Fock or Kohn–Sham orbitals ϕ_i

$$D(\mathbf{r}) = \frac{1}{2}\sum_i |\nabla\phi_i(\mathbf{r})|^2 - \frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \qquad (8)$$

and

$$D_h(\mathbf{r}) = C_F\rho(\mathbf{r})^{5/3} \qquad (9)$$

$D(\mathbf{r})$ has the physical meaning of the excess of local kinetic energy density due to Pauli's repulsion,[15] and $D_h(\mathbf{r})$ is the Thomas–Fermi kinetic energy density, which can be regarded as a "renormalization" factor. In eq 9, C_F is the Fermi constant with value $C_F = 2.871$ au. The range of values of η is $0 \leq \eta \leq 1$.

Where electrons are alone or form pairs of antiparallel spins, the Pauli principle has little influence on their behavior and the excess local kinetic energy has a low value, whereas at the boundaries between such regions the probability of finding parallel spin electrons close together is rather high and the excess local kinetic energy has a large value.

The Silvi–Savin[7] approach of chemical bonding based on the topological analysis of the $\eta(\mathbf{r})$ function achieves a partition of the molecular space into basins of attractors having a clear chemical signification. These basins are either core basins organized around nuclei (with $Z > 2$) or valence basins in the remaining space. We will also make a distinction between the valence basins according to their *synaptic order* σ, that is by the number of core basins with which they share a common boundary;[16] see Table 3. The molecular graph, built from the $\eta(\mathbf{r})$ gradient field critical points, provides a complete representation of the bonding in a molecule accounting for the bonds, the lone pairs, and their organization around the cores.

TABLE 3: Nomenclature of Valence Basins: The Expression between Parentheses Corresponds to the List of the Core Basins Sharing a Boundary with the Valence Basin

synaptic order	nomenclature	symbol
0	asynaptic	V
1	monosynaptic	$V(X_i)$
2	disynaptic	$V(X_i, Y_j)$
≥3	polysynaptic	$V(X_i, Y_j, ...)$

Considering now any chemical process, our method provides basically three levels of information.

Current Level. In this kind of description only the number μ of basins in each region of structural stability is considered. According to the variation of this number (*morphic number*) between products and reactants three types of reaction are possible; we propose calling them *plyomorphic* ($\Delta\mu > 0$), tautomorphic ($\Delta\mu = 0$), and miomorphic ($\Delta\mu < 0$). Tautomorphic processes are either *isosynaptic* if the basin synaptic order is not changed or *diffeosynaptic* otherwise.

Medium Level. Here the evolution of the complete molecular graph is considered, which means the changes of the number and type of all the critical points.

Accurate Level. In this case the universal unfolding involved in the chemical process is determined.

The classification of the processes given above may be useful to determine whether a process is or is not a chemical reaction. Reactions involving only tautomorphic isosynaptic processes, such as the dissociation of van der Waals complexes, are not chemical reactions, whereas plyomorphic, miomorphic, and tautomorphic diffeosynaptic processes characterize a chemical reaction.

2.4. Molecular Graph. The concept of a molecular graph has been introduced by Bader. The molecular graph of the density is the set of the unstable manifolds of the (3, −1) critical points which connect bonded atom attractors to each other. This kind of molecular graph provides a complete description of the connectivity of critical points since attractors correspond to single points, (3, −1) saddle points to lines, (3, +1) to rings, and (3, +3) to cages. In the case of the ELF function $\eta(\mathbf{r})$ a straightforward generalization of Bader's scheme is hampered by a great number of critical points and also by peculiar connections that are possible between attractors. Therefore we have been led to complement Bader's rules for constructing molecular graphs, and so the $\eta(\mathbf{r})$ molecular graphs are obtained according to the following recipe.

1. Attractors are represented by points and labeled according to the nomenclature given in Table 3.
2. (3, −1) saddle points are represented by full lines that correspond to their unstable manifold
3. Exceptional (3, +1) saddle points, those linking several attractors to one (3, −1) critical point, are represented by empty triangles, and their connection with attractors by dashed lines.

