Pramāṇa, Vol. 23, No. 6, December 1984, pp. 803–808. © Printed in India.

Quasisymmetry and classification of molecular structures

M KONDALA RAO and Ch. SURYANARAYANA
Department of Applied Mathematics, Andhra University, Waltair 530003, India

MS received 30 April 1984

Abstract. Exploring the concept of quasisymmetry, a simple and elegant method, for the classification of molecular structures, has been developed. Examples are given. Results are identified with those of Pople.

Keywords. Quasisymmetry; framework group; minor quasisymmetry group.

PACS No. 02·20+b

1. Introduction

The information available about symmetry of a molecule provided by its point group is generally scarce. Pople (1980) therefore introduced the concept of framework group and provided a notation for complete specification of the symmetry properties of any molecular structure. He systematically enumerated all distinguishable framework groups for a molecule of given composition and developed an algorithm for such enumeration in general case. Pointing out that the information contained in a framework group is available in the cycle structure of the permutation group of a molecule of known structure, Mcdaniel (1981) showed how one may go from framework group notation to the permutation group notation and vice versa. Flurry (1981) recast the framework group formalism in terms of site symmetry groups mentioning a few advantages. An alternative definition of a framework group as a pair 'point group—morphism' is given by Kryachko (1982). In this paper, it is shown that the framework groups derived by Pople are none other than the full minor quasisymmetry (p-symmetry) groups with the point group of the molecule as the generator group and the appropriate symmetric group S_n—n depending on the number of identical, nuclei in the molecule—as the substitution group. A simple method to derive the framework groups as full minor quasisymmetry groups is given. A few examples are worked out and advantages of the present method are discussed.

2. Framework groups of a molecule

The point groups specify the symmetry properties of a general body of finite extension and apply them to all types of bodies including those with a continuous distribution of matter. If the body consists of only a finite number of particles, further classification is possible. Such a body is called a framework and its set of symmetry elements then

constitutes a framework group. Complete specification of the symmetry elements would include the geometrical transformation (rotation, reflection, etc) and information about the way in which particles are permuted by the operation. Thus a full description of the molecular symmetry requires specification of nuclear positions relative to their symmetry elements of the point group. Framework groups describe the full symmetry of a framework $A_i B_j \ldots$ containing i nuclei of type A, j nuclei of type B, etc. Molecules with different sets i, j will belong to different framework groups. Thus, the elements of a framework group are specified in two parts:
(a) geometrical operations (rotations, reflections, etc) and
(b) as consequent permutations of nuclei of the same type.
The classification beyond that of the point group arises because of (b). A method for the systematic generation and enumeration of framework groups is given by Pople (1980).

3. Quasisymmetry groups and their construction

Let each point of a given figure be assigned at least one index i, i taking on values $(i = 1, 2, \ldots, p)$ $p > 2$. With these p indices, fix some group P of substitutions. Then the quasisymmetry transformation (p-symmetry transformation) given by the group P will refer to that isometric transformation of the figure which translates each point with index i into a point with index k_i so that the resulting substitution of indices

$$\varepsilon = \begin{pmatrix} 1\,2\,3 \ldots p \\ k_1 k_2 k_3 \ldots k_p \end{pmatrix}$$

belongs to the group P of substitutions. The set of all quasisymmetry transformations of a given figure forms a group called the quasi-symmetry group G of the figure (Zamorzaev 1968). The set S of all the symmetry transformations of a given figure is a subgroup of its quasisymmetry group G and is called the generating group of G. Similarly, the set P of all index substitutions (also known as p-identical transformations) forms a subgroup of its quasisymmetry group G and is called the group of index substitutions (or permutations).

Let G be an arbitrary quasisymmetry group. Let S and P_1, denote, respectively, the generator group and the index substitution group. Then the group G is called a group of full or partial P-symmetry according as $P_1 = P$ or $P_1 \neq P$. Zamorzaev (1968) gave a method, of deriving all groups of full P-symmetry from the generating groups, in the form of a theorem.

Theorem: Any group G of full P-symmetry is derivable from its generator group S by the following steps:

(i) Search for normal divisors H and Q, of the groups S and P such that $S/H \cong P/Q$.
(ii) Carry out pairwise multiplication of sH and pQ, the corresponding classes with respect to the isomorphism and
(iii) Combine the resulting products.

The P-symmetry group obtained by the above procedure is called major, minor or intermediate according as $Q = P$, $Q = [I]$ or Q is a nontrivial normal subgroup of P.

