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On Some Point Groups

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Abstract: In this note, we indicate the coincidence as abstract groups of some point groups which belong to different molecular orbitals. This elucidates somewhat vague presentation in many existing textbooks on molecular orbitals, thus abridging between group theory and quantum chemistry.

Keywords: Point Group Molecular Orbitals, Symmetry Transformations: Characters

1. Introduction

Point groups are indispensable tools for analysis of molecular orbitals. However, there is one point missing in most of the textbooks (given in references) to the effect that one group is associated to several orbitals, cf. e.g. Example 4, which has been a tradition in the theory because there is always associated a figure of the molecule. Since one group is associated to many molecules, it would be preferable to have a clear description of the correspondence between the molecules and the point group. In this note we shall show that some of the point groups which have different labels are isomorphic as abstract groups. Classification being the strong point of mathematics, this manifestation of the classification of point groups hopefully gives rise to better and clear understanding of the theory of point groups. We have treated the easiest case and apparently, we may go on classifying all the point groups, which task will be conducted subsequently.

In the remainder of this section, we assemble fundamentals on group theory for readers' convenience.

We are concerned with finite groups only. We take basic definitions of a group for granted. The number of elements of a group G is called the order of G denoted |G|. A subgroup H of a group H is a subset of G, which itself forms a group under the operation (called product) of G. A group with commutative product is called an Abelian group (or a commutative group).

For finite groups, the following is fundamental.

Lemma 1 (Lagrange). *Let G be a finite group and let H be its subgroup. Then the order of H divides that of G:*

$$|\mathrm{H}| \mid |G|.$$

Lemma 1 is used e.g. in the following context.

Recall that the cyclic subgroup <a> generated by a in a group G is the set of all powers of a:

$$< a >= \{a^m | m \in \mathbb{Z}\}$$

Since there are only finitely many different powers of a, we must have $a^k = a^l$, whence we may conclude that $X = \{m \in \mathbb{N} | a^m = 1\} \neq \emptyset$. Choosing $l = \min X$, we may conclude that l divides all members of X and that all elements $1, a, \dots, a^{l-1}$ are distinct, so that $| < a > | = l, | < a > | = min\,\{m \in \mathbb{N} | a^m = 1\}$. The order of the subgroup generated by <a> is called the order of a and denoted by $o(a)$.

By Lemma 1, $l \mid |G|$ and so $a^{|G|} = (a^{|<a>|})^{|G|/|<a>|} = 1$. Thus, we have the generalized Fermat's little theorem:

$$a^{|G|} = 1. \tag{1.1}$$

Corollary 1. A group G of prime order is cyclic.

For, any element a of G generates a cyclic subgroup whose order $o(a)$ divides the prime $p = |G|$, and so either $o(a) = 1$ or $o(a) = p$. The former case leads to $a = e$ (identity) and the latter case leads to $G =< a >$.

Lemma 2 (Sylow) For the highest prime power p^rthat divides the order of a group G, there exists a subgroup S of order p^r, called a Sylow p subgroup of G. All the subgroups of G of prime power order p^s are contained in the Sylow p subgroup S. All Sylow p subgroups are conjugate.

Notation. To avoid confusion with the rotary reflection S_n, we denote the nth symmetric group by $\mathcal{S}_n$. Care must be taken also in treating the dihedral group D_n which is denoted by $\mathcal{D}_{2n}$ in mathematics. $\mathcal{D}_{2n}$ is the semi-direct product of a cyclic group of order n and one of order 2: $\mathcal{D}_{2n} =< b > \rtimes < a >$, where o(b)=n, o(a)=2 and there is the relation $a^{-1}ba = b^{n-1}$.

2. Point Groups

By [7, p.8] point groups are rotational parts of the space group which leave the molecule (lattice) invariant and in the case of crystals there are 32 of them.

Definition 1. We choose the principal axis of symmetry as the one which goes through the maximum number of molecules (lattice points). If there are some of them, then we choose the one. If there is no such an axis we choose it arbitrarily. The plane of symmetry is chosen so that it contains the maximum number of molecules. The intersection of the principal axis and the plane of symmetry is chosen to be the origin.

- C_n is the rotation w.r.t. the principal axis through $2\pi/n$.
- σ is a reflection. σ_h (*h*=horizontal) is a reflection through a plane perpendicular to the axis of symmetry; σ_v (*v*=vertical) is a reflection through a plane containing a principal axis of symmetry; σ_d (*d*=dihedral) is a reflection through a plane containing a principal axis of symmetry and bisects the angle between two 2-fold axes perpendicular to the principal axis. They are all of order 2.
- *i* is the inversion w.r.t. the origin.
- S_n is the rotation through $2\pi/n$ followed by a reflection through a plane perpendicular to the axis of rotation, and is called rotary reflection (improper rotation).