These rules have been applied to draw the molecular graphs of NH_3, CH_3, BH_3, C_2H_6, and NH_3BH_3, represented in Figure 1. In all cases except for NH_3 and BH_3 only Bader's rules are necessary, so the numbers of vertices, edges, rings, and cages are identical to those of the critical points (in the case of CH_3, 5, 9, 7, 2, respectively). In NH_3, the eight full line segments correspond to the eight (3, −1) critical points. To get the number of (3, +1), one has to consider the seven rings involving at most one dashed line and for the three (3, +3) points the cages which do not contain any attractors. Finally considering the BH_3, the two particular (3, +1) points give rise to two cages.

3. Examples

As examples, we will successively consider the inversion of ammonia, the breaking of the ethane C−C bond, and the breaking of the B−N bond in BH_3NH_3. The Gaussian 94 software[17] has been used to carry out the calculations. They have been performed with polarized split valence basis sets either at the DFT (NH_3, BH_3NH_3) or CASSCF (CH_3CH_3) levels.

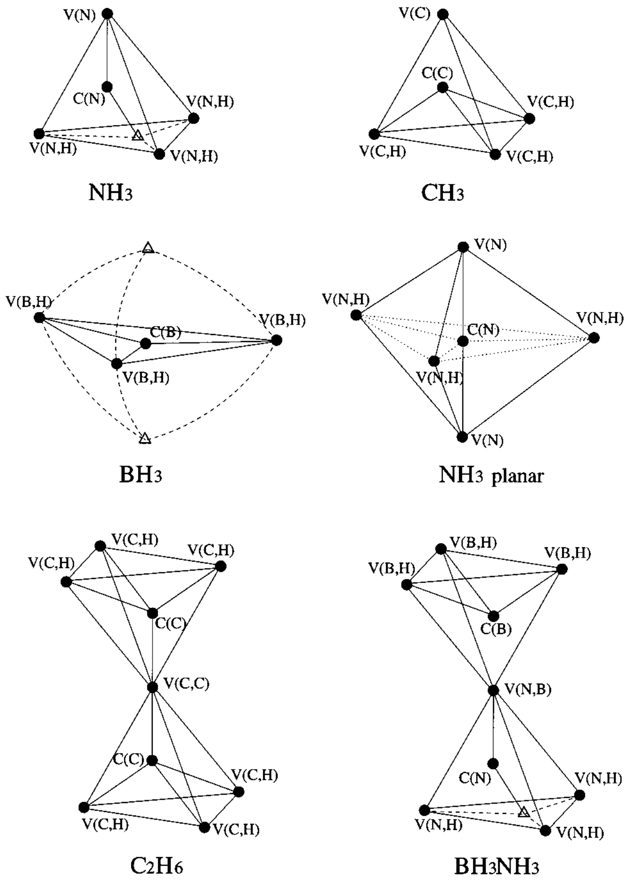

Figure 1. Molecular graphs of NH_3, CH_3, BH_3, NH_3 planar, C_2H_6, and BH_3NH_3. The attractors are represented by ● and the exceptional critical points of index 2 by △. Full lines correspond to index 1 critical point unstable manifolds, dashed lines to trajectories linking critical points of index 2 to attractors.

3.1. The Inversion of NH_3. The ammonia inversion can be considered as a simple unimolecular chemical reaction in which the nitrogen lone pair is transferred from one half-space to the other. The reaction coordinate is the angle, $\theta = (\pi/2) + \phi$, between the C_3 axis of the molecule and the N−H bonds. The initial equilibrium ground state geometry corresponds to $\phi = -21.6°$, the final to $\phi = +21.6°$, and the planar geometry to $\phi = 0$. The ammonia inversion is symmetrical with respect to $\phi = 0$, so only the interval of ϕ = -21.6° to $\phi = +21.6°$ will be explored. The evolution of the number and type of basins is represented in Figure 2A as a function of ϕ. In terms of the current level of description, a plyomorphic step takes place for $\phi = -15.2°$ which brings the system from the $-21.6° \leq \phi < -15.2°$ domain of structural stability (Figure 2A, α and β) to the $-15.2° < \phi < +15.2°$ one (Figure 2A, γ). Then for $\phi = +15.2°$ we have a miomorphic step which brings the system into a third domain of structural stability ($+15.2° < \phi \leq +21.6°$). The whole process of ammonia inversion is a tautomorphic one. Table 4 reports the numbers of critical points of each type in the three successive bonding states.

