

POINT SYMMETRY GROUPS OF ALL DISTORTED CONFIGURATIONS OF A MOLECULE FORM A LATTICE

Paul G. MEZEY

*Department of Chemistry and Department of Mathematics,
University of Saskatchewan, Saskatoon, Canada S7N 0W0*

Abstract

A generalization of the catchment region point symmetry theorem is given within the framework of lattice theory. The symmetry conditions, formulated in terms of lattice theory, interrelate all stationary and distorted configurations of various ground state and electronic excited state molecular species, transition structures, excimers and exciplexes.

1. Introduction

A brief review of the terminology required for the general results of this paper is given below.

Each point of a nuclear configuration space corresponds to a relative arrangement of the nuclei, specified by some internal coordinates [1]. Each nuclear configuration space belongs to a specified overall stoichiometry, representing the family of all possible arrangements of a given collection of atoms. The configuration space can be chosen as a metric space M , with a metric d expressing the dissimilarity of configurations as distance within space M [2]. For a stoichiometric family of molecular systems of N nuclei (with $N \geq 3$), the internal degrees of freedom are $3N - 6$, that is, the dimension of M is $3N - 6$. In any electronic state, the molecular energy is a function of the nuclear configuration, and this function can be regarded as a potential energy surface over the configuration space M .

Various molecular species of the given stoichiometry may be represented by *domains* within the configuration space M : minor distortions of configurations in the vicinity of the equilibrium configuration do not alter the chemical identity of the species. For a specified electronic state, e.g. for the electronic ground state, these domains can be chosen as the catchment regions of the corresponding potential energy surface [2-4]. With reference to a given electronic state, a catchment region is defined as the collection of all those distorted configurations for which an infinitely slow, vibrationless relaxation of the nuclear arrangement leads to the same equilibrium nuclear configuration. If within a region of this space M the internal coordinates are

derived from the mass-weighted Cartesian coordinates of the nuclei, where the x_i , y_i , and z_i coordinates of each nucleus are multiplied by the square root $m_i^{1/2}$ of the corresponding nuclear mass m_i , then the above relaxations correspond to steepest descent paths on the potential energy surface, describing the collective nuclear motions in dynamic models. Then, an equivalent definition of a catchment region can be given as the collection of all those points of the configuration space M from where steepest descent paths lead to the same critical point of the given potential energy surface.

Each catchment region represents a formal chemical species, accounting for the conformational flexibility and all distortions that preserve the chemical identity of the species. For a given electronic state, the catchment regions generate a subdivision of the nuclear configuration space M .

Each catchment region $C(\lambda, i)$ is specified according to the corresponding critical point $K(\lambda, i)$, where λ is the critical point index (that is, the number of negative eigenvalues of the local Hessian matrix), and i is a serial index. A $(3N - 6)$ -dimensional catchment region $C(0, i)$ of a minimum $K(0, i)$ represents the i th stable species, whereas a $(3N - 7)$ -dimensional catchment region $C(1, j)$ of a simple saddle point $K(1, j)$ represents the j th transition structure of the given electronic state. The conformational freedom and the extent of distortions that preserve chemical identity are determined by the shape and extent of catchment regions. Large distortions typically lead to a different catchment region, that is, to a different chemical species.

In general, for each electronic state, the shape of the potential surface is different. Consequently, for each electronic state, the stable chemical species are associated with a different partitioning of the nuclear configuration space into domains; hence the catchment regions are different. By contrast, for any given nuclear configuration, the point symmetry of the nuclei is fixed and is not affected by the electronic state. One may study the interrelations among the chemical identity, stability, and symmetry of nuclear configurations by comparing two subdivision schemes of the nuclear configuration space M . For a given electronic state, the first subdivision scheme is based on the catchment regions $C(\lambda, i)$, and the second one is based on the point symmetry domains G_{kl} of M . The point symmetry domain G_{kl} is the l th maximum connected component of subset G_k of M , where each G_k set contains the points of nuclear configurations having point symmetry group g_k . Only the catchment region subdivision is dependent on the electronic state. The point symmetry of the nuclear frameworks is a link among all electronic states of a fixed stoichiometry that has been utilized as a tool in the search for critical points of potential energy surfaces [2,5-7].

We shall make the usual assumption: the potential energy surfaces are everywhere differentiable within the configuration domains we consider; hence, energy gradient is well defined at each configuration. This assumption does not place any serious limitation on our analysis, since by applying an infinitesimal distortion of the potential energy surface at points of nondifferentiability, it can be converted into a function that is differentiable [2] and describes faithfully most of the chemically important topological properties of the original surface (see also ref. [8]).

2. A lattice model of point symmetry groups based on the catchment region point symmetry theorem

The following result, referred to as the catchment region point symmetry theorem, has been proven recently [2,7]:

Each critical point $K(\lambda, i)$ has all the symmetry elements of the corresponding catchment region $C(\lambda, i)$.

An equivalent formulation [7] is one that suggests more directly the approach of the present paper:

Within each catchment region $C(\lambda, i)$, the nuclear configuration corresponding to the critical point $K(\lambda, i)$ has the highest point symmetry.

The catchment region point symmetry theorem interrelates two very different molecular properties. The location of critical points and catchment regions of the potential energy surface depend on energy relations; by contrast, the point symmetries of nuclear configurations are purely geometrical properties.

The theorem is general for the potential energy surfaces and catchment regions of all electronic states. The point symmetry group of nuclear configurations provides a condition that interrelates the catchment regions of different electronic states.

