J Math Chem (2016) 54:552–558
DOI 10.1007/s10910-015-0577-4

ORIGINAL PAPER

On the algebraic structure of central molecular chirality

Francisco M. Fernández[1]

Received: 18 March 2015 / Accepted: 13 November 2015 / Published online: 19 November 2015

Abstract We show that a group of 24 4×4 permutation matrices that proved suitable for the study of chirality is a reducible representation of the group $\mathcal{T}_d$. Consequently, all the mathematical properties of the former matrices can be easily inferred from the table of characters of the latter group. We also show that the group of 4×4 permutation matrices is isomorphic to a group of 3×3 ones that form an irreducible representation of the elements of the group $\mathcal{T}_d$. We discuss the one-to-one correspondence between the two sets of matrices. A similar analysis can be carried out with the point group $\mathcal{O}$.

Keywords Chirality · Permutation matrices · Group theory · Homomorphism

1 Introduction

With the purpose of studying the important problem of molecular chirality, Capozziello and Lattanzi [1,2] proposed an algebraic approach based on the well-known Fisher projections that leads to 24 4×4 matrices that are the representations of the 4! permutations of four objects. According to the authors these 24 matrices are representations of the elements of the group $\mathcal{O}(4)$ and can be divided into a set of 12 matrices with determinant $+1$ corresponding to the rotation group $\mathcal{SO}(4)$ and a set of 12 matrices with determinant -1 that do not constitute a group. Before proceeding with present discussion we want to point out that it is customary to name $\mathcal{S}_4$ the group of 24 permutations of 4 objects and $\mathcal{A}_4$ the group of the 12 even permutations of 4 objects (the

✉ Francisco M. Fernández
fernande@quimica.unlp.edu.ar

1 División Química Teórica, INIFTA (UNLP, CCT La Plata-CONICET), Blvd. 113 S/N, Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina

latter having 4×4 matrix representations with determinant $+1$). We will adhere to this later notation from now on.

The authors argued that the 24 matrices "are not all independent: They can be grouped as different representations of the same operators" [2]. Similar matrices share the same characteristic polynomial and the authors found that there are just six independent eigenvalues. In a series of subsequent papers the authors applied this algebraic method to several molecular properties associated to chirality [3–6].

If we think of the permutation of the four objects as the permutation of the four vertices of a tetrahedron we conclude that the 24 matrices should be representations of the elements of the group $\mathcal{T}_d$ that describes the symmetry of such a polyhedron (see, e.g. [7]). In fact, the table of characters of the group $\mathcal{T}_d$ exhibits exactly 24 symmetry operations grouped into 5 classes. It is therefore reasonable to assume that the mathematical properties of the permutation matrices introduced by Capozziello and Lattanzi should be derived from those of the symmetry operations of the point group $\mathcal{T}_d$ commonly discussed in books on group theory (see, e.g. [7]).

The purpose of this paper is to establish a connection between the group $\mathcal{S}_4$ and the group $\mathcal{T}_d$ in order to show that all the features of the permutation matrices already follow from the well known results for the symmetry operations of the latter point group. The main results are shown in Sect. 2 and in Sect. 3 we summarize them and draw conclusions. In Appendix 1 we show the group of 24 4×4 permutation matrices proposed by Capozziello and Lattanzi [2] and in Appendix 2 an isomorphic group of 24 3×3 matrices that are an irreducible representation for the elements of the group $\mathcal{T}_d$.

2 Permutation matrices as representation of the symmetry elements of the group $\mathcal{T}_d$

In order to facilitate the discussion of the connection between the permutation matrices of the group $\mathcal{S}_4$ and the symmetry operations of the group $\mathcal{T}_d$ we resort to the notation introduced by Capozziello and Lattanzi [2] for the permutation matrices $G = \{\chi_i,\ i = 1, 2, \ldots, 24\}$ that we show in the Appendix 1 for completeness.

In general, two group elements χ_j and χ_k are said to be conjugate if

$$\chi_i \chi_j \chi_i^{-1} = \chi_k, \tag{1}$$

for some $\chi_i \in G$. If χ_l and χ_k are each conjugate to χ_j then they are conjugate to each other. All the mutually conjugated elements of a group are collected into a class, and it can be proved that the number of classes equals the number of irreducible representations (irreps) of the group (see, e.g. [7]). Table 1 shows the character table for the group $\mathcal{T}_d$. It follows from (1) that $\det(\chi_j - \lambda \mathbf{I}) = \det(\chi_k - \lambda \mathbf{I})$, where $\mathbf{I} = \chi_1$ is the identity matrix. It is clear that all the matrices χ_j belonging to the same class share the same characteristic polynomial and, consequently, the same eigenvalues.