The symmetrical catastrophes occurring at $\phi = -15.2°$ and $+15.2°$ are also shown in Figure 2B. They correspond to the interconversion of two critical points, located in the center, of index 2 and 0, respectively, which is accompanied by a rotation of three critical points of index 1 around the molecular axis, (Figure 2B, a and b). This corresponds in a first step to the

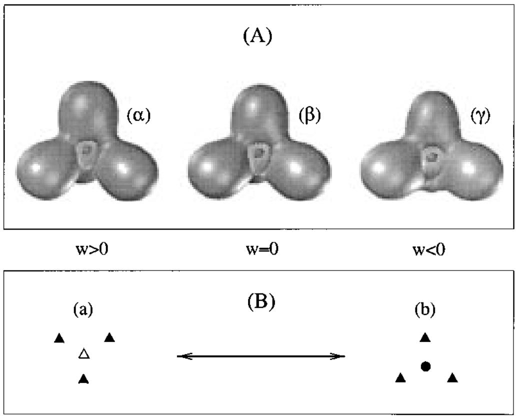

Figure 2. Representation of the ammonia inversion. In the upper part of the figure (A) the ELF = 0.8 isosurface[22] of ammonia shows the domains associated with the localization attractors for different values of the angle θ: left $\theta = 70°$, center $\theta = 74.8°$, right $\theta = 80°$. The lower part of the figure (B) sketches the elliptic umbilic catastrophe in the xy plane perpendicular to the C_3 axis. This figure, presented here in black and white, is available in color on the World Wide Web. Color code: magenta = core, red = valence monosynaptic, green = valence disynaptic, blue = protonated valence disynaptic. The critical points of index 0, 1, 2, and 3 are represented by the ●, ▲, △, and ○ symbols, respectively.

TABLE 4: Number of Critical Points for the Three-Domain, Two-Step Process of the Ammonia Inversion and the Poincaré−Hopf Theorem

domain of structural stability	$I = 3$	$I = 2$	$I = 1$	$I = 0$	P−H
$68.4° \le \theta < 74.8°$	3	7	8	5	1
$74.8° < \theta < 105.2°$	3	6	8	6	1
$105.2° < \theta \le 111.6°$	3	7	8	5	1

appearance of a second monosynaptic basin (plyomorphic step, see Figure 2A, γ) and in a second step to the annihilation of the first one (miomorphic step). The local behavior of $\eta(\mathbf{r})$ in the neighborhood of the critical points involved ($x = 0$, $y = 0$, $z = -1.0$) for $\phi = -15.2°$ and ($x = 0$, $y = 0$, $z = +1.0$) for $\phi = +15.2°$ is given, after a translation to the origin and a smooth change of variables by the unfolding:

