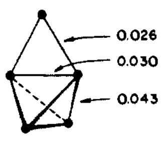
inner Cu in an adjacent stella quadrangula and has the same bond length as that within the metal tetrahedron. The calculated overlap populations are shown in **30**. The difference between the top and side bond strengths in the metal tetrahedron is increased. It is because more bonding states for the top edge are pushed up by interactions such as **31**. The bonding σ orbital in **26** has its electron density localized at the center of the bond, thus it interacts better with the $\mathrm{Cu_I}$ atom than other antibonding orbitals such as n.



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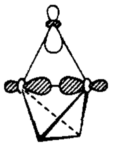

31

We have performed calculations on the stella quadrangula chain in which all inner sites or all outer sites are filled. When only all inner sites are filled, there are not enough M–X bonds to hold the structure from collapsing. If all outer sites are filled, there is the crowding effect between the metal atoms between adjacent stella quadrangula which gives unreasonably large negative overlap population values. The structure seems to be best filled alternatively, unless it expands to relieve the crowding effect. Figure 8 shows the COOP curves for the expanded structure, in which the shortest Cu–Cu and Cu–Te contacts are around 2.6 and 2.7 Å, respectively. Here again, the mixing of the Cu s,p band into the d band has reduced the antibonding feature at the top of the d band. Thus high occupancy of the d band is possible, even for an expanded structure with all outer or all inner and outer sites filled.

In this paper we have fleshed out the beautiful, seductive geometry of a spiral chain of face-sharing tetrahedra, by adducing several molecular realizations. The optimal electron counts for these hypothetical one-dimensional arrays are computed.

Still another, even more speculative potentiality for realizing the tetrahedral chain is to have each tetrahedron centered by a water molecule, with hydrogen bonds piercing the shared tetrahedral faces. Such a helical $(H_2O)_n$ chain would contain alternating nonequivalent water molecules, the chain formed by their O–H bonds and lone pairs. Stacking of such structures could lead to geometries related to the clathrates and gas hydrates.[25]

Acknowledgment. We are grateful to the National Science Foundation for its support of this work through Research Grant CHE8406119 and DMR85-16616-AO2, to Jane Jorgensen and Elisabeth Fields for their drawings, and to Joyce Barrows for the typing.

Appendix

The extended-Hückel method[26] was used in the calculations. The Bloch sum in the helical structure is $\sum_R e^{ik\cdot R} T_R \phi_i$, where ϕ_i is the atomic wave function in the unit cell, T_R is the translation-rotation operator, and k is the Bloch wave vector. The summation is over all cells. The energies and overlap populations are calculated with 100K points along the one-dimensional reciprocal space.

The interatomic distances used are the following: B–H = 1.28 Å, B–B = 1.80 Å,[27] Pt–Pt = 2.85 Å, Pt–C = 2.1 Å, C–O = 1.16 Å.[19] The extended-Hückel parameters are listed in Table I.

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A Global Approach to Molecular Symmetry: Theorems on Symmetry Relations between Ground- and Excited-State Configurations

Paul G. Mezey

Contribution from the Department of Chemistry and Department of Mathematics, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, S7N 0W0. *Received June 6, 1989*

Abstract: Several simple rules have been derived, providing new insight into the role of point symmetry in controlling the energetic stability of molecules and excited-state species. General symmetry conditions have been found that interrelate the ground-state and electronic excited-state energy minima, transition structures and other stationary nuclear arrangements of neutral molecules and ions, and excimers and exciplexes. By testing the point symmetry of a family of nuclear arrangements, one can predict the existence of stationary nuclear configurations within domains of a whole series of ground- and excited-state potential energy surfaces. The *catchment region point symmetry theorem* and various *vertical symmetry theorems* provide new tools for the analysis of potential surfaces and a rational strategy for the search for stationary points. The applications of the theorems are illustrated by examples.

The usual question asked when studying molecular symmetry problems is the following: what is the point symmetry group of some specified nuclear configuration? If the point symmetry is determined, then various conclusions can be drawn concerning the properties of the specified molecular species.[1–6]

In this study we shall view the problem from a different perspective and ask different questions: if all possible configurations of a collection of atoms is considered, then which are those configurations that have a specified symmetry? What predictions

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can be made concerning molecular stability and the presence of transition structures using symmetry as the only tool? It is tempting to assume that all is known that can be learned about molecules when using symmetry alone, without additional data. However, this is not the case, as it can be demonstrated by taking a global approach. Considering all nuclear configurations, many of which are highly unstable and have little direct physical significance, may appear a rather wasteful approach. However, this approach offers some unexpected shortcuts: it allows an easy recognition of many general features of potential energy surfaces, and it leads to a series of new relations of practical significance.

We shall consider symmetry in the context of potential energy surfaces. In dynamic studies the molecular potential energy is regarded as a function of a reaction coordinate, where the quantum mechanical adiabatic energy of all other coordinates (nonreactive modes) orthogonal to the reaction path is considered.[7,8] Here we shall use the nuclear configuration space approach where the potential energy surface is defined by assigning an energy value to each formal nuclear configuration.

The family of all possible arrangements of a given collection of atoms is regarded to form a *nuclear configuration space*, where each *point* of this space represents a *nuclear configuration*. The nuclear geometries of molecular systems of N atoms can be characterized by $3N$ cartesian coordinates of the nuclei in a $3N$-dimensional nuclear configuration space. Alternatively, the relative mutual arrangements of the N nuclei ($N \geq 3$) can be described by various choices of $3N-6$ *internal coordinates*, hence the dimension of a *reduced* or *internal* nuclear configuration space for the given *stoichiometric family* of molecular species is $3N-6$. Configuration spaces of the latter type are advantageous, since each relative nuclear arrangement corresponds to precisely one point of the space.

Most minor distortions of nuclear configurations do not change the chemical identity of molecular species; consequently, the various *stable molecules* of this stoichiometry as well as the *transition structures* of their interconversion reactions may be represented by *subsets* within the configuration space. With reference to the potential energy surface of a specified electronic state, for example, to that of the electronic ground state, these subsets can be chosen as various *catchment regions* of the nuclear configuration space:[9-11] the infinitely slow, vibrationless relaxation of each distorted nuclear arrangement within a catchment region leads to the same equilibrium nuclear configuration. In an approximate, classical sense, a catchment region may be regarded as the range of distorted configurations that preserves chemical identity. Note that in the above definition the equilibrium configuration is not necessarily an energy minimum; the definition applies for *any* stationary point, in particular, for saddle points of transition structures. The mathematical concept of catchment regions has been developed by Cayley[12] and Maxwell[13] who have applied it to geographical watersheds, hills, and dales. Other approaches to the subdivision of a configuration space, involving domains overlapping at their boundaries[14] or a differential geometrical approach based on the meta-IRC (intrinsic reaction coordinate) and on analogies with the cells of an organism[15,16] have been defined only with respect to stable species and not for transition structures. However, transition structures can also be defined directly, without reference to the stable species they mediate. The main advantage of the general catchment region definition[9-11] is that it applies equally to stable species and transition structures of the given electronic state, and it provides a single principle for a unique assignment of chemical identity labels to each point of a configuration space. One additional advantage is of particular relevance to our present study: there exists an important relation between catchment regions and molecular point symmetry.

For each electronically excited state (of each overall electronic charge), the stable chemical species are generally associated with a different partitioning of the nuclear configuration space into a different set of catchment regions. However, for any given nuclear configuration, the point symmetry of the nuclei is fixed and is not affected by the electronic state or net charge. Consequently, point symmetry is a link among all electronic states of neutral and ionic species of a fixed stoichiometry in a global sense, that is, for all possible nuclear configurations. We shall study the following questions: *which are those nuclear arrangements that have a specified symmetry, and can one deduce conditions on the energetic stability of these arrangements by using symmetry as the only tool*?

Some of the rules we shall derive will apply to individual catchment regions of a selected potential surface, some others to a whole family of potential surfaces of ground and electronically excited states of neutral and ionic species. By considering energy as a formal "vertical" dimension over the configuration space, these latter results will be summarized in "vertical symmetry theorems". Furthermore, by restricting the analysis to a few important internal coordinates, new symmetry theorems can be derived for relaxed cross sections of potential surfaces of ground and excited electronic states. The approach presented here complements well-known earlier results on the connections between stability and three-dimensional (3D) point symmetry of nuclear configurations, such as the extensive studies on the Jahn–Teller effect, on the symmetries of transition states, and on the more general problem of vibrations within potential wells.[17-25]

The Symmetry Domain Partitioning and Catchment Regions of the Nuclear Configuration Space

In this section we shall discuss two principles for the classification of nuclear arrangements: one based on symmetry and another on energetic stability.

The results we shall obtain are based on physical properties, hence they are independent of the actual coordinate representation of the configuration space. However, these results are easier to derive in some representations than in others. We shall use paths of infinitely slow relaxations and paths of steepest descent; depending on the representation, these two types of paths may differ, especially, if chemically motivated internal coordinates such as bond stretching and bond bending are used. The paths of relaxation represent physical conditions, hence any coordinate transformation converts a relaxation path into a relaxation path. A steepest descent path, however, is defined by the partial derivatives of the energy surface in the given coordinate representation, and the steepest descent property is not invariant to coordinate transformations. If in the transformation two of the coordinates are scaled differently, then on the scaled potential surface the ratio of partial derivatives according to the new coordinates may differ from the ratio of force components. Consequently, steepest descent paths and infinitely slow relaxation paths are not necessarily equivalent.[26]

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In particular, only in special, e.g., properly mass-weighted coordinate systems can one associate the infinitely slow relaxation of nuclei with a path of steepest descent on a potential surface. Since relaxation paths are special with respect to both catchment regions and symmetry conservation, the steepest descent path in a mass-weighted system is a tool that simplifies our treatment. Furthermore, as the term *symmetry* indicates, a global analysis of symmetry domain distributions is simpler if the configuration space has a *global metric*, that is, a suitable distance function defined for all possible pairs of nuclear configurations.

