

New rules on potential surface topology and critical point search

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The topology of potential energy surfaces provides a unified framework for the study of individual molecular properties, all conformational changes as well as chemical reactions. Molecular behavior, electronic and vibrational properties, conformational freedom, reactivity bond formation and bond breaking are all energy dependent, and the potential energy surface approach provides an elegant, conceptually convenient, although rather complicated representation of this energy dependence. Topology as a mathematical tool is exceptionally suitable for the extraction of the most essential features of complicated representations. By applying topological methods for potential surface analysis, a new, global perspective of many aspects of chemistry emerges. Some of these topological results also have important practical, computational significance. A family of new topological rules and symmetry relations will be adapted for applications in low dimensional relaxed cross-sections of configuration spaces, with a special emphasis on their role in the search for critical points, primarily energy minima and saddle points of transition structures of potential energy surfaces and hypersurfaces.

1. Introduction

When considering distorted forms of molecules, one must make a choice of reference form against which all other forms are compared. In a classical model of molecules, with a geometrically defined ideal form, all other forms may be compared to the ideal one. However, molecules are quantum-mechanical, topological entities which do not possess a geometrically defined nuclear configuration in the classical sense. The nuclei, just as the electrons, are subject to the Heisenberg uncertainty, hence the concept of nuclear position within a molecule is not a rigorously valid one. Nevertheless, by taking a pragmatic approach involving a form of the Born–Oppenheimer approximation for geometrically defined nuclear positions and introducing quantum mechanical uncertainty by defining families of such nuclear configurations as open sets of a topological space [1], one may use geometrical concepts without violating the quantum mechanical nature of the model. This model is compatible with the concept of equilibrium nuclear configuration for energetically stable conformations of molecules. The equilibrium nuclear configuration may be used as reference for distortions.

The problems of molecular deformations are related to energetic properties and the study of molecular identity requires the explicit consideration of the deformability of molecules. This requirement naturally leads to the potential energy surface model and to the global analysis of deformability of a whole range of formal nuclear arrangements. In a global approach to the study of molecular identity, it is advantageous to use the nuclear configuration space approach where all possible arrangements of a given stoichiometric family of nuclei are considered. Each stoichiometric family of chemical species is defined by a set of nuclei which may take any relative arrangement. These arrangements include all isomers, reaction intermediates, transition structures, and decomposition products of all molecules with a given atomic composition, as well as all distorted conformations of the above.

One may regard nuclear arrangements obtained from one another by rigid translation and rigid rotation as equivalent, and focus on the internal configuration K of the arrangement. The family of all possible internal configurations of a set of nuclei may be thought to form an internal configuration space. The space we shall use is the metric space M of internal configurations [1]. Since relative arrangements of $N \geq 3$ nuclei can be described by $3N - 6$ internal coordinates, the dimension of M is $3N - 6$. The metric of M is interpreted as the distance $d(K, K')$ between any two points K and K' of the space M , representing a measure of dissimilarity of the corresponding two internal nuclear configurations K and K' . Here we use the same notation, K , for the internal configuration (the 3D relative arrangement of the nuclei) and for the point representing it within the configuration space M .

By considering a given electronic state and infinitely slow motion for the nuclei, a potential energy value can be assigned to each nuclear configuration K ; this defines a potential energy hypersurface $E(K)$ over M . A point K of M where the gradient of $E(K)$ vanishes (where the tangent hyperplane to $E(K)$ is "horizontal") is called a critical point, denoted by $K(\lambda, i)$. Here, λ is the critical point index (and not the "order of critical point" as it is sometimes incorrectly called), defined as the number of negative eigenvalues of the Hessian matrix $\mathbf{H}(K(\lambda, i))$ of second derivatives of the energy, while i is a serial index.