In what follows we often write the group itself by its typical element.

Remark 1.

(1) In the case of crystals, rotations are only those which rotate through integral multiples of $\pi/3$, $\pi/2$ or the products of such rotations and the inversion. $\sigma = iC_2$, where C_2 is the rotation through $2\pi/2$.

(2) It seems that the introduction of the rotary reflection S_n leads to confusion because it is the product of two operations:

$$S_n = \sigma_h C_n \tag{2.1}$$

and $S_n^m = \sigma_h^m C_n^m$ for any integer *m*. Hence

$$S_n^m = C_n^m \qquad m \quad \text{even}, \tag{2.2}$$

$$S_n^m = \sigma_h C_n^m \qquad \text{m} \quad \text{odd and } S_1 = \sigma_h C_1 = \sigma_h.$$

Example 1. We have

$$C_{2v} \cong C_4.$$

Example 2. The group C_4 consists of the following 4 elements whose multiplication table is given below.

(i) C_4 is the rotation through $2\pi/4$ and $C_4^4 = e$ is the identity.
(ii) $C_4^2 = C_2$ is the rotation through π.
(iii) C_4^3 is the rotation through $3\pi/2$.

***Table 1.** Character table of C_4*

χ	e	C_4	C_4^2	C_4^3
χ_0	1	1	1	1
χ_1	1	-1	1	-1
χ_2	1	i	i^2	i^3
χ_3	1	i^3	i^2	i

Example 3. The group C_6 consists of 6 elements whose multiplication table is given below.

(i) C_4 is the rotation through $\pi/6$ and C_6^6 is the identity.
(ii) C_3 is the rotation through $2\pi/3$ and $C_3 = C_6^2$.
(iii) C_2 is the rotation through $2\pi/2$ and $C_2 = C_6^3$.
(iv) C_3^2 is the rotation through $4\pi/3$ and $C_3^2 = C_6^4$.
(v) C_3^5 is the rotation through $5\pi/3$.

***Table 2.** Multiplication table of C_6 (r indicates C_6).*

o	e	r	r^2	r^3	r^4	r^5
e	e	r	r^2	r^3	r^4	r^5
r	r	r^2	r^3	r^4	r^5	e
r^2	r^2	r^3	r^4	r^5	e	r
r^3	r^3	r^4	r^5	e	r	r^2
r^4	r^4	r^5	e	r	r^2	r^3
r^5	r^5	e	r	r^2	r^3	r^4

***Table 3.** Multiplication table of $\mathcal{S}_3$*

o	e	r	r^2	s	r^2s	rs
e	e	r	r^2	s	r^2s	rs
r	r	r^2	e	rs	s	r^2s
r^2	r^2	e	r	r^2s	rs	s
s	s	r^2s	rs	E	r	r^2
r^2s	r^2s	rs	S	r^2	E	r
rs	rs	s	r^2s	r	r^2	e

***Table 4.** Regular multiplication table of $\mathcal{S}_3$*

o	e	t_3	t_2	t_1	r^2	r
e	e	t_3	t_2	t_1	r^2	r
t_3	t_3	e	r^2	r	t_2	t_1
t_2	t_2	r	e	r^2	t_1	t_3
t_1	t_1	r^2	r	e	t_3	t_2
r	r	t_2	t_1	t_3	e	r^2
r^2	r^2	t_1	t_3	t_2	r	e

*Theorem 1. W*e have $C_{3v} = D_3$, *and they are* $\cong \mathcal{S}_3$.

Example 4. To C_{3v} belong ammonia NH_3, chloroform $CHCl_3$, cyclopropenylcation radical, phosphorus sesqui -sulfide P_4S_3, etc. To D_3 belong Boron trifluoride BF_3, triphenylmethyl radical, trans-perhydrotripolyphenylene, staggered conformation of ethane, etc.

We note that the following table appears on [9, p.29] and the elucidation appears on [9, p.6].