Both mass-weighting and a global distance function (metric) are easily available in a $3N$-dimensional configuration space. Unfortunately, in this space identical relative nuclear arrangements related to one another by rigid translation or rotation appear as different points, and their distance may take any value. On the other hand, a global metric is not in general possible for internal configuration spaces defined by bond angle and bond length internal coordinates; in fact, all global *internal* configuration spaces for polyatomic systems ($N > 3$) have counterintuitive properties,[11] with consequences that are not universally appreciated. These properties hinder or make impossible the global application of routine mathematical methods. Even for the simplest, one-dimensional internal configuration space of a diatomic system, where a global metric is available if one takes the bond length as coordinate, the space is only a half line, since no negative bond distances are possible. In general, internal configuration spaces with a global metric do not have vector space properties; for example, they have boundaries or singularities at points representing configurations with coincident nuclei.[11] Consequently, many of the powerful techniques of differential geometry[15,16] are applicable only to local domains but not globally to the entire internal configuration space.

In spite of this, it is possible to construct a $(3N-6)$-dimensional internal configuration space M (a metric space) with both a faithful representation of relaxations by steepest descent paths and a global distance function.[10,11,27] For our present purposes it is sufficient to know that such distance function d exists, and an actual construction[11] is not required. Proper relaxation paths and global distance function are used only to *prove* our theorems for the general case of a multidimensional internal configuration space M, and in actual applications, such as the examples of this study, one may use the more familiar bond length and bond angle internal coordinates to represent M.

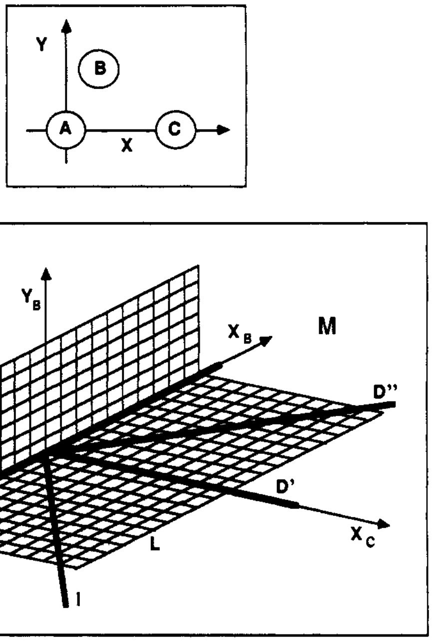

Figure 1. The family of all internal configurations of a triatomic system ABC, that is, the ABC configuration space M, can be represented by a formal "quarter" of the 3D space. The origin corresponds to the united atom configuration, along plane D and lines D′ and D″ some nuclear pairs are coincident, whereas plane L contains all linear triatomic configurations.

An example for the representation of the nuclear configuration space M of a triatomic stoichimetric family ABC is shown in Figure 1. This is a model that has been used extensively for illustrating some fundamental properties of nuclear configuration spaces.[11] The dimension is 3 × 3 − 6 = 3, and all possible nuclear configurations can be generated by varying just three of the nine Cartesian coordinates of the nuclei. One may take X_C, X_B, and Y_B as the three selected coordinates and fix all remaining coordinates at zero

$$X_A = Y_A = Y_C = Z_A = Z_B = Z_C = 0 \tag{1}$$

The family of all coordinate triplets (X_C, X_B, Y_B) fullfiling either one of the two conditions (i) or (ii)

$$\text{(i) } X_C > 0,\ Y_B \geq 0, \text{ or} \tag{2}$$

$$\text{(ii) } X_B = 0,\ X_C = 0, \text{ and } Y_B \geq 0 \tag{3}$$

is a formal "quarter" of a three-dimensional (3D) space spanned by the three coordinates X_C, X_B, and Y_B. This "quarter" represents the configuration space M of the stoichiometric family ABC of chemical species. Note that along boundary half-plane D nuclei A and C coincide, hence this plane actually represents a diatomic system. Each configuration of this half-plane is equivalent to a point on the Y_B axis, and only the origin and the positive Y_B axis of this plane is regarded as a part of M. All other linear configurations are found in the open half-plane L that is a part of M. Within L one finds the diatomic configurations with coincident nuclei A and B (along half-line D′) and those with coincident nuclei B and C (along half-line D″). The united atom configuration is the origin of the X_C, X_B, and Y_B coordinate system shown, the only point of line V that belongs to M.

The first classification we consider for nuclear arrangements is based on symmetry. Each nuclear configuration K can be characterized by its point symmetry group, g(K). We shall classify nuclear configurations into families, where within each family, the group is the same for all configurations. This is equivalent to considering subsets G_i of the nuclear configuration space M, where within each subset all points K correspond to nuclear configurations having the same point symmetry group g_i, $g(K) = g_i$. Within the configuration space M, a given group g_i may occur in several, separate, disjoint regions of the space, that is, there may exist different subfamilies of configurations of the same point symmetry that are separated by configurations of some different point symmetry. In such cases G_i is disconnected, and we shall use a second index j to distinguish the separate subsets G_{ij} (the so-called maximum connected components) of G_i. If there is only one such G_{ij} subset, that is, if $G_i = G_{ij} = G_{i1}$, then the index $j = 1$ may be omitted. The collection of all sets G_{ij} covers the entire configuration space M, and since they do not overlap, the

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(26) Considering a general coordinate transformation, the potential energy values assigned to corresponding points of the two surfaces agree, hence both the original and the transformed surfaces represent the same physical potential. This justifies considering all these representations as generalized potential surfaces, for example, those expressed in terms of bond bending and bond stretching internal coordinates. However, the energy function expressed in terms of the new coordinates is not necessarily a true potential surface in the strict sense, since different partial derivatives may transform differently, and the negative gradient vector at a given point of the surface (with components the partial energy derivatives in the new coordinate representation) may differ from the force at the same point. Consequently, a path that follows the steepest descent on a surface defined in an arbitrary coordinate system may deviate from the classical relaxation path. For example, in a spherical potential, all steepest descent paths are straight lines through the center. Scale one of the coordinates by a factor of two: this linear transformation generates an ellipsoidal representation of the same physical potential and converts all the original steepest descent paths into straight lines. Yet all lines that are neither orthogonal to nor parallel with the scaled coordinate will lose their steepest descent property in the new, ellipsoidal representation, where most paths of steepest descent will be curved lines, converging to the center along the scaled coordinate. Only the lines along the eigenvectors of the transformation will preserve their steepest descent property in the new representation of the potential. For an illustration see, e.g., ref 11, p 99.

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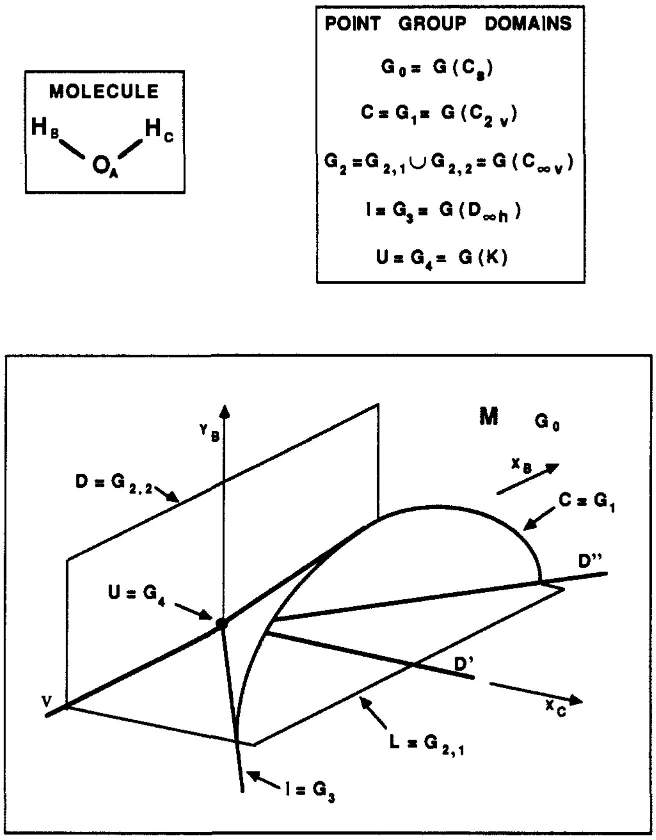

Figure 2. Symmetry domains of the nuclear configuration space M of the water stoichiometric family of chemical species, using the configuration space representation of Figure 1.

point symmetry domains G_{ij} generate a subdivision of M.

An illustration of the point symmetry domain subdivision for the triatomic stoichiometric family H_2O is shown in Figure 2. The representation of M is that given in Figure 1 for the general triatomic case, with the choice of the O = A, H = B, and H = C assignment for the nuclei. For the stoichiometric family H_2O there are five possible point symmetry groups:

$$g_0 = C_s,\ g_1 = C_{2v},\ g_2 = C_{\infty v},\ g_3 = D_{\infty h},\ \text{and}\ g_4 = K$$

The distribution of subsets G_i corresponding to these point symmetry groups is shown in Figure 2. The highest point symmetry group K, the spherical group, belongs to the united atom, represented by the origin. Point symmetry $D_{\infty h}$ is found along line I within the half-plane L, and all other points of the (open) half-plane L have the lesser $C_{\infty v}$ symmetry, the same symmetry found along the positive Y_B axis. Note that these latter two subsets $G_{2,1}$ and $G_{2,2}$ of set $G_2 = G(C_{\infty v})$ are *disjoint*, that is, it is impossible to change any $C_{\infty v}$ configuration from family $G_{2,1}$ to another $C_{\infty v}$ configuration in family $G_{2,2}$, without encountering some intermediate configuration of some *different* symmetry. The origin is the only point of the line V (where the two half-planes D and L meet) that belongs to M, and there the point symmetry is different, K, hence the origin does separate the two parts of $G_2 = G(C_{\infty v})$ within M. All C_{2v} configurations are found along the conical surface C = G_1, which, of course, does not include the origin or any point of half-plane L of linear configurations. All other points of M have only trivial C_s symmetry.