The second formulation of the theorem invokes directly the existence of a *highest* point symmetry group within each catchment region. In general, there exists no natural linear order for point symmetry groups, based upon their group-subgroup relations (where each group is regarded as one of its own subgroups), since in a pair of point symmetry groups each group may contain elements not present in the other group; hence, neither one is a subgroup of the other. Consequently, in an arbitrary collection of point symmetry groups, it may be impossible to decide which group represents the highest or lowest symmetry.

However, according to the catchment region point symmetry theorem, within a catchment region $C(\lambda, i)$, the point symmetry group $g_k = g[K(\lambda, i)]$ of the critical point $K(\lambda, i)$ contains as subgroups all other groups occurring in $C(\lambda, i)$. Consequently, within each catchment region $C(\lambda, i)$ there exists a "highest" point symmetry. The theorem does not imply that the critical point $K(\lambda, i)$ is unique within $C(\lambda, i)$ in having the highest point symmetry: other, possibly all points K of the catchment region $C(\lambda, i)$ may have this point symmetry, $g[K] = g_k = g[K(\lambda, i)]$.

The important conclusion is the following: for any two point symmetry groups occurring for configurations within any catchment region $C(\lambda, i)$ there exists a configuration with a point symmetry group that is a common supergroup of the two groups, that is, a group that contains both groups and subgroups. Considering the group-subgroup relation as a partial order, any two point symmetry groups of $C(\lambda, i)$ have a join (supremum); consequently, the family of all point symmetry groups of $C(\lambda, i)$ is a higher semilattice. The catchment region point symmetry theorem guarantees the higher semilattice property for all catchment regions.

For an arbitrary family of point symmetry groups, there does not have to exist a unique lowest point symmetry group either. However, for a catchment region $C(0, i)$ of a minimum point $K(0, i)$, the dimension is $3N - 6$, and all infinitesimal distortions of the minimum energy configuration will lead to configurations K that are still within the same catchment region, since a typical catchment region $C(0, i)$ is an open set of the configuration space. Among these distortions, some will preserve some of the symmetry elements of the minimum configuration $K(0, i)$; however, most distortions necessarily lead to configurations with trivial point symmetry only. It is evident that the trivial point symmetry group C_1 (for triatomic systems C_s) is a subgroup of all point symmetry groups occurring within a catchment region. Combining this with the result of the catchment region point symmetry theorem, one concludes that in a catchment region $C(0, i)$ of a minimum point $K(0, i)$ there exist both a smallest common subgroup and a largest common supergroup for all point symmetry groups occurring within $C(0, i)$. Consequently, by taking the group-subgroup relation as the partial order relation, the family of point symmetry groups occurring within a catchment region $C(0, i)$ of a minimum point $K(0, i)$ has both "join" (supremum) and "meet" (infimum) for any of the pairs of point symmetry groups. This implies that the family of point symmetry groups occurring within a catchment region $C(0, i)$ of a minimum point $K(0, i)$ is both a higher semilattice and a lower semilattice: consequently, it is a *lattice*.

Lower dimensional catchment regions, for example, catchment regions $C(1, i)$ of transition structure saddle points $K(1, i)$, do not necessarily have the above property. Since the dimension is lower, in the above special case $3N - 7$, it follows that not all infinitesimal distortions of the critical point $K(1, i)$ are confined within its catchment region $C(1, i)$; consequently, it is possible that no configuration K with a trivial point symmetry group occurs within $C(1, i)$. This applies to the family of point symmetry groups within a catchment region $C(1, i)$ of a transition structure, or to that within a catchment region $C(\lambda, i)$ of a critical point $K(\lambda, i)$ with a higher index $\lambda > 1$.

3. Summary

The catchment region point symmetry theorem implies that the family of point symmetry groups of configurations occurring within any catchment region has an algebraic structure: they form a higher semilattice. The catchment regions of energy minima, representing stable molecules, must contain configurations of trivial symmetry; hence, it is especially easy to show that the family of the point symmetry groups of configurations occurring in them is not only a higher semilattice, but also a lower semilattice: consequently, it is a lattice. Since a catchment region of a minimum contains all configurations that preserve the chemical identity of a stable species, the above result can be restated in terms of the family of all distorted configurations of a molecule: *the point symmetry groups of the equilibrium and all distorted configurations of a molecule form a lattice, with the dominant element the point symmetry group of the minimum configuration.*

Acknowledgement

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

References

- [1] D.G. Truhlar (ed.), *Potential Energy Surfaces and Dynamics Calculations* (Plenum, New York, 1981).
- [2] P.G. Mezey, *Potential Energy Hypersurfaces* (Elsevier, Amsterdam, 1987).
- [3] P.G. Mezey, *Theor. Chim. Acta* 58(1981)309.
- [4] P.G. Mezey, *Theor. Chim. Acta* 63(1983)9.
- [5] P.G. Mezey, Reaction topology and quantum chemical molecular design on potential surfaces, in: *New Theoretical Concepts for Understanding Organic Reactions*, ed. J. Bertrán and I.G. Csizmadia (Kluwer Academic, Dordrecht, 1989), p. 55.
- [6] P.G. Mezey, Three-dimensional topological aspects of molecular similarity, in: *Concepts and Applications of Molecular Similarity*, ed. G.M. Maggiora and M.A. Johnson (Wiley, New York, in press).
- [7] P.G. Mezey, *J. Amer. Chem. Soc.* 112(1990)3791.
- [8] P.G. Mezey, *Int. J. Quant. Chem.* 38(1990), in press.