For a given potential energy hypersurface $E(K)$, the range of deformations that preserves chemical identity of a chemical species defines a subset of the nuclear configuration space M . This subset, regarded as representing the chemical species within M , can be chosen as a *catchment region* $C(\lambda, i)$ of the corresponding potential energy hypersurface. Each catchment region $C(\lambda, i)$ is defined as the collection of all those nuclear configurations K from where the path of an infinitely slow relaxation (a steepest descent path in a mass-weighted coordinate system) leads to a common critical point $K(\lambda, i)$. (See original references in [1] and [2].) A catchment region $C(0, i)$ of a minimum point $K(0, i)$ represents the i th stable molecular species of the given stoichiometry and of the electronic state associated with the given potential energy hypersurface $E(K)$. The steepest descent paths from all points of the catchment region $C(0, i)$ lead to the minimum point $K(0, i)$; the dimension of $C(0, i)$ is

$3N - 6$. A $(3N - 7)$ -dimensional catchment region $C(1, j)$ of a saddle point $K(1, j)$ of critical point index $\lambda = 1$ represents the j th transition structure. Catchment regions $C(\lambda, i)$ of critical points $K(\lambda, i)$ of higher indices, $\lambda > 1$, and of dimensions lower than $3N - 7$, are of lesser direct chemical significance (and are not true chemical species); nevertheless, for the sake of uniformity in the terminology, they are also referred to as formal chemical species.

Let us denote by G_k the collection of all nuclear configurations of M which have a given point symmetry group g_k . Such a set G_k may be disconnected, since it is possible that two nuclear configurations K_1 and K_2 of the same point symmetry cannot be connected by a path with all configurations K along it having the same symmetry. In such cases, we shall consider the maximum connected components G_{kj} of each set G_k . Both the catchment regions $C(\lambda, i)$ of each potential energy hypersurface $E(K)$ and the configuration space symmetry domains G_{kj} generate rigorous partitionings of the entire nuclear configuration space M into subsets. Whereas there is a one-to-one correspondence between critical points $K(\lambda, i)$ and catchment regions $C(\lambda, i)$, there is no such simple correspondence for the symmetry partitioning, although other useful relations can be found [2].

An important earlier result is the rule on the conservation of point symmetry elements along segments of steepest descent paths falling between critical points [3], as well as the conservation of framework group elements along such segments (a framework group element is a pair of point symmetry elements and the nuclear permutation that reverses its effect). This result is valid if the potential surface is defined in terms of mass-weighted coordinates, and it has been used to derive some global relations within the nuclear configuration space M [1,2].

Molecular point symmetry is an important tool for the characterization of nuclear configurations, and it serves as a guide in the search for critical points of potential energy hypersurfaces. In an earlier study [2], a global approach to nuclear point symmetry within a configuration space was proposed, leading to new rules. Versions of these rules, restricted to subsets (relaxed cross-sections) of the nuclear configuration space, were also described but only an outline of their proofs was given [2]. In particular, theorems 1–5 we shall describe in this study have been listed, without detailed proof, as theorems 6–10 of ref. [2]. In the present study, we shall provide an explicit formulation and detailed proof of all of these theorems, including the relaxed cross-section catchment region point symmetry theorem and the relaxed cross-section vertical point symmetry theorem. In addition, some new rules will be derived.

2. Relaxed cross-sections and some of their properties

First we shall review the definition and some properties of relaxed cross-sections. The motivation for studying relaxed cross-sections of a configuration space M and of an energy hypersurface $E(K)$ is that not all internal coordinates of a molecule participate equally in some chemical processes. The changes in some

coordinates, such as C–H bond lengths in methyl groups, are often unimportant or negligible. This allows the reduction of the dimension of the problem, that can be accomplished by taking relaxed cross-sections.

We choose an electronic state and consider chemical processes along the corresponding potential energy surface $E(K)$. We assume that a subset A of the configuration space M is provided with a local coordinate system, where the first n of the internal coordinates ($n \leq 3N - 6$) are the chemically important *active coordinates* for the chemical processes considered, whereas the remaining n' coordinates ($n' = 3N - 6 - n$) are taken as the *passive coordinates*. For each possible fixed choice of the n active coordinates within set A , the n' passive coordinates can be chosen so that a fully relaxed n -dimensional surface C is obtained, where C is characterized by its points having zero gradient components orthogonal to C . Note that simple energy minimization along the passive coordinates does not necessarily lead to such a relaxed surface C , since along C the passive coordinates may also change, although, by assumption, only slightly. The condition of vanishing energy gradients along the passive coordinates leads to a fully relaxed cross-section C only if C is everywhere locally orthogonal to the subspace of the passive coordinates [2], a condition only seldom fulfilled. If all of the nuclear configurations K corresponding to the passive coordinates selected by the correct relaxation condition are found within set A , then this set C is called an n -dimensional *relaxed cross-section* of A according to the given potential energy surface $E(K)$.