Although it is much more difficult to visualize parts of multidimensional functions and spaces, one may generate an analogous subdivision of a higher dimensional configuration space M of any polyatomic ($N > 3$) stoichiometric family,[11] where within each symmetry domain G_{ij} of M the point symmetry group of all nuclear configurations is g_i. The very purpose of the theorems and rules we shall present below is to make our intuitive understanding less dependent on visualization attempts and to provide alternative tools for the search and analysis of molecular species along potential surfaces.

If the number of nuclei is greater than three ($N > 3$), then most of the nuclear configurations have only trivial point symmetry, even in the case of a homonuclear stoichiometry, hence most of the points of M belong to the subset G_0 of the trivial point group g_0. However, even if all the nuclei are different, there are still various subsets G_i of M where the point symmetry group g_i is nontrivial, as it is in the case, for example, in planar or linear configurations. Hence symmetry and the results we shall discuss below have relevance for all stoichiometries.

The second classification of nuclear arrangements is based on an *energy criterion* that leads to various, formal chemical identity labels one may assign to the configurations. For each specified electronic state the energy changes along the potential energy surface account for molecular stability, endothermicity, or exothermicity of reactions as well as for conformational and reaction barriers, for all species and processes confined to the given potential surface. Each catchment region represents a formal chemical species, regarded as a *family* of nuclear configurations with the common property that a concerted, infinitely slow relaxation converts each nuclear configuration of the family into the same stationary configuration. Proper mass-weighting of coordinates is the condition for the energy gradient to represent internal forces, and for a steepest descent path to represent concerted relaxation of the nuclei, that simplifies both the definition of catchment regions and the description of symmetry conservation properties. If mass-weighted coordinates are used, then the definition of catchment regions by relaxation paths can be replaced by a definition given in terms of steepest descent paths: a chemical species is represented by a *catchment region* of the potential energy surface, where from each point of the catchment region the steepest descent path leads to a common stationary point of energy.[9-11] We may assign the stationary point as a "chemical identity label" to each point of a given catchment region. Some examples for actual catchment regions will be shown in the following sections of this report.

Conformational rigidity and conformational softness are determined by the shape and extent of catchment regions, that are in turn determined by the curvature properties of the potential energy surface. If the stationary point $K(0,i)$ is the ith minimum of the potential surface, then the corresponding $(3N - 6)$-dimensional catchment region $C(0,i)$ represents the ith stable species of the given electronic state. If the stationary point is the jth simple saddle point, denoted by $K(1,j)$, then the corresponding $(3N - 7)$-dimensional catchment region $C(1,j)$ represents the jth transition structure. For critical points (also called stationary points) $K(\lambda,k)$ of some higher critical point index λ, $\lambda \geq 2$, the corresponding $(3N - 6 - \lambda)$-dimensional catchment regions $C(\lambda,k)$ represent formal, unstable "species" of little direct (but of some indirect) chemical significance, for example, single points of (0-dimensional) energy maxima. The catchment regions may be different for each electronic state, since in general the shapes of potential energy surfaces vary with electronic excitation. For a given electronic state the catchment regions generate a subdivision of the nuclear configuration space M. Most of the fundamental properties of catchment regions are reviewed in.[11]

Within the context of nuclear configuration space M the interrelations between symmetry and stability (chemical identity) of nuclear configurations can be studied by comparing the two subdivision schemes of space M: one in terms of the point symmetry domains G_{ij} and another based on catchment regions $C(\lambda,k)$. An important difference between the two subdivisions will be exploited: *only the second subdivision is dependent on the overall electronic charge and on the electronic state.*

For sake of simplicity in deriving the proofs, we shall assume that the potential energy surfaces are everywhere differentiable within the configuration domains we consider, that is, the concept of energy gradient is meaningful at each configuration considered. Note, however, that all our results are easily generalized to the case where a steepest descent path terminates as a consequence of reaching a point of nondifferentiability, such as a branch-cut point of a conical intersection, by replacing the phrase "critical point" with the phrase "critical point or a point of

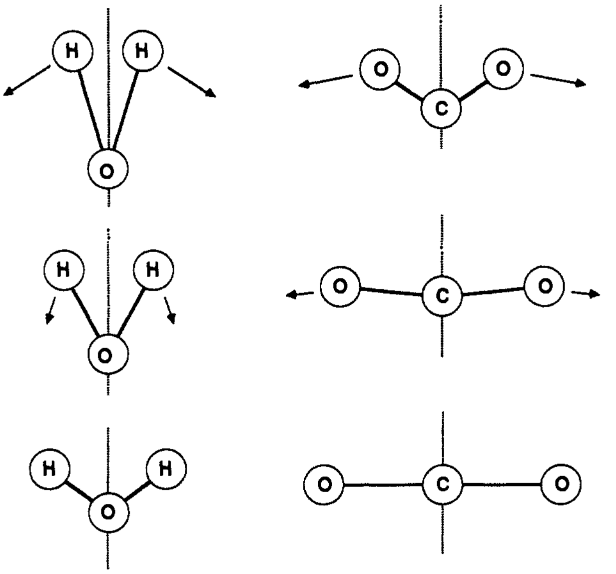

Figure 3. The symmetry of the pattern of forces acting on the nuclei as well as the point symmetry of configurations are preserved during an infinitely slow, vibrationless relaxation of distorted molecules. New symmetry elements may appear only at configurations where the net forces vanish, that is, at critical points of potential surfaces. At equilibrium all symmetry elements of configurations along the relaxation path are present. In the case of water, no new symmetry element appears at equilibrium; however, for carbon dioxide the symmetry increases at the linear equilibrium structure.

nondifferentiability" in the statements and proofs of the theorems. In the following derivations we shall not refer to nondifferentiabilities, but one should keep in mind the above generalization. Alternatively, at each point of nondifferentiability one may apply an infinitesimal distortion of the potential energy surface that makes it differentiable; this is a technique that has been applied in a different context.[11] Most of the essential topological properties of the surface are not affected by this distortion, and it allows one to apply these theorems in their original forms.

The Catchment Region Point Symmetry Theorem

The theorem discussed in this section is the simplest in a series of results concerning point symmetry properties within a family of nuclear configurations. It has been first stated[28] in the following form: *the critical point* $K(\lambda,i)$ *has all the symmetry elements of its catchment region* $C(\lambda,i)$. An equivalent formulation has been given with respect to the hierarchy of point symmetry groups within a catchment region,[29] and this is the approach we shall use for generalizations.

It what follows below we shall present a somewhat stronger variant of the theorem, with use of tools that are also suitable for the proofs of the new "vertical" symmetry theorems interrelating various electronic states.

First we shall make a simple observation, by using the two examples shown in Figure 3, representing the two possible cases of symmetry conservation. Consider two, nonequilibrium configurations of the H_2O and CO_2 molecules, obtained from the respective equilibrium configurations by bending, accompanied by a symmetric stretching or shortening of the bond pairs. Both distorted nuclear geometries belong to the point symmetry group C_{2v}. If the distortions are small enough, then within a semiclassical molecular model the formal, infinitely slow relaxations of both systems will lead to their respective equilibrium structures. While restoring the equilibrium configuration, all the forces are expected to act symmetrically, according to the symmetry elements of the C_{2v} point symmetry. For example, the forces acting upon the two hydrogen nuclei stay confined to the plane of the water molecule, and they also maintain being the mirror images of one another with respect to the reflection plane perpendicular to the molecular plane and passing through the oxygen nucleus. Consequently, by analogy with distorted macroscopic objects, we expect that during a formal, infinitely slow relaxation of the nuclei all the symmetry elements will be preserved. For example, at no stage of the infinitely slow, vibrationless relaxation process will one OH bond become longer than the other. In the case of the H_2O system no symmetry change occurs at all, and the equilibrium configuration also has the symmetry C_{2v}. No symmetry change occurs for the CO_2 system either until it reaches the linear equilibrium configuration, where the symmetry suddenly changes to $D_{\infty h}$. A *new symmetry element*, for example, a C_∞ symmetry axis of the linear equilibrium configuration of CO_2, *may appear only* when the relaxation process is completed, that is, *when the net internal forces vanish*. The above, rather evident conclusions can be summarized as follows: (i) The pattern of nonzero net forces acting upon the nuclei during a formal, infinitely slow relaxation must have all the symmetry elements of the actual, nonequilibrium nuclear configuration. Consequently, these forces cannot lower the symmetry of the configuration in the relaxation process, and neither can the negatives of these forces lower the symmetry in the reverse process; hence the point symmetry is preserved as long as the forces do not vanish during a configuration change. (ii) Since in a relaxation process, an equilibrium configuration can be approached arbitrarily close by a nonequilibrium configuration for which the symmetry is preserved, the equilibrium configuration must also have all the symmetry elements present during the relaxation. (iii) Zero net forces, however, can be regarded to have arbitrary directions, hence any conceivable symmetry; consequently, it is possible that the same equilibrium configuration is reachable by another relaxation process along which some different symmetry elements are preserved. Consequently, at an equilibrium configuration new symmetry elements may appear.

Note that actual molecules never follow the above model, since a relaxation involves vibrational motion, molecules possess zero point energy, and molecular configurations never stay relaxed at a potential minimum with all net internal forces equal to zero. However, the above model is suitable for interrelating the point symmetries of various configurations, and the conclusions can be generalized for all molecules.

