A CHEMIST LOOKS AT THE STRUCTURE OF SYMMETRY GROUPS

On a generic scheme of important point groups for rigid molecular frames

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Abstract

A practical method for generating larger symmetry groups from smaller ones is presented. It is based upon the construction of the abstract-unique group H(G) called the holomorph of a given starting group G. The extension of G by its full automorphism group A(G) is given in great detail as permutation realizations for both the cyclic and the abelian group of order 4. A selection of point groups generated by this method of the holomorph is given for some important symmetries.

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1. Introduction

Symmetry considerations have always been important in various branches of chemistry from both qualitative (or geometrical) and quantitative (i.e. group theoretical) points of view. It is the concept of structural symmetry or (mentioning L. Pauling's words about)the "architecture of molecules", resp., that is relating experimental observations like optical spectra, dipole moments, electric and magnetic susceptibilities, optical activity and chirality, etc., to theoretical calculations based upon quantum mechanics. Therefore, group theory is connecting very efficiently the world of problems in chemical statics and dynamics to the world of abstractly operating computational machinery supplied by physics and mathematics.

The traditional interest of chemists in group theory stems from areas as classification of molecules by means of point groups, normal vibrations analysis, MO theory, crystal and/or ligand field theory (a terrible semantics since these topics have nothing to do with a physical "field theory"), selection rules, and so forth. The tools needed are: character systems of the various groups involved in the chemical problem, classification of wave functions and state vectors (i.e. the orbital business), and some capability in understanding energy level diagrams. It is probably true that character tables will maintain their leading position in practical applications also in the near future. The same is true for the use of the 32 crystallographic point groups in solid state chemistry and some other special groups like $O^+(3)$, SU(2), and some members of the family of the symmetric group $G = S_m$ on m symbols.

In the last five years, however, there is an increasing interest in the chemical literature for more abstract concepts from group theory. Among others are topics like symmetry adaption[1], the role of the group S_m in the m-electron problem[2], and, recently, the molecular dynamics of the so-called non-rigid molecules[3], respectively. The last example forces chemists to the idea of feasible symmetry operations[4] which are combinations of permutations of identical entities within the nuclear framework and traditional operations (rotations, inversions, etc.). Because of these features new symmetry operations together with unconventional symmetry groups appear whose character tables are not known beforehand.

The work of the present author is following along these lines having objectives from both scientific and educational view points simultaneously. In the science area, we are looking at simple methods to generate symmetrized states for the many-body problem(important for optical and magnetic spectral data). On the other hand for teaching purposes, we can control the proper level of abstractness in courses of both theoretical chemistry and chemical physics by the feedback of the audience being bombarded by group theoretical "food"[5].

In this first paper out of a planned series a technique for the construction of chemical relevant point groups from the simplest possible subgroups is presented. We use the method of the holomorph that is relating in an abstractly unique manner a given group G (in principle arbitrary concerning both order and structure) to a strongly related group H(G) via the full automorphism group A(G) of G. This construct stems from the early days of group theory[6] and has not been used consciously in theoretical chemistry. In the following sections we are exploiting the method with typical examples from the area of finite point groups that are of importance for rigid molecular frameworks. The treatment of the non-rigid molecules is postponed to a forthcoming paper. Furthermore, after having looked at the chosen examples some general remarks are given. In conclusion of this section, the present author must mention that he is addressing mainly those readers using group theory for chemical applications.

2. Method of the Holomorph

As examples are taken the two structural different groups of order 4, i.e. in the chemical notation the cyclic group $G = C_4$ and the Abelian group $G = D_2$ (= F. Klein's "Vierergruppe"), resp. As point groups, we have the realizations

$$\begin{aligned} C_4 &= \text{gp}\left\{C_4 / C_4^4 = E\right\} = \left\{E, C_4, C_2, C_4^{-}\right\} \ , \\ D_2 &= \text{gp}\left\{2_z, 2_y / 2_z^2 = 2_y^2 = E\right\} = \left\{E, 2_z, 2_y, 2_x\right\} \ ; \end{aligned} \qquad (2.1)$$

here, E is the identity operation; x,y,z refer to the orientation of the Cartesian axes for the symmetry elements in question. For the following arguments it is convenient to represent both groups as regular permutation groups (due to the Cayley-theorem[7]) defined by the multiplication tables, that is

$$\begin{array}{lll} \underline{C_4}: & E \longleftrightarrow (E)(C_4)(C_2)(C_4^{-}) = (E) & = P(E) \ , \\ & C_4 \longleftrightarrow (EC_4C_2C_4^{-}) & = P(C_4) = P(C_4^{-})^{-1} , \qquad (2.2) \\ & C_2 \longleftrightarrow (EC_2)(C_4C_4^{-}) & = P(C_2) \ ; \qquad \text{and} \\ \underline{D_2}: & E \longleftrightarrow \qquad (E) & = P(E) \ , \\ & 2_z \longleftrightarrow (E2_z)(2_y2_x) & = P(2_z), \ \text{and so on.} \end{array}$$