At every point K in the n -dimensional surface C , the gradient vector is tangential to C ; consequently, the "gradient flux" is zero across C . The potential energy hypersurface $E(K)$ may be restricted to this set C , and $E(K)$ 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 $E(K)$.

Evidently, a relaxed cross-section C depends on the choice of the electronic state, that is, on the potential surface $E(K)$, since relaxation is defined along $E(K)$. On the other hand, one may repeat the relaxation procedure of the passive coordinates for several electronic states using the *same* collection of n active coordinates. In this case, one obtains a series of cross sections C_i , one for the potential energy surface $E_i(K)$ of each electronic state. These relaxed cross-sections C_i may differ only in the passive coordinates. The n (active) components of all coordinate vectors in each C_i are common for all of the electronic states, and they generate a common set C^n of n -dimensional vectors. Individually, each cross-section C_i is a (possibly) curved surface that cuts across the configuration space M , and it depends on the potential energy surface (the electronic state) according to which it is "relaxed". On the other hand, the projection C^n of each of these sets C_i onto the n -dimensional subspace of the active coordinates is the same, that is, C^n is independent of the potential energy hypersurface $E_i(K)$ (electronic state) used for relaxation. Consequently, all these relaxed cross-sections C_i of potential energy surfaces $E_i(K)$ of all electronic states are defined over the same set C^n of n -dimensional coordinate vectors, that is, they are functions of the same n active coordinates.

It is important to realize that an n -dimensional surface C of points with zero gradient components orthogonal to C does not require that the energy is near minimum with respect to all of the passive coordinates. In a relaxed cross-section C , the energy may be near maximum along some of the passive coordinates. A rope relaxing along a mountain ridge is such an example.

If the set A is finite, then a cross-section C of A is also limited to a finite configurational domain, hence it may have a boundary. If the cross-section C itself has no boundary, then C^n may cut across the entire configuration space; in this case, C and its projection C^n to the subspace of the active coordinates represent a *complete relaxed cross-section*. No steepest descent path can leave a complete relaxed cross-section; however, if the cross-section is not complete, then it is possible for a steepest descent path to leave it, but only along a direction locally tangential to the cross-section at one of its boundary points.

If the point symmetry domain G_{ij}^n of C^n has no points falling on the boundary of C^n , then G_{ij}^n is an *interior point symmetry domain* of C^n . Since a complete relaxed cross-section C^n has no boundary, all its point symmetry domains G_{ij}^n are interior symmetry domains.

If a critical point $K(\lambda, i)$ falls within a relaxed cross-section C^n , then the *catchment region* $C^n(\lambda, i)$ of the relaxed cross-section C^n is defined as the collection of all the nuclear configurations of C^n from where steepest descent paths lead to the critical point $K(\lambda, i)$. This concept is justified by the following two considerations. A steepest descent path passing through any point K of a relaxed cross-section C either stays within C , or it leaves C at the boundary of C along a direction of tangential extension of C . Furthermore, all points K which fall within the intersection of the catchment region $C(\lambda, i)$ of the full configuration space M and the relaxed cross-section C^n , and also have the property that the entire steepest descent path segment between K and $K(\lambda, i)$ is contained within C^n , form a connected set.

The set $C^n(\lambda, i)$ is an *interior catchment region* of C^n if $C^n(\lambda, i)$ is a catchment region of C^n that has no points falling on the boundary of C^n . All catchment regions of a complete relaxed cross-section are interior catchment regions. As a function of the size and shape of a relaxed cross-section C^n , the common parts of some catchment region $C(\lambda, i)$ of M and the relaxed cross-section C^n may be disconnected, implying that their common parts do not necessarily coincide with the corresponding catchment region $C^n(\lambda, i)$ of the relaxed cross-section C^n . For a complete relaxed cross-section C^n , the common part of $C(\lambda, i)$ and C^n is $C^n(\lambda, i)$.