Table 5. *Multiplication table of* C_{3h}

$\mathbf{o}$	$\boldsymbol{e}$	$\boldsymbol{S_3^1}$	$\boldsymbol{S_3^5}$	$\boldsymbol{C_3^1 = S_3^4}$	$\boldsymbol{C_3^2 = S_3^2}$	$\boldsymbol{\sigma_h = S_3^3}$
e	e	S_3^1	S_3^5	S_3^4	$S_3^2 = C_3^2$	S_3^3
S_3^1	S_3^1	C_3^2	e	S_3^5	S_3^2	C_3^1
S_3^5	S_3^5	e	$S_3^4 = C_3^1$	$S_3^3 = \sigma_h$	S_3^1	$S_3^2 = C_3^2$
$C_3^1 = S_3^4$	C_3^1	S_3^5	$S_3^3 = \sigma_h$	$S_3^2 = C_3^2$	e	S_3^1
$C_3^2 = S_3^2$	C_3^2	$S_3^3 = \sigma_h$	S_3^1	e	$S_3^4 = C_3^1$	S_3^5
$\sigma_h = S_3^3$	σ_h	$S_3^4 = C_3^1$	$S_3^2 = C_3^2$	S_3^1	S_3^5	e

Theorem 2.

$$C_{3h} \cong C_6. \tag{2.3}$$

Theorem3. We have $D_{3h} \cong D_6 \cong \mathcal{D}_{12}$ and $D_{3v} \cong D_3 \cong \mathcal{D}_6$ is its subgroup. Consequently, we may treat planar molecules belonging to D_{3h} as those belonging to D_3.

3. Characters

Definition 2. In a (matrix) representation Γ of a finite group G, the trace of the matrix S_σ corresponding to $\sigma \in G$ is called a character of Γ and denoted by $\chi(\sigma)$.

$$\chi(\sigma) = \mathrm{Tr}(S_\sigma)$$

There are |G| characters of G. Those which corresponding to irreducible representations are called simple characters.

$$\chi_0(\sigma), \quad \dots, \quad \chi_{h-1}(\sigma).$$

Theorem 4. Any irreducible representation of a finite Abelian group must be of degree 1, and so the representation ρ itself is equal to the trace of the representation matrix, i.e. it is a character.

Theorem 5. Any finite Abelian group is expressed as a direct product of cyclic groups of prime power order.

Lemma 3. Any cyclic group C_n of order n is isomorphic to the additive group of residue classes modulo n:

$$C_n \cong \mathbb{Z}/n\mathbb{Z}.$$

Theorem 6. Suppose $C_n =< a >$ be a cyclic group of order n. Since $a^n = e$ it follows that the values of a character $\chi: C_n \to \mathbb{C}^\times$ must be the nth roots of 1. Hence it suffices to restrict the range to the torus group $\mathbb{T} = \{z \in \mathbb{C} \,||z| = 1\}$. Then the character χ is determined by its value at a, say $\chi(a) = e^{2\pi i/n}$, the piervotny primitive root of 1. The correspondence $\chi \to j + n\mathbb{Z}$ gives rise to the isomorphism

$$\mathrm{X}(C_n) \cong \mathbb{Z}/n\mathbb{Z} \cong C_n.$$

This theorem follows from Lemma 3 since the correspondence $a \leftrightarrow e^{2\pi i/n}$ give rise to an isomorphism between the groups <a> and μ_n of the group of *n*th roots of *1*.

Now combining Theorem 5 and Theorem 6, we deduce

Theorem 7. Any finite Abelian group is isomorphic to its character group $\mathrm{X(G)} = \{\chi: \mathrm{G} \to \mathbb{T} | \chi \text{ is a homomorphism}\}$:

$$G \cong \mathrm{X}(G).$$

Let $\rho = e^{2\pi i/3}$ be the piervotny primitive 3rd root of unity and let $\omega = e^{2\pi i/6}$ the piervotny primitive 6th root of unity. Table XXI [7, p.16] after changing the columns of C_3 and S_3 reads.

Table 6. *Character table of* C_3

$\boldsymbol{\chi}$	**e**	$\boldsymbol{S_3}$	$\boldsymbol{S_3^2 = C_3^2}$	$\boldsymbol{S_3^3 = \sigma_h}$	$\boldsymbol{S_3^4 = C_3}$	$\boldsymbol{S_3^4 = \sigma_h C_3^2}$
χ_0	1	1	1	1	1	1
χ_2	1	ρ	ρ^2	1	ρ	ρ^2
χ_3	1	ρ^2	ρ	1	ρ^2	ρ
χ_1	1	-1	1	-1	1	-1
χ_5	1	$-\rho$	ρ^2	-1	ρ	$-\rho$
χ_4	1	$-\rho^2$	ρ	-1	ρ^2	$-\rho^2$