In the case of finite groups it is common to introduce the concept of order or period of a group element χ_i that is the smallest positive integer such that $\chi_i^{\nu} = \mathbf{I}$. All the elements that belong to the same class have the same period as follows from

Table 1 Character table for T_d point group

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$\left(2z^2-x^2-y^2, x^2-y^2\right)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xz, yz, xy)

$\left(\chi_i \chi_j \chi_i^{-1}\right)^\nu = \chi_i \chi_j^\nu \chi_i^{-1} = \chi_k^\nu$. In addition to it, the eigenvalues of a matrix of order ν satisfy $\lambda^\nu = 1$.

The properties outlined above enable us to establish the connection between the permutation matrices χ_i and the elements of the group $\mathcal{T}_d$:

$$\begin{aligned} \chi_1 &\rightarrow E \\ \chi_2, \chi_3, \chi_4, \chi_6, \chi_8, \chi_9, \chi_{10}, \chi_{12} &\rightarrow 8C_3 \\ \chi_5, \chi_7, \chi_{11} &\rightarrow 3C_2 \\ \bar{\chi}_1, \bar{\chi}_2, \bar{\chi}_3, \bar{\chi}_6, \bar{\chi}_8, \bar{\chi}_{11} &\rightarrow 6\sigma_d \\ \bar{\chi}_4, \bar{\chi}_5, \bar{\chi}_7, \bar{\chi}_9, \bar{\chi}_{10}, \bar{\chi}_{12} &\rightarrow 6S_4. \end{aligned} \tag{2}$$

Since $C_3^3 = C_2^2 = \sigma_d^2 = S_4^4 = E$ it is clear why all the eigenvalues of the permutation matrices χ_i found by Capozziello and Lattanzi [2] are given by the roots of $\lambda^3 = 1$, $\lambda^2 = 1$ and $\lambda^4 = 1$.

The class labelled $8C_3$ is given by four pairs of rotations by angles $2\pi/3$ (C_3) and $4\pi/3$ (C_3^2). This fact explains why $\chi_2^2 = \chi_3$ (and similar expressions for other pairs of matrices belonging to the same class). A consequence of this result is that $[\chi_2, \chi_3] = 0$. The class labelled $6S_4$ is given by three pairs of improper rotations by angles $\pi/2$ (S_4) and $3\pi/2$ (S_4^3) which explains why $\bar{\chi}_4^3 = \bar{\chi}_{10}$, etc., that leads to $[\bar{\chi}_4, \bar{\chi}_{10}] = 0$, etc.. These results extend those of Capozziello and Lattanzi [2] (Eqs. (12)-(15)) who only mentioned the commutation among the $3C_2$ matrices.

We have recently resorted to group theory in order to study the properties of a non-Hermitian anharmonic oscillator with symmetry $\mathcal{T}_d$ [8]. In order to construct a suitable matrix representation for the symmetry elements X_i of that group we resorted to a group of 3×3 matrices $\mathbf{M}_i$, $i = 1, 2, \ldots, 24$, that are shown in the Appendix 2. These matrices carry out the coordinate transformations $\mathbf{x}_i = \mathbf{M}_i \mathbf{x}$ for every symmetry operation, where $\mathbf{x}_i = (x_i \; y_i \; z_i)^T$ and $\mathbf{x} = (x \; y \; z)^T$. The effect of X_i on a function $f(\mathbf{x})$ is given by

$$X_i f(\mathbf{x}) = f\left(\mathbf{M}_i^{-1}\mathbf{x}\right). \tag{3}$$

The groups of matrices in the appendices 1 and 2 are isomorphic. In order to appreciate their connection we define the vector

$$\mathbf{t}(\mathbf{x}) = \begin{pmatrix} t_1(\mathbf{x}) \\ t_2(\mathbf{x}) \\ t_3(\mathbf{x}) \\ t_4(\mathbf{x}) \end{pmatrix} = \begin{pmatrix} x + y + z \\ -x - y + z \\ -x + y - z \\ x - y - z \end{pmatrix}, \tag{4}$$

that satisfies

$$\begin{aligned} \mathbf{t}.\mathbf{t} &= 4\mathbf{x}.\mathbf{x}, \\ \sum_{i=1}^{4} t_i &= 0. \end{aligned} \tag{5}$$

The one-to-one correspondence between the 4 × 4 matrices χ_i and the 3 × 3 matrices of Appendix 2 is given by $\chi_i \mathbf{t} = \mathbf{t}(\mathbf{M}_i^{-1}\mathbf{x})$ that follows from Eq. (3). Two particular examples of this mapping are

$$\begin{aligned} \chi_3 &\rightarrow \begin{pmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}, \\ \bar{\chi}_4 &\rightarrow \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \end{aligned} \tag{6}$$

the first case belonging to the class $8C_3$ and the second one to the class $6S_4$. The remaining pairs can be found exactly in the same way. χ_i and $\mathbf{M}_i$ share the same determinant and period but $\mathbf{M}_i$ exhibits one eigenvalue less that χ_i (see below).