The above, intuitively evident conclusions can be stated in a form more convenient for the purposes of configuration space analysis by recalling that an infinitely slow, vibrationless molecular relaxation can be represented by the steepest descent path of a potential surface. Pechukas[25] has presented an elegant proof for the following, equivalent result: along each path of steepest descent of a potential surface, defined in terms of a mass-scaled coordinate system, all symmetry elements are preserved, and additional symmetry elements may appear only at critical points (endpoints) of the steepest descent path, that is, at points corresponding to configurations where the net internal forces vanish. Among such critical points one finds those of energy minima and saddle points of transition structures ("transition states"). The main result of Pechukas[25] also implies that the transition structure symmetry elements have an important role interrelating product and reactant configurations, a result that can be extended to chiral configurations.[30]

Catchment regions of potential energy surfaces are defined with respect to steepest descent paths; consequently, one expects that by combining the above property of steepest descent paths with properties of catchment regions, one may obtain significant results.[28,29] Consider a catchment region $C(0,i)$ of a minimum point $K(0,i)$, representing a stable chemical species. The minimum point $K(0,i)$ is the only critical point within $C(0,i)$, and from all other points K of $C(0,i)$ the path of steepest descent must lead to $K(0,i)$. Consequently, the configuration represented by the minimum point $K(0,i)$ must have all the symmetry elements of all configurations represented by points K of the catchment region $C(0,i)$. That is, the point symmetry group of the configuration at the minimum

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(28) Page 367 in ref 11.

(29) Mezey, P. G. Reaction Topology and Quantum Chemical Molecular Design on Potential Surfaces. In *New Theoretical Concepts for Understanding Organic Actions*; Bertrán, J., Csizmadia, I. G., Eds.; Kluwer Academic: Dordrecht, 1989; p 55.

point K(0,*i*) must contain the point symmetry groups of all other configurations of the catchment region C(0,*i*) as subgroups; in other words, K(0,*i*) has the highest point symmetry within its catchment region C(0,*i*). Precisely the same applies to all critical points K(λ,*i*) of catchment regions C(λ,*i*) of the potential surface, such as the simple saddle point K(1,*j*) of a catchment region C(1,*j*), representing a transition structure.

The above proof allows one to recast the original statement[28] of the *catchment region point symmetry theorem* as follows.

Theorem 1. Within each catchment region C(λ,*i*) the nuclear configuration corresponding to the critical point K(λ,*i*) has the highest point symmetry.

Note that the adjective "highest" needs some explanation, since in general it is not always possible to decide which one of a pair of point symmetry groups represents the "higher" point symmetry, for each group may contain elements not present in the other group. However, within a catchment region C(λ,*i*) there always exists a point symmetry group (that of the critical point K(λ,*i*)) which contains as subgroups all other groups occurring in C(λ,*i*); hence within a catchment region it is meaningful to refer to the "highest" point symmetry. Also note that the theorem does not imply that the critical point K(λ,*i*) is the only point within C(λ,*i*) that has the highest point symmetry; some other and possibly all points of the catchment region C(λ,*i*) may have the same (and by default, the highest) point symmetry. In this context one should recall that each point symmetry group is considered to be one of its own subgroups.

Two aspects of the above theorem are of special interest: (i) The distribution of catchment regions and their critical points are the properties of the potential energy surface, that is, they depend on *energy relations*, whereas the point symmetries of various nuclear configurations are purely *geometrical properties*, not directly dependent on energy. Consequently, *the theorem interrelates two very different molecular properties.* (ii) The point symmetry of a fixed nuclear configuration is independent of the net charge and the electronic state of the molecule. Consequently, the above result is general for the potential energy surfaces and catchment regions of all electronic states of the neutral and all ionic species of the given stoichiometry. The point group symmetry of nuclear configurations provides a condition that interrelates the *catchment regions of different electronic states of neutral and ionic species.*

In Figure 4 the example of symmetry conservation along steepest descent paths within the configuration space of the H_2O stoichiometric family is shown. The ground state equilibrium C_{2v} structure of the water molecule corresponds to the critical point K(0,1), that falls on the cone C of all C_{2v} structures within M. Evidently, this critical point K(0,1) has the highest symmetry, C_{2v}, within the water catchment region C(0,1). Steepest descent paths p_1, p_2, and p_3 stay within the cone C, and the C_{2v} point symmetry is preserved along them. Paths p_4, p_5, p_6, and p_7 originate from points of distorted water configurations of trivial symmetry C_s. The C_s symmetry is preserved along these paths as long as the energy gradient does not become zero; however, the gradient converges to zero as the paths approach the critical point (minimum) K(0,1), where the symmetry suddenly increases to C_{2v}.

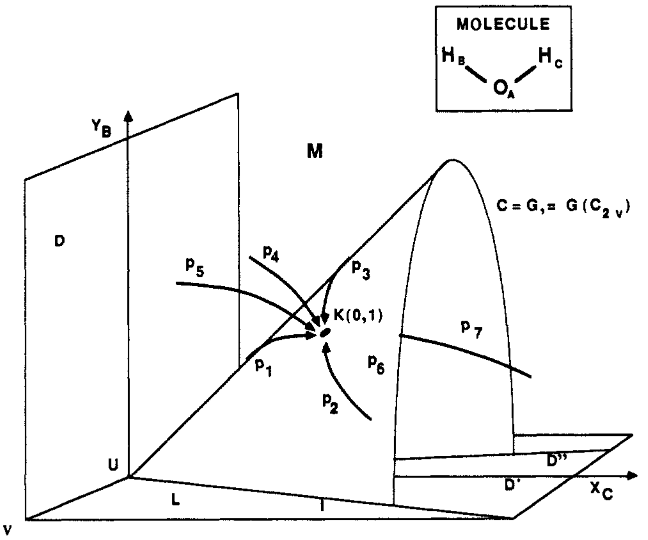

Figure 4. The configuration space model of Figure 2 is applied for water, showing various relaxation paths leading to the C_{2v} equilibrium configuration K(0,1). Paths p_1, p_2, and p_3, originate at points of the cone C of configurations of C_{2v} point symmetry, hence all these paths must stay confined to the cone, preserving C_{2v} symmetry, while approaching the equilibrium point K(0,1). The origin points of paths p_4, p_5, p_6, and p_7 have only trivial, C_s point symmetry, hence all points along these paths, except their endpoint at K(0,1), must also have only trivial, C_s point symmetry. In particular, no relaxation path can cross the conical surface C.

One generalization of the above theorem to pairs of symmetry and nuclear permutation operators[28,29] is motivated by the preservation of such operator pairs along steepest descent paths.[25] For each symmetry operator R of a nuclear configuration K, there exists a permutation operator P, assigned to R by the following rule: the rearrangement of identical nuclei caused by the symmetry operator R is undone by the permutation P of identical nuclei.[25] Although the two operators, R and P, are of different types, the net effect of applying R followed by P on the given nuclear configuration is equivalent to the effect of the identity operation I. Note, however, that for some other configurations the application of R followed by P may have an effect different from that of I. For two different configurations, K_1 and K_2 of the same set of nuclei, both having a given symmetry operator R, the assigned permutation operators P_1 and P_2 may be different, that is, R does not determine P in general. For each configuration K the pairs (R,P) of associated operators form a group, that is also preserved between critical points along steepest descent paths, defined in terms of mass-weighted coordinates.[25] Consequenly, as it has been pointed out earlier,[28,29] the catchment region point symmetry theorem can be generalized for groups having the (R,P) pairs as elements. In fact, all the proofs and general results we shall state in this contribution with reference to point symmetry operators and groups are equally valid for the pairs (R,P) of operators and their groups.

The second generalization of the results allows one to nearly "double" the information gained. In all the theorems and general results discussed in this paper, the steepest descent paths can be replaced with steepest ascent paths, and all the new conclusions obtained are equally valid. In the context of the catchment region point symmetry theorem, this is equivalent to considering the formal catchment regions of the inverted potential energy surface, -E(K). Note that the two subdivisions of the configuration space M according to the catchment regions of E(K) and -E(K) are in general different and their interrelation is far from trivial. Consequently, the generalization does provide new information.

A partial "converse" of the catchment region point symmetry theorem is also true for all electronic states of neutral and charged species of the given stoichiometric family. We shall refer to this result as the *catchment region minimum theorem*, stated as follows.

Theorem 2. If within a catchment region C(λ,*i*) there is a point K with a symmetry element R not present anywhere else in the catchment region, then this point K must have the *lowest energy value within the catchment region*, and point K is the critical point K(λ,*i*) of C(λ,*i*).

The proof of this statement follows from the fact that each catchment region C(λ,*i*) contains precisely one critical point. Since this critical point K(λ,*i*) is the endpoint of all steepest descent paths originating anywhere within C(λ,*i*), it must have the lowest energy within C(λ,*i*). If a point K of the catchment region C(λ,*i*) has a symmetry element R then, by the conservation of symmetry elements along steepest descent paths, this symmetry element must also be present at the critical point K(λ,*i*). If this symmetry element R occurs only at point K of C(λ,*i*), then K is identical with K(λ,*i*); consequently, K must have the lowest energy within C(λ,*i*).

Vertical Symmetry Theorems for a Sequence of Electronic States

In studies of neutral and ionic molecular species of ground and various excited electronic states, excimers and exciplexes, and transition structures, one often faces the following question: how similar are these species to one another? In this section we shall derive a series of relations for the relative nuclear configurations of stationary points of various electronic states, by using the tools described above. For simplicity, we shall regard the net charge as being part of the specificiation of the electronic state, and it will be mentioned explicity only if emphasis is needed.

Collectively these rules are referred to as vertical symmetry theorems. One may regard energy as a formal "vertical" dimension over a nuclear configuration space M. In general, electronic excitation affects the energy of a molecular system, hence relations among various electronically excited state potential surfaces may be regarded as formal vertical relations over M.

We take a given collection of nuclei, that is, a given stoichiometry, and consider the corresponding nuclear configuration space M that contains all possible nuclear arrangements. We choose any surface B that divides the nuclear configuration space M into two parts, M_1 and M_2, as illustrated in Figure 5. We assume that the set M_1 of configurations contains surface B as its boundary (that is, M_1 is a so-called closed set). In the simplest case, any two points K_1 and K_2 of B represent configurations that can be converted into one another continuously, without leaving set B, whereas any configuration represented by some interior point K_3 in M_1 *cannot* be converted into any configuration represented by some point K_4 in M_2 without passing through boundary B.