Table 7. *Character table of* C_6

$\boldsymbol{\chi}$	$\boldsymbol{e}$	$\boldsymbol{C_6}$	$\boldsymbol{C_6^2 = C_3}$	$\boldsymbol{C_6^3 = C_2}$	$\boldsymbol{C_6^4 = C_3 - 2}$	$\boldsymbol{C_6^5}$
χ_0	1	1	1	1	1	1
χ_1	1	-1	1	-1	1	-1
χ_2	1	$\omega^2 = \rho$	$\omega^4 = \rho^2$	1	$\omega^2 = \rho$	$\omega^4 = \rho^2$
χ_3	1	$\omega^4 = \rho^2$	$\omega^2 = \rho$	1	$\omega^4 = \rho^2$	$\omega^2 = \rho$
χ_4	1	$\omega = -\rho^2$	$\omega^2 = \rho$	-1	$-\omega = \rho^2$	$-\omega^2 = -\rho^2$
χ_5	1	$-\omega^2 = -\rho$	$-\omega = \rho^2$	-1	$\omega^2 = \rho$	$\omega = -\rho$

By changing the 5th and 6th rows in Table 5, it coincides with Table 6, so that these character groups are isomorphic. By Theorem 7, we reprove Theorem 2.

4. Rotations as Matrices

In this section we elucidate the rotations and reflections as matrices.

Theorem 7.

Let

$$A_\theta = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \tag{4.1}$$

and

$$B_\phi = \begin{pmatrix} \cos\phi & \sin\phi \\ \sin\phi & -\cos\phi \end{pmatrix}. \tag{4.2}$$

Then the linear transformation $\mathbf{y} = A_\theta \mathbf{x}$ by A_θ means the rotation (in the positive direction, i.e. counterclockwise)

w.r.t. the origin by θ and that the linear transformation $\mathbf{y} = B_\phi \mathbf{x}$ by B_ϕ means the reflection w.r.t. the line ℓ which goes through the origin and is subtended to the positive direction of the x -axis by the angle $\frac{\phi}{2}$.

Proof. We give a proof that makes full use of Euler's identity. Expressing the Cartesian coordinates as the complex number in polar coordinates:

$$\begin{pmatrix} r\cos\Theta \\ r\sin\Theta \end{pmatrix} = \begin{pmatrix} x \\ y \end{pmatrix} = \mathbf{z} \Leftrightarrow z = x + iy = r\cos\Theta + ir\sin\Theta,$$

we see that the rotation $e^{i\theta}z = ze^{i\theta}$ of z by θ is

$$\begin{aligned} e^{i\theta}z &= re^{i(\Theta+\theta)} = r\cos(\Theta+\theta) + ir\sin(\Theta+\theta) \\ &= r\cos\Theta\cos\theta - r\sin\Theta\text{s}-\text{in}\,\theta \\ &+i\left(r\sin\Theta\cos\theta - r\cos\Theta\sin\theta\right) \\ &= x\cos\theta - x\sin\theta + i\left(x\sin\theta + y\cos\theta\right), \end{aligned}$$

which is the linear transformation

$$\begin{pmatrix} x\cos\theta - \text{y}\sin\theta \\ x\sin\theta + \text{y}\cos\theta \end{pmatrix} = A_\theta \begin{pmatrix} x \\ \text{y} \end{pmatrix}.$$

Of course,

$$\arg A_\theta z = \Theta + \theta. \tag{4.3}$$

For the treatment of B_ϕ we note that

$$B_\phi = A_\phi B_0, \tag{4.4}$$

which we now check. Since B_0 means the reflection w.r.t. the x -axis, it corresponds to taking the complex conjugate.

Therefore, the effect of B_ϕ on z corresponds to $e^{i\theta}\overline{z}$. Hence with $\arg z = \Theta$, we have

$$\arg B_0 z = \theta - \Theta. \tag{4.5}$$

Now since $B_\theta z$ is the vector obtained from $\mathbf{z}$ by the rotation by $-\left(\Theta - \frac{1}{2}\theta\right)$, it follows that $\arg B_\theta z = \frac{1}{2}\theta - \left(\Theta - \frac{1}{2}\theta\right)$, which is equal to (4.5). Hence (4.4) follows.

Corollary 1. We have the following identities which have the geometric meaning.

$$A_\theta A_\phi = A_\phi A_\theta = A_{\theta+\phi}, \tag{4.6}$$

$$A_\theta B_\phi = B_{\theta+\phi}, \tag{4.7}$$

$$B_\theta A_\phi = B_{\theta-\phi}, \tag{4.8}$$

and

$$B_\theta B_\phi = A_{\theta-\phi}. \tag{4.9}$$

It is easy to deduce (4.7) etc. from (4.3) and (4.5). Indeed, we find that

$$\arg A_\theta B_\phi \mathbf{z} = \theta + \phi - \Theta, \tag{4.10}$$

which is $B_{\theta+\phi}$, i.e. (4.7).