Note that the term "relaxed cross-section" is often used in the literature somewhat incorrectly for not fully relaxed cross-section, where simple energy minimization along some of the less important coordinates is used as a criterion. Unless these coordinates are constant throughout the cross-section, this criterion does not lead to a truly relaxed cross-section, and the results are often dependent on the coordinate representation. A more detailed discussion of this problem is given in [4].

For the sake of simplicity, we shall assume that the potential energy hypersurfaces are twice differentiable in all the domains considered. This condition is

usually satisfied, at conical intersections and at other special points, even first derivatives may fail to exist. Note that conical intersection points often behave as extreme cases of critical points, and some of the global point symmetry theorems have been generalized for some non-differentiable potential surfaces having conical intersections [5].

3. Relaxed cross-section symmetry theorems

Consider a catchment region $C^n(\lambda, i)$ of a relaxed cross-section C^n . The critical point $K(\lambda, i)$ is the only critical point within $C^n(\lambda, i)$. From all other points K of $C^n(\lambda, i)$, the path of steepest descent must stay within the relaxed cross-section C^n , it must stay within $C^n(\lambda, i)$, and it leads to $K(\lambda, i)$. By the conservation of point symmetry elements along steepest descent paths between non-critical points, all point symmetry elements must also be present arbitrarily close to the critical point $K(\lambda, i)$. Hence, the configuration represented by the critical point $K(\lambda, i)$ must have all the point symmetry elements of all configurations represented by points K of the catchment region $C^n(\lambda, i)$. Consequently, the point symmetry group of the configuration at the critical point $K(\lambda, i)$ must contain the point symmetry groups of all other configurations K of the catchment region $C^n(\lambda, i)$ of the relaxed cross-section C^n as subgroups. If one interprets the term “higher point symmetry” by group–subgroup relations, and regards each group as one of its (trivial) subgroups, then the above is a direct proof of the *relaxed cross-section catchment region point symmetry theorem*:

THEOREM 1

Within each catchment region $C^n(\lambda, i)$ of relaxed cross-section C^n , the nuclear configuration corresponding to the critical point $K(\lambda, i)$ has the highest point symmetry.

As in the general case of catchment regions within the full configuration space M [2], the theorem does not imply that the critical point $K(\lambda, i)$ is the only point within the catchment region $C^n(\lambda, i)$ of the relaxed cross-section C^n that has the highest point symmetry. Some other points K , and possibly all points of the relaxed cross-section catchment region $C^n(\lambda, i)$ may have the same, highest point symmetry.

Also note that, similarly to the case of the full configuration space [2], this theorem holds for the potential surfaces, relaxed cross-sections, and catchment regions of all electronic states of neutral and all charged species of the given stoichiometric family.

It is not necessary for $C^n(\lambda, i)$ to be an interior catchment region of the relaxed cross-section C^n ; it is sufficient that the catchment region $C^n(\lambda, i)$, hence its critical point $K(\lambda, i)$, exists within C^n .

The following *relaxed cross-section catchment region minimum theorem* may be regarded as a partial converse of the above relaxed cross-section catchment region point symmetry theorem:

THEOREM 2

If within a catchment region $C^n(\lambda, i)$ of a relaxed cross-section C^n there is a point K with a symmetry element R not present anywhere else in the catchment region $C^n(\lambda, i)$, then this point K must have the *lowest energy value within the catchment region*, and point K is the critical point $K(\lambda, i)$ of $C^n(\lambda, i)$.