4. Method for the derivation of framework groups

From the very definition of the framework group, it may be observed that an element of the framework group is not simply a point group operation *viz.* rotation or rotation reflection, but it consists of the consequent permutations, of the identical nuclei, that arise when the point symmetry operation is performed on the framework. This observation allows us to identify the elements of the framework group as the elements of the full minor quasisymmetry group (Zamorzaev 1968). In what follows we develop a method for deriving framework groups as full minor quasisymmetry groups. Consider a molecule of the type A_n—molecule consisting of n identical nuclei A—having the point symmetry, say, G. All the framework groups for this molecule will be derived by the following procedure:

Consider all the normal subgroups H_i, of the point symmetry group G. Write down all the factor groups G/H_i of different orders. Take any factor group G/H_k and find all the subgroups P_k of S_n, the symmetric groups on n symbols, that are isomorphic to G/H_k and construct the full minor quasisymmetry groups, following the method outlined in §3, with G as generator group and P_k as substitution groups. Repeat the procedure for all the other factor groups G/H_i. The totality of all these full minor quasisymmetry groups gives the required framework groups. However, because of the generality of method of construction of the full minor quasisymmetry groups, not all the groups thus obtained actually represent a framework group. We have to eliminate some of these groups using the following three rules:

(i) If in a minor quasisymmetry group any two distinct operations interchange two or more nuclei in a way that makes the fixation of the nuclei in the molecule impossible, then the quasi-symmetry group does not represent a framework group and hence it is to be eliminated.

(ii) If a minor quasisymmetry group can be obtained from the other by a mere renumbering of the nuclei labels, then it does not give rise to a different framework group and hence it is to be eliminated.

(iii) If the movement of the labelled nuclei, under the permutations of all the operations, fix the location of the nuclei in the molecule in such a way that it leads to a possible higher symmetry for the molecule as a whole, such a group is to be eliminated.

Following the above procedures, along with the elimination rules, we can get all the possible framework groups in a systematic way. By noticing the movements of the labelled nuclei, as exhibited through the permutation part of the quasisymmetry operation, we can identify each group, constructed by the present procedure, with that given by Pople (1980).

We explain the method of deriving all the framework groups by explicitly working out an example. Consider a molecule of the type A_4 having C_{2v} symmetry.

Here $G = C_{2v} = \{E, C_2, \sigma_v, \sigma_{v'}\}$

Normal subgroups are:
$$H_1 = C_2 = \{E, C_2\}$$
$$H_2 = C_s = \{E, \sigma_v\}$$
$$H_3 = \{E\}$$

Consider the factor group $G/H_1 = C_{2v}/C_2$

Now each permutation group P, ($\subset S_4$) on four symbols 1, 2, 3, 4 of the same order as that of C_{2v}/C_2 possibly gives rise to a framework group.

Consider $P = P_1 = \{I, (12)\}$

Construct a full minor quasisymmetry group with C_{2v} as the generator group and P_1 as the substitution group. Thus

$$G/H_1 \cong P_1/I \text{ i.e., } \{H_1, \sigma_v H_1\} \to \{I, (12)\}.$$

Hence, the full minor quasisymmetry group is

$$\{EI, C_2 I, \sigma_v(12), \sigma_{v'}(12)\}.$$

This group will not represent a framework group and is to be eliminated by rule (i). Let

$$P = P_2 = \{I, (12)(34)\}, \text{ therefore } G/H_1 \cong P_2/I$$

So, $\{H_1, \sigma_v H_1\} \to \{I, (12)(34)\}$.

The full minor quasisymmetry group is

$$\{EI, C_2 I, \sigma_v(12)(34), \sigma_{v'}(12)(34)\}.$$

This group is to be eliminated by rule (i). Next, consider the second factor group $G/H_2 = C_{2v}/C_s$. Because this group is of the same order as that of G/H_1, we need consider the same P_1 and P_2.

$$G/H_2 \cong P_1/I \quad \text{i.e.,} \quad \{H_2, C_2 H_2\} \to \{I, (12)\}.$$

The full minor quasisymmetry group is

$$\{EI, \sigma_v I, C_2(12), \sigma_{v'}(12)\}. \tag{1}$$

Next, $G/H_2 \cong P_2/I$ i.e., $\{H_2, C_2 H_2\} \to \{I, (12)(34)\}$.