$$\eta(x,y;u,v,w) = x^3 - 3xy^2 + w(x^2 + y^2) + ux + vy \qquad (10)$$

These two catastrophes are elliptic umbilics in Thom's classification.[10,18] The unfolding above contains three control parameters (u, v, w) and two space variables (x, y) also called in general variables of behavior in catastrophe theory.[18] Equation 10 provides a local description of the behavior of the dynamical system $\nabla_{\mathbf{r}}\eta(\mathbf{r},\phi)$. The variables of behavior are generalized coordinates. Those retained in the unfolding are those for which the characteristic exponents (the Hessian matrix eigenvalues for gradient dynamical systems) of the critical point change of sign. In the actual case of the ammonia inversion, x and y are the Cartesian coordinates in a plane perpendicular to the C_3 axis. The parameter w is identified with the umbrella opening angle ϕ and is of the form $\pm(\phi_c - \phi)$, ϕ_c denoting the bifurcation value. These are $\phi_c = -15.2°$ and $\phi_c = +15.2°$, for the first and second catastrophes, respectively. The parameters u and v account for distorsion from the C_{3v} point group symmetry of the molecule. When the D_{3h} symmetry is conserved along the reaction path, u and v are equal to zero. During the umbrella opening the population of the monosynaptic basins[16] (i.e. the one-electron density integrated over these basins) increases from 2.12e to 2.62e, whereas the total population of the NH disynaptic basins decreases from 5.76e to 5.25e, indicating an appreciable contribution of these latter basins to lone pair transfer.

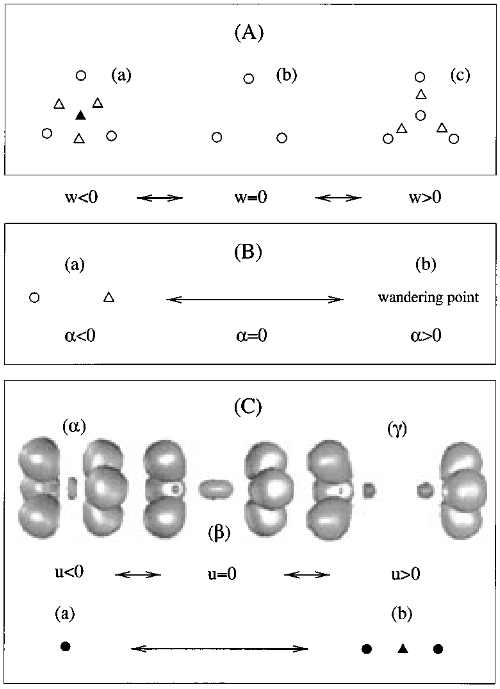

Figure 3. Representation of the ethane dissociation. (A and B) Core rearrangement: (A) elliptic umbilic catastrophe in the xy plane perpendicular to the reaction path, (B) fold catastrophe, (C) dual cusp catastrophe corresponding to the bond breaking. This figure, presented here in black and white, is available in color on the World Wide Web.

3.2. The Breaking of the Ethane C−C Bond.

The breaking of a single covalent bond is a typical plyomorph chemical process and can be illustrated by the case of ethane. The reaction coordinate is the C−C internuclear distance R. The dissociation involves three domains of structural stability separated by two bifurcation processes. The first step is a tautomorphic one and rearranges the valence basins around the carbon cores. It is composed of an elliptic umbilic (Figure 3A, a → Figure 3A, c), with $w = R - R_c$ and $R_c \approx 1.83$ Å, followed by three simultaneous fold catastrophes, Figure 2B, described by the unfolding below:

$$\eta(x;\alpha) = x^3 + \alpha x \qquad (11)$$

for which $\alpha = R - R_c$ and $R_c = 1.85$ Å and x is the direction joining the critical points of index 2 and 3, which give rise to a wandering point. The second step is a plyomorphic one and identified as a dual-cusp catastrophe,[18] which splits the C−C bond disynaptic attractor (Figure 3C, α, and Figure 3C, a) into two monosynaptic attractors and a saddle point of index 1 (Figure 3C, γ, and Figure 3C, b). This step characterizes the ethane dissociation. Its unfolding is given by

$$\eta(x;u,v) = -(x^4 + ux^2 + vx) \qquad (12)$$

In the actual case $v = 0$, $u = R_c - R$, and x is the reaction path direction. This step increases the number of basins by 1, as ethane becomes a biradical. The bifurcation state is located at $R_c = 3.34$ Å, a value which is close to the critical configuration as defined by Bunker and Panttengill[19,20] (i.e. the value of the reaction coordinate that minimizes the number of accessible internal states). In this region, the energy difference, with respect to the fully dissociated species, is on the order of 10 kJ mol^{-1}.[21]