Some symmetry elements are present for all nuclear configurations K′ along B, and we denote a family of such symmetry elements, $R'_1, R'_2, \ldots R'_p$, by R′

$$R' = \{R'_1, R'_2, \ldots R'_p\} \tag{4}$$

We choose a nuclear configuration K from set M_1 and denote by R a family of symmetry elements, $R_1, R_2, \ldots R_q$, that are present at point K:

$$R = \{R_1, R_2, \ldots R_q\} \tag{5}$$

Note that if one takes *all* common symmetry elements from B, then the family of symmetry operators corresponding to the family R′ of symmetry elements is a group, and, evidently, if one extends family R to *all* symmetry elements of configuration K, then the corresponding symmetry operators form the point symmetry group of K. Our results, however, are valid even if one includes only *some* of the eligible symmetry elements in families R′ and R.

The *vertical point symmetry theorem of nuclear configuration spaces* states the following.

Theorem 3. If (i) no configuration along B possesses the family R of symmetry elements or if (ii) configuration K does not have all the symmetry elements of family R′, then the family M_1 of configurations must contain at least one critical point *for the potential energy surface of each electronic state* (*of each possible overall electronic charge*).

Note that if either one of conditions (i) and (ii) is fulfilled, then K must be an interior point of M_1, that is, K cannot fall on the boundary B.

In order to prove this theorem, we choose a potential energy surface corresponding to any one of the possible electronic states. There are two possibilities: if the chosen point K of set M_1 is a critical point of this potential surface, then for this potential surface the statement of the theorem follows. If K is not a critical point, then there must exist a steepest descent path that passes through K. We show now that this steepest descent path cannot leave set M_1. By assuming that the path does leave M_1, we shall find a contradiction. If the path would leave set M_1, then it would have to reach the boundary B at some point K′. This point K′ could not be a critical point itself, since then the path would terminate there, hence it could not leave M_1 (recall that M_1 contains its boundary B). If the path would leave set M_1, then this point K′ could not be an ordinary, noncritical point either, since this would imply (by the conservation of symmetry elements along steepest descent paths) that configurations K and K′ would have precisely the same symmetry elements. However, this is impossible, since it contradicts both of the conditions (i) and (ii) of the theorem. Consequently, there exists no point K′ at the boundary B that can be reached by the steepest descent path from K, hence the path must terminate within set M_1. Since each steepest descent path must terminate at a critical point, set M_1 must contain at least one critical point of the potential energy surface of the chosen electronic state. Since the electronic state has been chosen arbitrarily, this conclusion is valid for each electronic state that proves the theorem.

The theorem does not specify the exact location or type of the critical point; all it states is that if for some (arbitrarily small) part M_1 of the configuration space M the condition of the theorem is fulfilled, then within M_1 there must exist some critical point for each electronic state (and net charge). It does not specify the number of critical points, hence some critical points may remain undetected by the theorem. For different electronic states the critical points may have different locations within M_1, and they may be of different types (e.g., minima or saddle points). Also note that the chosen test point K itself does not have to be a critical point for any one of the potential surfaces.

An intriguing feature of this theorem is that it provides direct information on the behavior of the potential energy surface (the presence of a critical point within some region), based on a property of the configuration space M (symmetry conditions on boundary B and a test point K). Evidently, this information can be obtained *without any quantum chemical calculation*, simply by checking the symmetry elements for a family of configurations. This result shows that *symmetry* has a strong influence on *energy* in a rather general way.

Since the conclusion is general for all electronic states, indicating the presence of a critical point within configuration domain M_1 for each potential surface, the theorem is suitable to study the *similarities within a whole family of potential surfaces of all electronic states*.

By using a different set of conditions one may obtain a similar conclusion. We choose a symmetry element R of some interior point K of subset M_1 and take the family S_B of *all* symmetry elements of nuclear configurations occurring along boundary B. The *vertical symmetry element theorem of nuclear configuration spaces* states the following.

Theorem 4. If M_1 contains a configuration K that has a symmetry element R *not present* in family S_B, then the *interior* of M_1 must contain at least one critical point *for the potential energy surface of each electronic state* (*of each possible* overall electronic charge).

Note that if there exist two point symmetry groups along boundary B, neither of which is a subgroup of the other, then it is impossible to choose class R′ of theorem 3 to coincide with class S_B. Consequently, the conditions of theorems 3 and 4 are, indeed, different. Also note that theorem 3 can guarantee only the existence of a critical point *somewhere* in set M_1 that may fall on the boundary B, as this latter possibility is compatible with condition (ii) (but not with condition (i)). By contrast, theorem 4 is somewhat stronger, since it implies that the critical point *must* fall within the interior of M_1, that is, it cannot fall on the boundary B.

In order to prove theorem 4, choose an electronic state and the corresponding potential energy surface. Furthermore, choose a point K of set M_1 that has a symmetry element R not present in family S_B. If K is a critical point, then for this potential surface the stateent of the theorem follows. If K is not a critical point, then there exists a steepest descent path passing through K. This path cannot reach the boundary B, since then it would have to have a common point with B, and then the family S_B would contain all the symmetry elements of K, including R, in contradiction with the conditions of the theorem. Consequently, the steepest descent path must terminate within the interior of M_1. Since each steepest descent path must terminate at a critical point, the interior of set M_1 must contain at least one critical point of the potential energy surface of the selected electronic state. Since this conclusion is valid for each electronic state, the statement of the theorem follows.

A partial "reverse" of these theorems is also valid. If one knows that no critical point exists within a given domain (for some electronic state), then this information can be used to obtain global conclusions concerning symmetry within an entire subset M_1 of the configuration space M.

Theorem 5. If the point symmetry group g_i contains the collection of all the symmetry operators of symmetry elements occurring at various points of the boundary surface B and if exists an electronic state (of any net charge) with a potential surface that has no critical point within set M_1, then no point K of set M_1 can have a point symmetry group g, $g \neq g_i$, that contains g_i as a subgroup.

Stated differently, the lack of a critical point within M_1 for any electronic state of any overall charge implies that no interior point of M_1 can have any symmetry element not present at the boundary B.

The proof of theorem 5 follows from the fact that if M_1 contains no critical point for a potential surface, then for this surface the steepest descent paths from all points of M_1 must leave M_1 passing through B. Hence all symmetry elements present at various points of M_1 must occur somewhere along the boundary B, and the statement of the theorem follows.

One consequence of theorem 5 implies that some critical points cannot have higher symmetry than that of other points along a steepest descent path leading to the critical point. If the potential surface of one electronic state has a critical point within M_1, then, in principle, this critical point can have new symmetry elements that are nowhere present along the boundary B. However, if there is another electronic state with a potential surface that has no critical point within M_1, then the critical point of the first potential surface cannot have a new symmetry element either, in addition to those occurring along the boundary B.

Symmetry Theorems on Relaxed Cross Sections of Potential Surfaces

It is often inconvenient as well as unnecessary to analyze the domains of a multidimensional configuration space in its entirety. Some internal coordinates, such as C–H bonds in methyl groups, change only very little in many chemical processes, hence in those cases their changes do not have to be considered explicity. Instead of the full, $(3N-6)$-dimensional problem, one may study lower dimensional, *relaxed cross sections* of the configuration space and of the potential energy surface. With this approach, only some of the internal coordinates are regarded as explicit variables, and all others are taken at their ("relaxed") optima that are dependent on the explicit variables. Techniques based on relaxed cross sections are often used in quantum chemical and other computations.

Our purpose is to adapt the catchment region point symmetry theorems and the vertical symmetry theorems to such relaxed cross sections. Since point symmetry is dependent on all of the internal coordinates, we need to define precisely the process of generating the cross sections and the relations of steepest descent paths within the cross section to the steepest descent paths within the full configuration space. In particular, the clear distinction between the relaxed cross section of a potential surface and the relaxed cross section of the nuclear configuration space is essential.

Let us assume that a subset A of the configuration space M is provided with a local coordinate system. We assume that the first n's of the internal coordinates ($n \leq 3N-6$) are the chemically important variables, and these are to be called the *active coordinates*, whereas the remaining ones ($n' = 3N-6-n$) are regarded as the *passive coordinates*. We choose an electronic state and the corresponding potential energy surface. For each value (in practice, for a finite number of values) of the n active coordinates within set A, the energy is repeatedly reoptimized with respect to the n' passive coordinates. If the optimization of passive coordinates is carried out for all possible fixed values of the active coordinates and if all these optima are found within set A, then the collection of all the resulting optimum points generates an n-dimensional surface, a subset C′ of A, relaxed along the directions of the passive coordinates. This surface C′ is fully relaxed only if it is everywhere orthogonal to the passive coordinates, a condition that is fulfilled only in exceptional cases. In the more common cases, a second optimization along directions locally orthogonal to C′ leads to a new, fully relaxed n-dimensional surface C, characterized by its points having zero gradient components orthogonal to C. This set C is called an n-dimensional *relaxed cross section* of A according to the given potential energy surface. The relaxed cross section C may be thought of as an n-dimensional surface within M, where at every point K of C the gradient vector is tangential to C, hence the "gradient flux" is zero across this n-dimensional surface C. If the potential energy surface is restricted to this set C, then it can be regarded as an energy function of the n active coordinates. This energy function is called an n-dimensional *relaxed cross section* of the original potential energy surface.