The full minor quasisymmetry group is

$$\{EI, \sigma_v I, C_2(12)(34), \sigma_{v'}(12)(34)\}. \tag{2}$$

No other full minor quasisymmetry group can be constructed with the factor group G/H_2. For the factor group $G/H_3 = G/E$.
Consider every P_3 of order four (order of G/E)
Let $P_3 = \{I, (12), (34), (12)(34)\}$. Therefore

$$G/H_3 \cong P_3/I.$$

The full minor quasisymmetry group is

$$\{EI, C_2(12), \sigma_v(34), \sigma_{v'}(12)(34)\}. \tag{3}$$

This group is to be eliminated by rule (i). Let $P_3 = \{I, (12)(34), (12), (34)\}$

$$G/H_3 \cong P_3/I.$$

The full minor quasisymmetry group is

$$\{EI, C_2(12)(34), \sigma_v(12), \sigma_{v'}(34)\}. \tag{4}$$

Let $P_3 = \{I, (12)(34), (13)(24), (14)(23)\}$,

$$G/H_3 \cong P_3/I.$$

The full minor quasisymmetry group is

$$\{EI, C_2(12)(34), \sigma_v(13)(24), \sigma_{v'}(14)(23)\}$$

This is to be eliminated by rule (iii).

One may note, however, that many new permutation groups P, of required order, other than those considered above can be considered for the purpose of the construction of some other full minor quasisymmetry groups. But all such full minor quasisymmetry groups will automatically be eliminated by rule (ii). For instance, let us construct a full minor quasisymmetry group with

$$P_3 = \{I, (13), (24), (13)(24)\}.$$

The full minor quasisymmetry group is

$$\{EI, C_2(13), \sigma_v(24), \sigma_{v'}(13)(24)\}$$

This is the same as (3) if we make the following relabelling

$$2 \to 3, \qquad 3 \to 2.$$

It may be noted that by actually fixing the location of the nuclei in the molecule as suggested by each quasisymmetry operation in the full minor quasisymmetry group we can identify the three full minor quasisymmetry groups got above with those given by Pople (1980), in the following way,

Consider $\{EI, \sigma_v I, C_2(12), \sigma_{v'}(12)\}$

$C_2(12)$ implies that 3, 4 are on C_2 axis

$\sigma_{v'}(12)$ implies that 1, 2 are in σ as $\sigma_{v'}$-images. Therefore

$$\{EI, \sigma_v I, C_2(12), \sigma_{v'}(12)\} \to C_{2v}[2100].$$

Similarly,

$$\{EI, \sigma_v I, C_2(12)(34), \sigma_{v'}(12)(34)\} \to C_{2v}[0200],$$

$$\{EI, C_2(12)(34), \sigma_v(12), \sigma_{v'}(34)\} \to C_{2v}[0110].$$

The method described above for obtaining the framework groups for a given molecule as the full minor quasisymmetry groups has been applied for a molecule of type A_i. As may be noted, the method can, straightaway be applied to the general molecules of the type $A_i, B_j \ldots$.

5. Discussion

As is evident from the way of construction, the present method is simple and quite elegant for compound molecules $A_m B_n \ldots$ consisting of $m, n, \ldots$ nuclei of types $A, B, \ldots$ where $m, n \ldots$ are not very large. Further, if the framework groups for the molecule $A_m B_n \ldots$ having the point symmetry group G, are found, the framework groups for the molecules $A_{m-1} B_{n-1} \ldots, A_{m-2} B_{n-2} \ldots$; etc having the same symmetry G, can straightaway be given from them. For example, framework group for the molecule of the type A_3 having C_{2v} symmetry can be obtained from (1), (2) and (4) just by making the nuclei labelled '4' unmoved or in other words by dropping the nuclei labelled '4' from the operations of the group. We get (1) as

$$\{EI,\ \sigma_v I,\ C_2(12),\ \sigma_{v'}(12)\} \rightarrow (1)'.$$

As far as (2) and (3) are concerned, the nuclei labelled '4' remains unmoved under σ_v implies that the nuclei labelled '3' also remains unmoved. Therefore

(2) gives $\{EI,\ \sigma_v I,\ C_2(12),\ \sigma_{v'}(12)\} \rightarrow (2)'$

(4) gives $\{EI,\ C_2(12),\ \sigma_v(12),\ \sigma_{v'}(I)\} \rightarrow (3)'$.

These three groups (1)', (2)' and (4)' give rise to only one framework group, after applying the elimination rules and is

$$\{EI,\ C_2(12),\ \sigma_v I,\ \sigma_{v'}(12)\} \rightarrow C_{2v}[1010].$$

This agrees with that given by Pople (1980).

Acknowledgements

The authors thank Drs T S G Krishna Murty and L S R K Prasad, for useful discussions and encouragement.

References

Flurry Jr R L 1981 *J. Am. Chem. Soc.* **103** 2901
Kyrachko E S 1982 *Int. J. Quantum Chem.* **22** 657
Mcdaniel Darl H 1981 *J. Phys. Chem.* **85** 479
Pople J A 1980 *J. Am. Chem. Soc.* **102** 4615
Zamorzaev A M 1968 *Sov. Phys. Crystallogr.* **12** 717