Proof

Each catchment region $C^n(\lambda, i)$ of a relaxed cross-section C^n contains precisely one critical point $K(\lambda, i)$. This critical point $K(\lambda, i)$ is the endpoint of all steepest descent paths originating anywhere within $C(\lambda, i)$; consequently, $K(\lambda, i)$ must have the lowest energy within $C^n(\lambda, i)$. If a point K of the catchment region $C^n(\lambda, i)$ has a symmetry element R then, by the conservation of symmetry along steepest descent paths, this symmetry element must also be present at the critical point $K(\lambda, i)$. If this symmetry element R occurs only at point K of $C^n(\lambda, i)$, then K must be identical to $K(\lambda, i)$ and then point K must have the lowest energy within the catchment region $C^n(\lambda, i)$ of the relaxed cross-section C^n . \square

This theorem also holds for the potential surfaces, relaxed cross-sections, and catchment regions of all electronic states of neutral and all charged species of the given stoichiometric family.

The following three theorems are the relaxed cross-section versions of the vertical symmetry theorems of ref. [2]. The terminology refers to the convention of regarding energy as a formal "vertical" dimension over a nuclear configuration space M . Similarly, if energy and symmetry relations restricted to a relaxed cross-section C^n are studied, then energy may be regarded as a vertical dimension over the relaxed cross-section C^n .

These theorems describe symmetry and critical point relations between various parts of a relaxed cross-section C^n . Choose any surface B^n within C^n that divides the relaxed cross-section C^n into two parts, C_1^n and C_2^n . We assume that the set C_1^n of configurations contains the chosen surface B^n as its boundary.

We denote by \mathcal{R}' a family of symmetry elements R'_1, R'_2, \dots, R'_p , present for *all* nuclear configurations K' along B^n ,

$$\mathcal{R}' = \{R'_1, R'_2, \dots, R'_p\}. \quad (1)$$

We select a nuclear configuration K from set C_1^n . Next, we select a family \mathcal{R} of symmetry elements R_1, R_2, \dots, R_q which are present at point K :

$$\mathcal{R} = \{R_1, R_2, \dots, R_q\}. \quad (2)$$

Note that the theorems we shall prove are also valid if one includes only some of the eligible symmetry elements in families \mathcal{R}' and \mathcal{R} . If, however, all eligible

symmetry elements are included in families \mathcal{R}' and \mathcal{R} , then both families of the corresponding symmetry operators are groups (with the usual group multiplication of symmetry operators).

The *vertical point symmetry theorem of relaxed cross-sections* states the following:

THEOREM 3

If either

- (i) no configuration along B^n possesses the family \mathcal{R} of symmetry elements, or
- (ii) configuration K does not have all the symmetry elements of family \mathcal{R}' ,

then the family C_1^n of relaxed cross-section configurations must contain at least one critical point for the potential energy surface of each electronic state (or 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 subset C_1^n of the relaxed cross-section C^n , that is, configuration K cannot fall on the boundary B^n .

Proof

Choose a potential energy surface corresponding to any one of the possible electronic states. There are two possibilities:

(a) If the chosen point K of set C_1^n is a critical point of this potential surface, then for this potential surface the statement of the theorem follows.

(b) If K is not a critical point, then there must exist a steepest descent path that passes through K . Since K is a point of the relaxed cross-section C^n , a path of steepest descent cannot leave C^n , except possibly along a locally tangential direction at a point of the boundary of C^n , if the relaxed cross section C^n is not a complete one. We now show a much stronger restriction: this steepest descent path cannot leave set C_1^n either. We shall prove this by contradiction. First we recall that C_1^n contains its boundary B^n . If the path would leave set C_1^n , then it would have to reach the boundary B^n of C_1^n at some point K' . This point K' could not be a critical point itself, since then the path would terminate there, hence the path could not leave C_1^n . If the path would leave set C_1^n , then this point K' could not be an ordinary, non-critical point either, since then the conservation of symmetry elements along steepest descent paths would imply that configurations K and K' would have precisely the same symmetry elements. However, this would contradict both of the conditions (i) and (ii) of the theorem. Consequently, there exists no point K' at the boundary B^n that can be reached by the steepest descent path from K . We conclude that the path must terminate within set C_1^n . Since each steepest descent path must terminate at a critical point, set C_1^n must contain at least one critical point of the potential energy surface of the chosen electronic state. Since the overall electronic charge and the electronic state have been chosen arbitrarily, this conclusion is valid for each electronic state; this proves the theorem. \square

Neither the exact location nor the type of the critical point is implied by the theorem. Furthermore, there may be more than one critical point within the subset C_1^n of the relaxed cross-section C^n , and some critical points may remain undetected by the theorem.