Note that the relaxed cross section C depends on the choice of the electronic state, that is, on the potential surface. However, one may repeat the optimization procedure of the passive coordinates for each electronic state, by using the *same* values of the active coordinates. One obtains a series of cross sections C: one for the potential energy surface of each electronic state, which may differ only in the passive coordinates. By taking the first n (active) components of all coordinate vectors in C, *for any one of the electronic states*, one obtains the *same* set C^n of n-dimensional vectors. Each cross section C, as a curved surface cutting across the configuration space M, does depend on the electronic state, that is, on the potential energy surface according to which it is "relaxed". By contrast, the projection C^n of each of these sets C onto the n-dimensional subspace of the active coordinates is the same, that is, C^n is independent of the electronic state. Consequently, it is meaningful to treat all the relaxed cross sections of potential energy surfaces of all electronic states collectively as functions of the same active coordinates. Hence, one may regard the relaxed cross sections of potential surfaces of all electronic states as being defined over the *same* set C^n of n-dimensional coordinate vectors. This allows direct comparisons of the relaxed cross sections of potential surfaces of different electronic states (of any net charge), an interesting application of vertical symmetry theorems to relaxed cross sections.

Note that an n-dimensional surface C, characterized by its points having zero gradient components orthogonal to C, does not require that the energy is minimized with respect to all of the passive coordinates. Just as a rope may relax along a mountain ridge, even if each of its points lies at a maximum along directions locally orthogonal to the rope, a relaxed cross section C may also be obtained by maximizing energy along some of the passive coordinates.

For some of the following results we need to clarify four additional concepts. A cross section may be limited to a finite configurational domain, hence it may have a boundary. If, by contrast, we require that the cross section itself has no boundary, for example, if C^n cuts across the entire configuration space, then C^n is a *complete* relaxed cross section. No steepest descent path can leave a complete relaxed cross section. If the cross section is not complete, then it is possible for a steepest descent path to leave it at one of its boundary points along a direction locally tangential to the cross section.

Another important concept is the *interior point symmetry domain* of a relaxed cross section C^n. If $G^n{}_{ij}$ is one of the point symmetry domains of C^n that has no points falling on the boundary of C^n, then $G^n{}_{ij}$ is an *interior* point symmetry domain of C^n. Since a complete relaxed cross section has no boundary, all its point symmetry domains are interior point symmetry domains.

The third concept is the *catchment region of a relaxed cross section* C^n. A catchment region $C^n(\lambda,i)$ of any relaxed cross section C^n is the collection of all the nuclear configurations of C^n from where steepest descent paths stay within C^n and lead to the critical point $K(\lambda,i)$. Note that along the passive coordinates, optimized individually for each electronic state, all gradient components vanish, hence a steepest descent path passing through any point K of the relaxed cross section C either stays within C or leaves

C at the boundary of C along a direction of tangential extension of C. In order to exist, for each catchment region $C^n(\lambda,i)$ of any relaxed cross section C^n the corresponding critical point $K(\lambda,i)$ must also fall within C^n. If $K(\lambda,i)$ is within C^n, then all points K of the common part of the catchment region $C(\lambda,i)$ of the full configuration space M and the relaxed cross section C^n, from where the entire steepest descent path segment between K and $K(\lambda,i)$ is contained within C^n, form a connected set. Hence it is meaningful to refer to a catchment region $C^n(\lambda,i)$ of a relaxed cross section C^n.

The fourth concept is the *interior catchment region* of a relaxed cross section C^n. If $C^n(\lambda,i)$ is one of the catchment regions of C^n that has no points falling on the boundary of C^n, then $C^n(\lambda,i)$ is an *interior catchment region* of C^n. Since a complete relaxed cross section has no boundary, all its catchment regions are interior catchment regions. Note that, depending on the extent and boundary of a relaxed cross section C^n, it is possible that the common parts of some catchment region $C(\lambda,i)$ of M and the relaxed cross section C^n are disconnected, which implies that the common parts do not necessarily coincide with the corresponding catchment region $C^n(\lambda,i)$ of the relaxed cross section C^n. However, for a complete relaxed cross section C^n, $C^n(\lambda,i)$ is the common part of $C(\lambda,i)$ and C^n.

The relaxed cross section versions of theorems 1–5, labeled as theorems 6–10, respectively, are obtained by replacing M, $C(\lambda,i)$, M_1, M_2, and B with their *n*-dimensional counterparts in the relaxed cross section, C^n, $C^n(\lambda,i)$, $C^n{}_1$, $C^n{}_2$, and B^n, respectively. Since steepest descent paths originating from any point K of $C^n(\lambda,i)$ must stay within $C^n(\lambda,i)$, all the steps of the proofs of theorems 1–5 can be repeated. For completeness, these relaxed cross section theorems are stated explicitly in the supplementary material, as Theorems 6–10, together with an additional result, applicable only to relaxed cross sections.

Examples and Applications

Whereas properly mass-scaled coordinates are convenient for the derivation of the above results, their use in actual studies of molecular configurations is often impractical. Conventional internal coordinates, such as bond angle and bond length coordinates, are more suitable for the recognition of chemically important conformational features. There is, however, some difficulty with such chemically motivated internal coordinate systems, since the transformation between them and the mass-scaled system is usually nontrivial, and even a simple linear transformation such as a nonuniform scaling of selected coordinates may transform a steepest descent path into a path that has no steepest descent property according to the gradient vectors defined in the new coordinate representation.[26] This may appear as a serious limitation of conventional internal coordinates. Note, however, that nondegenerate coordinate transformations of local regions of the nuclear configuration space convert catchment region into catchment region and a closed boundary surface B into a closed boundary surface. Only our actual proofs require the use of steepest descent paths directly. For applications, it is sufficient to analyze the symmetry properties in catchment regions, along boundary surfaces and within their interiors, by using any coordinate system as long as it can be derived by a continuous and differentiable (nondegenerate) transformation from the mass-scaled coordinates. Within local regions of the configuration space most of the usual internal coordinates satisfy this condition as guaranteed, for example, by the existence of a Riemannian space description of such local regions.[15,16]

The examples of water and carbon dioxide, shown in Figure 3, and the 3D representation for water in Figure 4 illustrate the catchment region point symmetry theorem: the energy minima have the highest point symmetry within the respective catchment regions. Note that linear H_2O structures do not belong to the water catchment region; they belong to a transition structure catchment region involved in the planar inversion process of water.

In Figure 5, a schematic 2D model is shown as an example for the vertical point symmetry theorem, indicating that the critical points of various excited electronic state potential surfaces do not have to be of the same type. In fact, they do not have to occur at the same configuration K either; however, all these critical points must belong to the family M_1 of configurations.

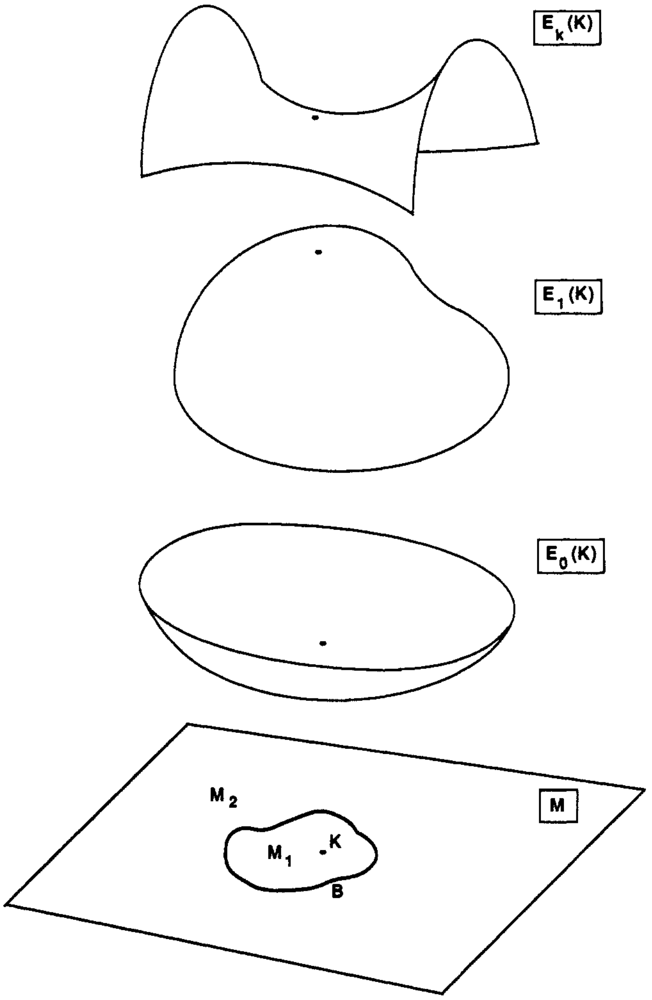

Figure 5. The vertical point symmetry theorem applied to a model of a 2D configuration space M. Boundary B divides the family M of all configurations into two subsets, M_1 (containing B) and M_2. If the point symmetries of configurations along B and at some interior point K of M_1 are sufficiently different (see text), then family M_1 must contain a critical point configuration for the potential energy surface of *each electronic state*. The critical points do not have to coincide with the test point K, and they may be of different types for the various excited-state potential surfaces. In the figure three potential surfaces, those of the ground state, $E_0(K)$, the first excited state $E_1(K)$, and the *k*th excited state $E_k(K)$, are shown, having a minimum, a 2D maximum, and a saddle point of a transition structure, respectively.

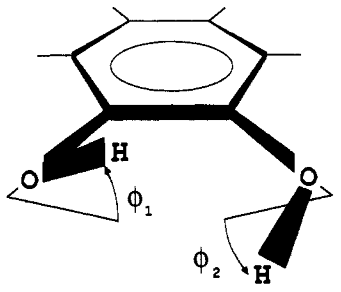

Figure 6. The definition of C–O bond rotation angles for the conformational problem of the catechol molecule.