3.3. The Breaking of the B−N Bond in BH_3NH_3.

The last example is the breaking of the B−N dative bond in BH_3NH_3. This reaction is an example of a tautomorphic

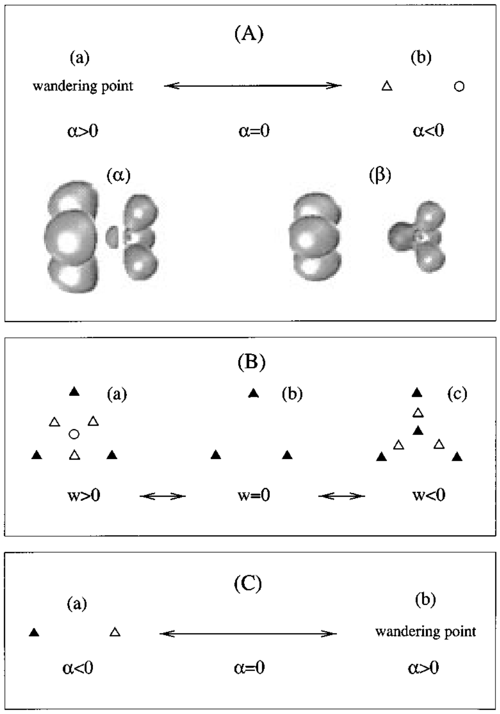

Figure 4. Representation of the NH_3BH_3 dissociation. (A) Fold catastrophe creating a second repellor and a saddle point of index 2; note that the green disynaptic domain becomes monosynaptic and red. (B and C) Boron core rearrangement. This figure, presented here in black and white, is available in color on the World Wide Web.

chemical process, the number of basins is constant, and the main feature is that the disynaptic basin of the B−N bond becomes monosynaptic. This is a two-step process. In the equilibrium nuclear configuration, the separatrix of the boron core basin and of the B−N disynaptic one is a single critical point of index 3, a repellor. The first step, at $R = 2.87$ Å, is a fold catastrophe in which a wandering point located in the disynaptic basin and in the neighborhood of the separatrix gives rise to a second repellor and to a saddle point of index 2, as shown of Figure 4A. This step transforms the disynaptic basin into a monosynaptic one. The second step, at $R_c = 3.83$ Å, is an elliptic umbilic (Figure 4B) followed by three simultaneous folds (Figure 4C), which completes the rearrangement of the hydrogen basins around the boron core.

4. Conclusions

The topological analysis sketched above provides a precise description of the evolution of the bonding associated with a chemical reaction. The method exhibits different steps, such as valence basin rearrangements, which cannot always be seen by other techniques, and emphasizes the importance of the topological properties of the space (i.e. the Poincaré−Hopf theorem). The unfolding of the catastrophes gives access to the dimension of the active control space. In the case of reaction for which the energy hypersurface has no saddle point defining the transition state, it is nevertheless possible to locate a bifurcation state on the basis of bonding criteria at the turning point corresponding to the catastrophe that breaks or forms a bond. In the previous static presentation of this approach,[7] no distinction was made possible between covalent and dative bonds. Both were referred to as belonging to the shared interaction. The analysis of bond breaking presented herein allows a clear characterization: in the covalent case, the dual-cusp catastrophe involves an attractor; in the dative one the fold catastrophe gives rise to a saddle point and a new repellor. Work is in progress to extend this approach to cases in which some of the control space parameters are discrete (for instance the label of the electronic state) in order to be able to treat in a consistent fashion reactions involving different channels and different energy hypersurfaces.

Acknowledgment. We wish to thank Prof. E. M. Evleth and Dr. A. Savin for their constant interest and Prof. M. L. Klein for critically reading and improving the draft manuscript. This work has been performed within the Groupement de Recherche Européen “Dynamique moléculaire quantique appliquée à la catalyse, à l’adsorption et à l’absorption”, supported by the Institut Français du Pétrole and the Centre National de la Recherche Scientifique (France).

Supporting Information Available: The color versions of Figures 2−4 (3 pages). Ordering information is given on any current masthead page.

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