In the next stage we construct the automorphism groups A(G) of G where the image group is G itself. Due to the properties of automorphisms and bijective mappings of groups onto itself one has to consider that two corresponding elements preserve their order under any mapping, and identity operations are always mapped onto itself[7]. Therefore, it is clear that all allowed automorphisms ϕ are permuting the group elements in a definite way. Again, the multiplication table, i.e. the structure of G, generates the complete set $\{\phi_i\}$ having group properties. The result is the group A(G) whose binary operation is the succession of the isomorphic mappings. In general the set consists of both outer and inner automorphisms (the latter being induced by conjugation, i.e. equivalence relations on the set). The subset of the inner automorphisms forms the normal subgroup I(G) of A(G), i.e. $I(G) \triangleleft A(G)$. This is all standard abstract group theory. To see how it works we return to our examples.

Instead of the abstract group A(G) it is more appropriate to work with the isomorphic permutation group $PA(G) = \{P(\phi_i)/i = 1 \text{ to } /A(G)/\}$, /A(G)/ being the order of the group. It can easily be shown that for $G = C_4$ there are only two allowed automorphic mappings, given by

$$\begin{aligned} \underline{PA(C_4)}:\ \phi_1 &\longleftrightarrow (E)(C_4)(C_2)(C_4^-) = (E) = P(\phi_1)\ , \\ \phi_2 &\longleftrightarrow (C_4C_4^-) \qquad\qquad\quad = P(\phi_2)\ . \end{aligned} \tag{2.3}$$

On the other hand, $G = D_2$ has three elements of order two, cf. Eq.(2.1), and we are dealing with six different permutations as representations of the allowed automorphisms, given by

$$\begin{aligned} &\underline{PA(D_2)}:\ \phi_1 \longleftrightarrow (E) = P(\phi_1), \phi_2 \longleftrightarrow (2_z2_x2_y) = P(\phi_2) = P(\phi_3)^{-1}, \\ &\qquad\qquad \phi_4 \longleftrightarrow (2_z2_y) = P(\phi_4), \text{ and so on,} \end{aligned} \tag{2.4}$$

which is isomorphic to the symmetric group S_3 on three symbols.

Looking at the cycle structures of the groups $P(C_4) =$

$= \{P(R_k)/k = 1 \text{ to } /C_4/\} \longleftrightarrow C_4$ and $PA(C_4)$ from Eqs.(2.2) and (2.3) on the one hand, and analogously for $P(D_2) \longleftrightarrow D_2$ and $PA(D_2)$ in Eqs.(2.2) and (2.4) on the other hand, we can extract the following important informations:

a) $P(C_4) \cap PA(C_4) = \{(E)\}$; $P(D_2) \cap PA(D_2) = \{(E)\}$,

b) $P(C_4)$ is invariant under the action of $PA(C_4)$; the same is due for $P(D_2)$ under the action of $PA(D_2)$,

c) the reverse statement of item b is not true.

As a reminder, the reader should have no difficulties to identify point groups that are isomorphic to the groups PA(G) and A(G), respectively. For instance, $PA(C_4) \longleftrightarrow C_2, C_s, C_i$ whereas $PA(D_2) \longleftrightarrow D_3, C_{3v}$.

Now we are interested to form a larger group from the subgroups P(G) and PA(G) encouraged by items a to c (see above). That means, one has to make the set of ordered pairs $\{P(R_k), P(\phi_i);$ all $R_k \in G$ and all $\phi_i \in A(G)\}$ into a group. Looking at our examples we are indeed successful; for convenience we list all elements of the new group $PH(C_4)$ that has been formed from $P(C_4)$, the elements of which are always taken first in the ordered pairs, and $PA(C_4)$, i.e. using Eqs.(2.2) and (2.3) one obtains:

$$\begin{aligned}
&P(E\phi_1) = (P(E),P(\phi_1)) = (E),\ P(E\phi_2) = (C_4C_4^{-}),\\
&P(C_4\phi_1) = (EC_4C_2C_4^{-}),\ P(C_4\phi_2) = (EC_4)(C_2C_4^{-}),\\
&P(C_2\phi_1) = (EC_2)(C_4C_4^{-}),\ P(C_2\phi_2) = (EC_2),\\
&P(C_4^{-}\phi_1) = (EC_4^{-}C_2C_4^{-}),\ P(C_4^{-}\phi_2) = (EC_4^{-})(C_4C_2).
\end{aligned} \tag{2.5}$$