The detailed example we shall consider is the 2D relaxed conformational cross section of catechol (1,2-dihydroxybenzene), involving the two C–O bond rotation angles ϕ_1 and ϕ_2 as active coordinates, defined in Figure 6. The ground-state potential energy surface for this cross section has been calculated by using

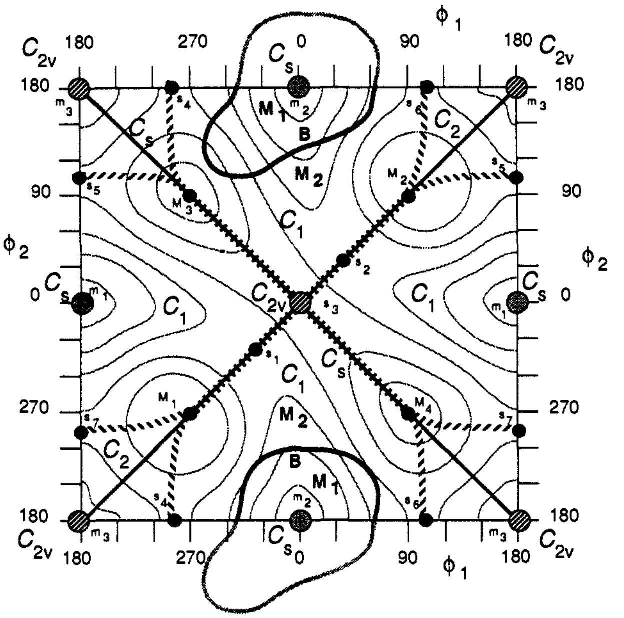

Figure 7. This figure shows a unit cell representation of the catechol conformational catchment regions for comparison with the symmetry domains and an illustration of the vertical point symmetry theorem. Letters m, s, and M stand for minimum, saddle point, and maximum, respectively. The faint solid lines are constant energy contours, calculated at the 3G ab initio level, and the crosshatched lines are the boundaries of 2D catchment regions of stable conformers. A catchment region is defined as the collection of all configurations from where a steepest descent path leads to a common critical point, in this instance, to a minimum point. Crosshatched line segments of the M–s–M or M–s–s pattern are 1D catchment regions, representing transition structures: from each point of the line segment a path of steepest descent leads to the saddle point near the middle of the line segment. The catchment region model provides a unique assignment of each internal configuration to a critical point, representing a stable or unstable, formal chemical species. The relaxed cross section version of the *vertical point symmetry theorem* applies to the boundary loop B that subdivides the conformational space M into two subsets, denoted by boldface letters $\mathbf{M}_1$ and $\mathbf{M}_2$, where $\mathbf{M}_1$ contains the boundary B. Along the boundary none of the configurations have a reflection plane symmetry element, whereas $\mathbf{M}_1$ contains an interior point, representing a configuration that has this symmetry element. The theorem implies that there must exist a critical point configuration within family $\mathbf{M}_1$ of configurations for the potential energy surface of *each electronic state* of the catechol system of any net charge. A property of potential energy surfaces, that is, information on energy, can be deduced by using no more than a simple test of symmetry.

the GAUSSIAN 86 program and the standard STO 3G basis set.[31] The topological shape characteristics of the 3D "body" of the catechol molecule, as a function of conformational changes, are discussed elsewhere.[32]

Due to the $\phi_1 = \phi_1 + 360°$ and $\phi_2 = \phi_2 + 360°$ equivalences for the bond rotation angles, the relaxed potential energy surface is periodic in both of the active coordinates. It is possible to represent all configurations of the cross section by a formal unit cell involving any 360° interval for each coordinate, as shown in Figure 7. However, for the actual conformational problem of the catechol molecule, it is not possible to choose a unit cell that would contain each conformational catchment region in a connected representation. For every choice, the boundary of the unit cell cuts into some of the catchment regions, hence an actual, connected catchment region may appear as two, disconnected pieces at opposite sides of the unit cell, and some catchment region may appear as four separate pieces at the four corners of the unit cell.

In Figure 7 the letters m, s and M stand for minima, saddle points of transition structures, and maxima, respectively, whereas the faint solid contour lines represent constant energy values. The first contour around minimum m_1 corresponds to $E = -375.573$ hartrees, and each subsequent line corresponds to an increment of 0.003 hartree, leading to the highest energy contour of $E = -375.555$ hartrees around maximum M_3. The domains enclosed by crosshatched lines are the catchment regions $C(0,j)$ of the three minima m_i, $i = 1, 2, 3$. These catchment regions represent the stable conformers of the catechol molecule (see also comments below). Crosshatched line segments of the M–s–M pattern are catchment regions $C(1,j)$ of transition structures. Note an unusual feature: the catchment regions $C(1,1)$ and $C(1,2)$ of saddle points s_1 and s_2 are the crosshatched line segments M_1–s_1–s_3, and M_2–s_2–s_3, respectively, involving steepest descent paths leading from one saddle point, s_3, directly to other saddle points, s_1 and s_2. Within the 2D relaxed cross section the maximum points are their own catchment regions. Two-dimensional catchment regions $C(0,1)$ and $C(0,2)$ of minima m_1 and m_2 are cut in halves by the boundaries of the unit cell, whereas the catchment region $C(0,3)$ of minimum m_3 appears in four pieces, one at each corner of the unit cell. Most one-dimensional catchment regions $C(1,j)$ of transition structures are cut in halves by the cell boundaries, with the exceptions of those of saddle points s_1, s_2, and s_3.

In the actual molecule the ring substituents in positions 3–6 are all hydrogens, implying that the two OH groups are in equivalent environments. Consequently, the following pairs of critical points as well as their catchment regions are equivalent: minima m_1 and m_2, maxima M_1 and M_2, maxima M_3 and M_4, and saddle points s_1 and s_2. Furthermore, all four saddle points, s_4, s_5, s_6, and s_7, as well as their catchment regions are equivalent. However, if any one of the ring hydrogens is replaced by some other substituent, then the above equivalences are lost, and all critical points of different indices become nonequivalent. Some of the essential topological features of the relaxed potential surface may remain unaffected by a substitution (especially for substitutions in ring positions 4 and 5), and the actual numbering of critical points has been adopted in order to cover these cases.

The point symmetry domains of the relaxed cross section are also shown in Figure 7. Most configuations have only trivial point symmetry, C_1. Along the solid straight line of the NW–SE (Northwest–Southeast) diagonal of the given representation of the unit cell, all configurations have a reflection plane symmetry element, accordingly, the point symmetry is at least C_s. These configurations can be derived from the reference configuration of $\phi_1 = 0$ and $\phi_2 = 0$ by simultaneous disrotatory motions of the OH groups. Two isolated configurations of C_s symmetry are also found at the two energy minima, m_1 and m_2, each represented twice in the figure, at opposite sides of the unit cell. In both of these two planar configurations only one of the OH bonds points toward the other, and any small change in the angles ϕ_1 and ϕ_2 does lead to a loss of the plane of symmetry.

All configurations with C_2 point symmetry are found along the NE–SW diagonal; these configurations can be derived from the reference configuration of $\phi_1 = 0$ and $\phi_2 = 0$ by simultaneous conrotatory motions of the OH groups. The C_2 symmetry axis passes through the midpoints of the C(1)–C(2) and C(4)–C(5) bonds.

There are only two isolated points, saddle point s_3 and minimum m_3, where both the reflection plane and the C_2 symmetry axis are present; at these configurations the point symmetry is C_{2v}. Saddle point s_3 falls within the interior of the chosen unit cell; consequently, it is represented by a single point of the figure. However, minimum point m_3 appears four times in the figure, as it happens to fall on the corners of the chosen unit cell. In fact, both isolated configurations of point symmetry C_{2v} may be regarded as points occurring at the intersections of the C_s (NW–SE) diagonal and the C_2 (NE–SW) diagonal. One should note that the C_s and C_2 symmetry sets represented by these two different diagonal lines do intersect at two different points, a feat that cannot be accomplished by ordinary straight lines in Euclidean geometry, indicating

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(30) Pages 91 and 93 in ref 11.

(31) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Feuder, E. M.; Pople, J. A. GAUSSIAN 86; Carnegie-Mellon Quantum Chemistry Publishing Unit; Pittsburgh, PA, 1986.

(32) Arteca, G. A.; Heal, J. A.; Mezey, P. G. *Theor. Chim. Acta* **1990**, *76*, 377.

that their straight line representations within a single unit cell do not convey all the relevant information.

There is a useful, alternative representation of the unit cell that avoids multiple occurrences of individual configurations. This representation is identical with that obtained in a standard topological transformation of periodic functions[33] that has been used extensively in various conformational potential surface studies and reviewed, for example, in ref 11. By identifying two opposite boundary lines of the unit cell, representing the same family of configurations, the potential map can be rolled up, forming a cylinder. The two end circles of this cylinder also represent a common family of configurations, and, by identifying these circles, the two ends of the cylinder are joined, forming a torus as shown in Figure 8. On this torus each nuclear configuration of the relaxed cross section is represented by precisely one point, and, at the same time, all the catchment regions appear as connected sets. By contrast to the conventional unit cell representation shown in Figure 7, where two distant points may represent very similar or even identical configurations, on the torus two points that are far apart always represent two very different configurations. Hence the conformational torus reflects better the interrelations among configurations. However, one disadvantage of the graphical representations of the conformational torus is that some of its parts are hidden from view. It is often useful to carry out parallel studies of the geometrical features on conventional unit cells and the general topological properties on conformational tori, keeping the dual representation in perspective.

As it is evident from Figure 7, the catchment region point symmetry theorem applies to each catchment region of the catechol relaxed cross section. For example, point symmetry C_{2v} is the highest one occurring within catchment region C(0,3), found at the minimum point m_3 = K(0,3). There exists only one such point of the highest symmetry within C(0,3).

The assertion of the relaxed cross-section catchment region minimum theorem (theorem 7) is found valid in the example, since the unique point of C_{2v} symmetry is indeed the lowest energy point of catchment region C(0,3).