Similarly, since $\arg A_\phi \mathbf{z} = \Theta + \phi$, we have

$$\arg B_\theta A_\phi \mathbf{z} = \theta - (\Theta + \phi) = (\theta - \phi) - \Theta,$$

whence (4.9).

Finally,

$$\arg B_\theta B_\phi \mathbf{z} = \theta - (\phi - \Theta) = (\theta - \phi) + \Theta,$$

whence (4.10) follows..

Lemma 4.

We have the following identities

$$B_0 A_\theta = B_{-\theta}, \tag{4.11}$$

$$B_\phi B_0 = A_\phi. \tag{4.12}$$

Proof. We make use of (4.4) to express B_ϕ as $A_\phi B_0$. E.g. (4.12) follows by writing $B_\phi B_0 = A_\phi B_0 B_0$ and noting that $B_0^2 = E$.

With aid of Lemma 4, we may give a lucid proof of Corollary 1.

$$A_\theta B_\phi = A_\theta A_\phi B_0 = A_{\theta+\phi} B_0 = B_{\theta+\phi}, \tag{4.13}$$

i.e. (4.7). To prove (4.8), we use (4,4), (4.11), (4.7) to deduce that

$$B_\theta A_\phi = A_\theta B_0 A_\phi = A_\theta B_{-\phi} = B_{\theta-\phi}, \tag{4.14}$$

whence (4.8). Finally,

$$B_\theta B_\phi = A_\theta B_0 A_\phi B_0 = A_\theta B_{-\phi} B_0 = A_\theta A_{-\phi} = A_{\theta-\phi} \tag{4.15}$$

by (4.11), (4.12) and (4.6) successively.

The following examples give rudiments of matrix representations of the group C_{3v}.

Example 5. Given a regular triangle *ABC*, let *O* be the center of gravity and let the mid points of *AB, BC*, *CA* be *D*, *E*, *F,* respectively and choose *DO* to be the x -axis. Let $E = E_2$,

$$C_3 = A_{\frac{2\pi}{3}}, \quad C_3^2 = A_{\frac{4\pi}{3}}, \tag{4.16}$$

and

$$\sigma_v(1) = B_{\frac{4\pi}{3}} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix},$$
$$\sigma_v(2) = B_{\frac{2\pi}{3}} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \quad (4.17)$$
$$\sigma_v(3) = B_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Then

$$G = \{E, C_3, C_3^2, \sigma_v(1), \sigma_v(2), \sigma_v(3)\} \quad (4.18)$$

forms a group w.r.t. the multiplication of matrices and is isomorphic to the group C_{3v} or the symmetric group of order 6 (cf. Theorem 1).

Example 6. Let $E = E_3$,

$$C_3 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \quad C_3^2 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad (4.19)$$

and

$$\sigma_v(1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \sigma_v(2) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix},$$
$$\sigma_v(3) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (4.20)$$

Then

$$G' = \{E, C_3, C_3^2, \sigma_v(1), \sigma_v(2), \sigma_v(3)\} \quad (4.21)$$

forms a group w.r.t. the multiplication of matrices and is isomorphic to the group C_{3v} (cf. Example 5).

Example 7. We find a regular matrix $X = \begin{pmatrix} a & b & 1 \\ b & a & 1 \\ 1 & 1 & 1 \end{pmatrix}$ such that

$$X^{-1} C_3 X = \begin{pmatrix} A_\theta & \mathbf{o} \\ \mathbf{o} & 1 \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (4.22)$$

i.e. similar to C_3.

To this end, it suffices to consider $C_3 X = X \begin{pmatrix} A_\theta & \mathbf{o} \\ \mathbf{o} & 1 \end{pmatrix}$ or

$$\begin{pmatrix} b & a & 1 \\ 1 & 1 & 1 \\ a & b & 1 \end{pmatrix} = \begin{pmatrix} a\cos\theta + b\sin\theta & -a\sin\theta + b\cos\theta & 1 \\ a\sin\theta + b\cos\theta & a\cos\theta - b\sin\theta & 1 \\ \cos\theta + \sin\theta & -\sin\theta + \cos\theta & 1 \end{pmatrix}$$

whence

$$\begin{cases} a = \cos\theta + \sin\theta \\ b = -\sin\theta + \cos\theta \end{cases}.$$

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