For different overall charges and different electronic states, the critical points detected by the theorem may have different locations within C_1^n , and these critical points may be of different types, for example, a minimum on one and a saddle point on another potential surface over the same subset C_1^n of the relaxed cross-section C^n . It is important to point out that the chosen test point K itself does not have to be a critical point for any one of the potential surfaces.

For the next result, choose a symmetry element R of some interior point K of subset C_1^n , and take the family S_B of *all* symmetry elements of nuclear configurations occurring along boundary B^n .

The *vertical symmetry element theorem of relaxed cross-sections* relies on a set of conditions different from those of the previous theorem to reach a similar (but not identical) conclusion. This theorem states the following:

THEOREM 4

If the subset C_1^n of the relaxed cross-section C^n contains a configuration K that has a symmetry element R *not present* in the family S_B of all point symmetry elements occurring along B^n , then the *interior* of C_1^n must contain at least one critical point for the potential energy surface of each electronic state (of each possible overall electronic charge).

Theorems 3 and 4 differ on two main points. If there exist two point symmetry groups along boundary B^n , neither of which is a subgroup of the other, then it is impossible to choose the class \mathcal{R}' of theorem 3 to coincide with family S_B . Theorem 3 detects the existence of a critical point somewhere in set C_1^n . As allowed by condition (ii) (but not by condition (i)), this critical point may fall on the boundary B^n . Theorem 4 is somewhat stronger, since the critical point detected must fall within the interior of C_1^n , that is, it cannot fall on the boundary B^n .

Proof

Choose a potential surface defined over the relaxed cross-section C^n , and a point K of set C_1^n that has a symmetry element R not present in family S_B . There are two cases:

(a) If K is a critical point, then for this potential surface the statement of the theorem follows.

(b) If K is not a critical point, then there exists a steepest descent path passing through K . A general steepest descent path cannot leave the relaxed cross-section C^n , except possibly along a locally tangential direction at a point of the

boundary of C^n , if the relaxed cross-section C^n is not a complete one. *This* steepest descent path cannot leave subset C_1^n , it cannot even reach the boundary B^n of C_1^n either, since then it would have to have a common point with B^n , and then the family S_B would contain all the symmetry elements of K , including R . This contradicts the conditions of the theorem. Consequently, the steepest descent path must terminate within the interior of subset C_1^n . Since each steepest descent path must terminate at a critical point, the interior of set C_1^n must contain at least one critical point of the potential energy surface of each electronic state. \square

The next theorem may be regarded as a partial “converse” of theorems 3 and 4. Information on the lack of presence of critical points within a given domain of a relaxed cross-section C^n (for some electronic state) can be used to obtain global conclusions concerning symmetry within an entire subset C_1^n of the relaxed cross-section C^n .

THEOREM 5

The lack of a critical point within C_1^n for the potential energy hypersurface $E(K)$ of any electronic state of any overall charge implies that no interior point K of C_1^n can have any symmetry element not present at the boundary B^n .

(If a point symmetry group g_i contains the family S_B of all the symmetry operators of symmetry elements occurring at various points of the boundary surface B^n , and if there exists an electronic state (of any net charge) with a potential surface that has no critical point within set C_1^n , then no point K of set C_1^n can have a point symmetry group g , different from g_i , $g \neq g_i$, that contains g_i as a proper subgroup.)

Proof

If C_1^n contains no critical point for a potential surface, then for this surface the steepest descent paths from all points of C_1^n must leave C_1^n passing through its boundary B^n . Consequently, all symmetry elements present at various points of C_1^n must occur somewhere along the boundary B^n . \square

An interesting corollary of this theorem is the following. If the potential surface of one electronic state has a critical point within C_1^n , then this critical point may have additional symmetry elements which are nowhere present along the boundary B^n . If, however, there is another electronic state with a potential surface that has no critical point within set C_1^n , 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^n .