The vertical point symmetry theorem (theorem 8) is illustrated by the conventional unit cell representation (Figure 7) and by a conformational torus representation (Figure 8) of the catechol relaxed cross section. In the notations used in the figures the indication of dimension 2 is omitted. Note that the C_s and C_2 symmetry sets appear as circles on the conformational torus. The relaxed conformational space, denoted by M in Figures 7 and 8, is divided into two subsets, labeled with boldface symbols $\mathbf{M}_1$ and $\mathbf{M}_2$, by a boundary line B that is contained in $\mathbf{M}_1$. Note that due to the limitations of the conventional unit cell representation, in Figure 7, the boundary line B appears disconnected; however, in the conformational torus representation (Figure 8), the boundary B is properly shown to be connected. Along the boundary B all configurations have only trivial C_1 point symmetry. Within the family $\mathbf{M}_1$ of configurations there exists a configuration of point symmetry C_s, that is, one with a symmetry element (reflection plane) that does not occur along B. Consequently, condition (i) of the theorem is fulfilled, and the theorem applies: in family $\mathbf{M}_1$ there must exist a critical point configuration for the relaxed cross section of the potential surface of *each electronic state*.

The very same choice of families $\mathbf{M}_1$ and $\mathbf{M}_2$ of configurations and boundary line B also serves as an example for the vertical symmetry element theorem, adapted to relaxed cross sections (theorem 9). The symmetry element of reflection plane, present at point m_3, is not a member of the family S_B of symmetry elements occurring along B (in this example, S_B contains only the trivial symmetry element, corresponding to the identity symmetry operation I). Consequently, the theorem applies, indicating the existence of a critical point in the interior of $\mathbf{M}_1$.

One may choose the families $\mathbf{M}_1$ and $\mathbf{M}_2$ of configurations and boundary line B in infinitely many different ways, some of which may lead to identical conclusions. Whereas in the above choice there is no variation of point symmetry along B, in the following choice the symmetry varies along B. This problem is the easiest to visualize on the conformational torus of Figure 8. One may take B as any loop falling on or in between the first and second energy contours around point m_3; for example, one may take B as the first energy contour. From the resulting two subsets of the torus take family $\mathbf{M}_1$ as the one that contains m_3. Along B, most configurations have only the trivial symmetry C_1; however, B must cross the circle of configurations of C_s symmetry as well as the circle of configurations of C_2 symmetry, both on at least two occasions and possibly a greater even number of times. Hence some configurations with a reflection plane and some configurations with a C_2 symmetry axis do occur along B. There exists a configuration within $\mathbf{M}_1$ that has C_{2v} symmetry, and there is no configuration along B that has all the symmetry elements corresponding to the C_{2v} point symmetry group. Consequently, the vertical point symmetry theorem applies, and there must exist a critical point in family $\mathbf{M}_1$ for the relaxed cross section of the potential surface of each electronic state. This critical point is m_3 that happens to be a minimum point of the ground electronic state relaxed potential surface.

Of course, the theorems are not restricted to energy minima. In order to illustrate this fact, consider, for example, the representation in Figure 7 and a circle drawn around saddle point s_3 by any positive radius of less than 180° (note that both coordinates of the unit cell are angles, hence distances on the conformational map, such as a radius, can be measured in degrees). We take this circle as the boundary B and take family $\mathbf{M}_1$ as the disk defined by the circle. The point symmetry groups occurring along B are C_1, C_2, and C_s. There exists a configuration within the disk $\mathbf{M}_1$ where the point symmetry group is C_{2v}, and the full set of symmetry elements corresponding to group C_{2v} does not occur anywhere along B. Hence the vertical point symmetry theorem implies that within the disk $\mathbf{M}_1$ there must exist at least one critical point for every electronic state. If the radius of the circle is large enough, then several actual critical points of the ground-state relaxed potential surface fall within $\mathbf{M}_1$. However, for smaller radii, e.g., for 30°, there is only one critical point of the ground-state surface, the saddle point s_3. In this case the theorem leads to the detection of a critical point that happens to be a saddle point of a transition structure.

In all of the above examples the critical point coincides with the test point K of set $\mathbf{M}_1$; however, this is not required in general. There may exist a whole family of interior points K of the same symmetry properties, and the critical point can be different from the actual test poin K. A coincidence is common in two dimensions, if there exists some variety of point symmetries within the cross section. These are the very 2D problems that serve best as illustrative examples in planar drawings. However, even in two dimensions, the point symmetry theorem may determine only a subset within which at least one critical point must occur for each electronic state. For different electronic states their location (as well as type, e.g., minimum, saddle point) may be different.

One such example can be found in Figure 7 if one takes a different choice for subsets $\mathbf{M}_1$ and $\mathbf{M}_2$. Take two parallel lines, 10° apart on both sides of the C_2 diagonal (NE–SW) in Figure 7, and their extensions which (by periodicity) are lines near the NW and SE corners, cutting off these corners from the rest of the unit cell. (Note that the "extended" lines appear as two distorted circles on the conformational torus of Figure 8 with the circle C_2 sandwiched between them.) This pair of lines separates the relaxed conformational unit cell into two subsets, $\mathbf{M}_1$ and $\mathbf{M}_2$. We take $\mathbf{M}_1$ as the subset that contains the NE–SW diagonal and take the pair of lines as its boundary B. In this case the boundary B has two parts (two maximum connected components), a fact that can be demonstrated easily on the conformational torus of Figure 8. Take point K as any point along the NE–SW diagonal; this point has at least C_2 symmetry. Since along B only C_1 and C_s point symmetries occur, the relaxed cross section vertical point symmetry theorem (theorem 8) applies, indicating that $\mathbf{M}_1$ must contain at least one critical point. The precise location of this critical point is not determined by the theorem, although by

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[33] Singer, I. M.; Thorpe, J. A. *Lecture Notes on Elementary Topology and Geometry*; Springer-Verlag: New York, 1976; p 64.

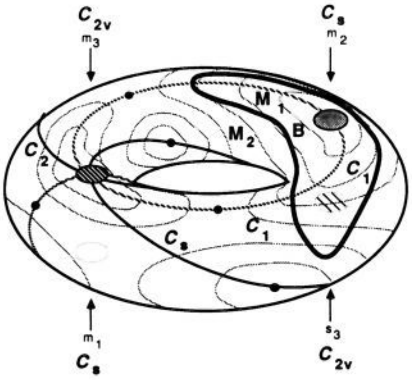

Figure 8. This figure shows illustration of point symmetry domains and the relaxed cross section vertical point symmetry theorem of the catechol conformational problem on a conformational torus. Note that the unit cell representation of Figure 7 does not reflect properly the connectedness of the boundary loop B, and, in general, very similar or even identical configurations may appear as distant points of the unit cell. The conformational torus avoids these difficulties and provides a faithful topological representation of the conformational problem.

reducing the distance of 10° between the two lines, the size of set M_1, hence the uncertainty in the location (as predicted by the theorem), can be reduced. Eventually, the critical point "caught" by the theorem can be confined to the NE–SW diagonal. However, if one takes a whole family of potential surfaces, then along this diagonal line some of the critical points may appear at different locations for each potential surface, depending on the net charge and the electronic state.

In three or higher dimensions the coincidence of the test point K and the critical point is no longer the most common case. For an illustration of this feature for the case of a simple 3D problem, one may consider a "breathing" motion of the catechol molecule, in addition to the C–O bond rotations. In order to be able to use a simple, visualizible extension of the 2D problem described above, we choose the breathing motion as a uniform scaling of all of the conformations of the molecule, affecting all internuclear distances by a common multiplying factor f. We take this factor f ($f > 0$) as the third active coordinate, in addition to the rotation angles ϕ_1 and ϕ_2. (In the strict sense, the $f = 0$ case of the united atom should also by included; however, the energy barrier of a nuclear reaction leading to this point is much too high, and it is safe to assume that no steepest descent path would lead there.) The new, 3D relaxed cross section may be imagined by taking coordinate f along a direction perpendicular to the plane of Figure 7. We take the new 2D boundary B as a tube, generated by translating the loop B shown in the figure parallel to the new coordinate axis f. Family M_1 of configurations are all those enclosed by and falling on the tube, whereas family M_2 contains all other configurations of the 3D relaxed cross section. Along tube B all configurations have only trivial C_1 point symmetry; however, tube B encloses a line along which all configurations have C_s point symmetry. If one chooses the test point K as any point along this line, then the relaxed cross section vertical point symmetry theorem (theorem 8) applies: there must exist a critical point within family M_1 of configurations for the 3D relaxed cross section of the potential energy hypersurface of each electronic state (of any net charge) of the catechol system. For most choices of coordinate f, the test point K and the critical point (m_2 in Figure 7) are different.

Summary

In this report we describe a new, global approach to the analysis of the relations between point symmetry of nuclear arrangements and energetic stability of chemical species. The approach leads to the recognition of several new symmetry theorems which provide surprisingly strong symmetry conditions on the shapes of ground and excited electronic state potential energy surfaces for both neutral and ionic systems. The catchment region point symmetry theorem and various "vertical" symmetry theorems may serve as predictive tools in the search for both neutral and ionic stable molecular species and transition structures on ground- and excited-state potential energy surfaces. The vertical symmetry theorems use only point symmetry information along the boundary B of a configuration family M_1 and at one interior test point K of M_1. Just as an "over the horizon radar", these theorems are suitable for the "remote detection" of a critical point, a feature important in the topological analysis of potential surfaces and, in general, in the topological approach to molecular species and chemical reactions.[34] The above theorems can serve as tools for detecting as well as locating some of the critical points. The mere presence of an interior point K of symmetry properties sufficiently different from those at the boundary B of a multidimensional domain M_1 leads to the detection, although not necessarily to the exact location of a critical point. However, by gradually decreasing the size of set M_1 by contracting its boundary B and by testing the conditions of the theorems, one may reduce the uncertainty in the location, and in some cases one may find the exact location of the critical point. The theorems are also adapted to lower dimensional, relaxed cross sections of multidimensional potential surfaces, important in actual potential surface computations. Their applications are illustrated by various examples.

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Supplementary Material Available: Basic discussion of theorems 6–11 (3 pages). Ordering information is given on any current masthead page.

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