This group $PH(C_4)$ is nothing else but the permutation realization of the isomorphic group $H(C_4)$ called the <u>holomorph of $G = C_4$</u>. The experienced reader will agree that our construction is identical with the formation of both a <u>semi-direct product</u> and/or a <u>split extension</u> of C_4 by $A(C_4)$. Reaching the aim of our efforts is, ultimately, equivalent to the finding of a point group isomorphic to the holomorph. By inspection, we find from Eq.(2.5) that $PH(C_4)$ is isomorphic to the dihedral group $D_4 = C_4 \circledS C_2'$.(The prime in the subgroup C_2 of the semi-direct product is for the relative orientation of the symmetry elements.) Furthermore, we learn from Eq.(2.5) the following properties:

$$/PH(C_4)/ = /P(C_4)//PA(C_4)/ \quad ; \quad P(C_4) \triangleleft PH(C_4) \quad ; \qquad (2.6)$$
$$PH(C_4)/P(C_4) \longleftrightarrow PA(C_4).$$

Lastly, we formulate the product of elements as ordered pairs for $PH(C_4)$, i.e. for all $R_k \in C_4$ and all $\phi_i \in A(C_4)$:

$$(P(R_k),P(\phi_i))(P(R_l),P(\phi_j)) = \qquad (2.7)$$
$$= (P(R_k)P(\phi_i)P(R_l)P(\phi_i)^{-1},P(\phi_i)P(\phi_j)) = (P(R_p),P(\phi_t)) \in PH(C_4).$$

The other example for $G = D_2$ can be treated in the same manner resulting in the permutation realization $PH(D_2)$ of the holomorph $H(D_2)$ that-with proper choice of axes for the subgroups-is found to be isomorphic to the octahedral rotation group O, that is:$O = D_2 \circledS D_3'$. Here too, it is found that $A(D_2) \longleftrightarrow D_3$ normalizes D_2 in O, and the factor group O/D_2 is isomorphic to the subgroup D_3, cf. Eq.(2.6).

3. Generalization of the concept

From the group theoretical point of view, a holomorph belongs to the category of extensions of a group G by other groups F having definite relations with G via special homomorphism conditions which are treated elsewhere[7-9]. In the special case of the holomorph these relations are trivial[6]. We have only to generalize Eq.(2.6) and find, that

$$H(G) = G \circledS A(G); \; /H(G)/ = /G//A(G)/; \qquad (3.1)$$
$$G \triangleleft H(G); \; H(G)/G \longleftrightarrow F; \; F \longleftrightarrow A(G).$$

The composition law for this split extension H(G) is given by

$$(R_k,\phi_i)(R_l,\phi_j) = (R_k\phi_i R_l \phi_i^{-1},\phi_i\phi_j) \; , \qquad (3.2)$$

fulfilling the closure condition, cf. Eq.(2.7). A general inverse element of H(G) is therefore

$$(R_k,\phi_i)^{-1} = (R_k',\phi_i') \text{ , with } R_k' = \phi_i^{-1}R_k^{-1}\phi_i \quad \text{and} \quad \phi_i' = \phi_i^{-1} \text{ .} \tag{3.3}$$

For our problem finding suitable pointgroups as extensions of certain given point groups using the method of the holomorph, one has to analyse both the group and class structure of G and H(G), respectively. The results are used to find new point or symmetry groups in general that are isomorphic to H(G), i.e. $H(G) \longleftrightarrow K = G \circledS F$, with $F \longleftrightarrow A(G)$. Some examples are given in Table 1 where the point groups K have been constructed along the lines of section 2.

Table 1. Generic scheme for some important point groups K ($K = G \circledS F$)

G	/A(G)/	F	/H(G)/	K	Remarks about K
C_2	1	C_1	2	C_2	trivial extension
C_3	2	C_2	6	D_3	
C_3	2	C_s	6	C_{3v}	$C_{3v} \longleftrightarrow D_3$
C_4	2	C_2	8	D_4	
C_4	2	C_s	8	C_{4v}	$C_{4v} \longleftrightarrow D_4$
C_5	4	C_4	20	?	
C_6	2	C_2	12	D_6	
C_6	2	C_s	12	C_{6v}	$C_{6v} \longleftrightarrow D_6$
C_∞	2	C_2	∞	D_∞	infinite dihedral group
C_∞	2	C_s	∞	$C_{\infty v}$	$C_{\infty v} \longleftrightarrow D_\infty$
D_2	6	D_3	24	O	octahedral group

The chemically interested reader will probably miss two interesting point groups, viz. the tetrahedral group T and the icosahedral group I with /T/ = 12 and /I/ = 60. Indeed, the group T that is very important in ligand field theory and chemistry in general cannot be generated by our method directly. If however one is considering that $T \triangleleft O$, it turns out: $T = D_2 \circledS C_3'$, with

$C_3 \triangleleft D_3$; cf. last line in Table 1. This semi-direct product (together with others not mentioned here) using certain isomorphic subgroups of A(G) for a given starting group G is important for extensions in the theory of space groups[9,10]. Finally, the group I is not tractable with our proposed method since it is simple[11].

In conclusion, we like to mention that this method of the holomorph is useful to generate the character systems of symmetry groups important in chemistry by "inducing" of representations from the starting group G that is normal in the holomorph.

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