Additional results can be derived if one considers the symmetry domain partitioning of a relaxed cross-section. An interior point symmetry domain G_{kj}^n of a relaxed cross-section C^n is defined as a maximum connected component of the

intersection of G_k with the relaxed cross-section C^n , having no common point with the boundary of C^n .

The following three results are generalizations of the supplementary material for ref. [2]. The generalizations below provide information on both the lowest and the highest energy points within a point symmetry domain of a relaxed cross-section.

An interesting property of interior point symmetry domains G_{kj}^n of a relaxed cross-section C^n is described by the following theorem:

THEOREM 6

If G_{kj}^n is an interior point symmetry domain of a relaxed cross-section C^n , and if the corresponding point symmetry group g_k is not a subgroup of any other point symmetry group occurring within C^n , then

- (i) G_{kj}^n must contain a critical point,
- (ii) the lowest energy point within symmetry domain G_{kj}^n is a critical point, and
- (iii) the highest energy point within symmetry domain G_{kj}^n is also a critical point.

Proof

Since G_{kj}^n is an interior point symmetry domain of C^n , and as a consequence of the restriction on group g_k , no other point symmetry domain G_{im}^n on the boundary of G_{kj}^n may have all the symmetry elements present in G_{kj}^n , all steepest descent paths as well as all steepest ascent paths from G_{kj}^n must terminate within G_{kj}^n . Consequently, G_{kj}^n must contain at least one critical point. Furthermore, one of the critical points must have the lowest energy within G_{kj}^n and one of the critical points must have the highest energy within G_{kj}^n . \square

The following *high–low rule* and *high–high rule* are two of the consequences of the above theorem for complete relaxed cross-sections:

HIGH–LOW RULE

If within a complete relaxed cross-section C^n there exists a *highest* point symmetry group g_k (that is, if all other point symmetry groups occurring within C^n are subgroups of g_k), then within C^n there must exist a critical point which has point symmetry g_k , and also the *lowest* energy among all points of C^n having this *highest* point symmetry.

By contrast, for a point symmetry group which is not the highest within C^n even the existence of a critical point within C^n and having this symmetry is uncertain.

HIGH–HIGH RULE

If within a complete relaxed cross-section C^n there exists a *highest* point symmetry group g_k , then within C^n there must exist a critical point which has point

symmetry g_k , and also the *highest* energy among all points of C^n having this *highest* point symmetry.

4. Conclusions

Relaxed cross-sections of a nuclear configuration space M , relaxed according to a specified potential energy hypersurface $E(K)$, provide computational advantages due to their reduced dimension, yet they carry the most essential chemical information. In this study, detailed proofs have been given for a series of relaxed cross-section symmetry theorems interrelating energetic properties, the presence of critical points of the potential energy hypersurfaces, and geometric properties, the point symmetry groups of various nuclear configurations. These theorems provide fundamental constraints in the search for critical points, where a preliminary (inexpensive) computation of point symmetries within a configurational domain, followed by applications of the theorems, can provide information on the presence of a critical point within a given subset of configurations.

All theorems and rules described in this study can be generalized by simply replacing all point symmetry groups and their elements by framework groups and their elements. Also, all results are equally valid for catchment regions and steepest descent paths of “upside down” potential energy hypersurfaces $-E(K)$.

Acknowledgement

This work was supported by both operating and strategic research grants from the Natural Sciences and Engineering Research Council of Canada.

References

- [1] P.G. Mezey, *Potential Energy Hypersurfaces* (Elsevier, Amsterdam, 1987).
- [2] P.G. Mezey, *J. Amer. Chem. Soc.* 112(1990)3791.
- [3] P. Pechukas, *J. Chem. Phys.* 64(1976)1516.
- [4] P.G. Mezey, New symmetry theorems and similarity rules for transition structures, in: *Theoretical and Computational Models for Organic Chemistry*, ed. S.J. Formosinho, I.G. Csizmadia and L.G. Arnaut (Kluwer Academic, Dordrecht, 1991).
- [5] P.G. Mezey, *Int. J. Quant. Chem.* 38(1990)699.