The 4 × 4 matrix representation Γ is reducible. Using a well known expression given by group theory (see e.g. [7]) we can easily decompose it into the irreps of the group $\mathcal{T}_d$ shown in Table 1. We obtain

$$\Gamma = A_1 \oplus T_2, \tag{7}$$

where the 3×3 part T_2 is given by the matrices already shown in the Appendix 2. All the matrices χ_i exhibit at least one eigenvalue $\lambda = 1$ that comes from the A_1 contribution and is missing in the matrices $\mathbf{M}_i$. For example, the characteristic polynomial for the matrices $6S_4$ is $(\lambda + 1)(\lambda^2 + 1)$ and that for $8C_3$ is $(1 - \lambda)(1 + \lambda + \lambda^2) = 1 - \lambda^3$ (compare with Eqs. (18) and (22) of Reference [2]).

We can transform the 4 × 4 matrices χ_i into the 3 × 3 matrices of Appendix 2 by means of the following matrix equation:

$$\begin{aligned} &\mathbf{R}_{xt}\chi_i\mathbf{R}_{tx} = \mathbf{M}_i, \\ &\mathbf{R}_{xt} = \frac{1}{2}\begin{pmatrix} 1 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 1 & 1 & 0 & 0 \end{pmatrix}, \; \mathbf{R}_{tx} = \begin{pmatrix} 1 & 1 & 1 \\ -1 & -1 & 1 \\ -1 & 1 & -1 \\ 1 & -1 & -1 \end{pmatrix} \end{aligned} \tag{8}$$

where $\mathbf{R}_{xt}\mathbf{R}_{tx} = \mathbf{I}$ is the 3 × 3 identity matrix.

3 Conclusions

We have shown that the 24 4×4 permutation matrices form a reducible representation for the group $\mathcal{T}_d$. Consequently, all the properties of the permutation matrices derived by Capozziello and Lattanzi [2] can be extracted with little calculation from the table of characters shown in Table 1. For example, the value of the determinant follows from the type of symmetry operation (rotation, reflection, improper rotation, etc.). The eigenvalues of each matrix are determined by the order of the corresponding group element which, together with the symmetry classes, are clearly indicated in the character table.

The representation of the group elements in terms of permutation matrices is reducible, one of the resulting irreps being associated to the matrix representation of dimension 3 of the elements of the group $\mathcal{T}_d$ in the basis set (x, y, z) for the irrep T_2. The 4×4 permutation matrices can be reduced to the 3×3 ones by means of a pair of rectangular transformation matrices.

Finally, it is worth mentioning that one can carry out a similar analysis by means of the point group $\mathcal{O}$ (see, e.g. [7]) and the following correspondence

$$\begin{aligned}
\chi_1 &\rightarrow E \\
\bar{\chi}_4, \bar{\chi}_5, \bar{\chi}_7, \bar{\chi}_9, \bar{\chi}_{10}, \bar{\chi}_{12} &\rightarrow 6C_4 \\
\chi_5, \chi_7, \chi_{11} &\rightarrow 3C_2 = \left(C_4^2\right) \\
\chi_2, \chi_3, \chi_4, \chi_6, \chi_8, \chi_9, \chi_{10}, \chi_{12} &\rightarrow 8C_3 \\
\bar{\chi}_1, \bar{\chi}_2, \bar{\chi}_3, \bar{\chi}_6, \bar{\chi}_8, \bar{\chi}_{11} &\rightarrow 6C_2.
\end{aligned} \tag{9}$$

Note that $\mathcal{S}_4$, $\mathcal{T}_d$ and $\mathcal{O}$ are isomorphic as well as $\mathcal{A}_4$ and $\mathcal{T}$.

Appendix 1: Permutation matrices

In this appendix we simply collect the 24 matrices, labelled according to the paper of Capozziello and Lattanzi [2], that produce all the permutations of the elements t_i of the vector $\mathbf{t}$ in Eq. (4).

$$\chi_1 = \begin{pmatrix} 1&0&0&0 \\ 0&1&0&0 \\ 0&0&1&0 \\ 0&0&0&1 \end{pmatrix}, \chi_2 = \begin{pmatrix} 0&0&1&0 \\ 0&1&0&0 \\ 0&0&0&1 \\ 1&0&0&0 \end{pmatrix}, \chi_3 = \begin{pmatrix} 0&0&0&1 \\ 0&1&0&0 \\ 1&0&0&0 \\ 0&0&1&0 \end{pmatrix} \tag{10}$$

$$\chi_4 = \begin{pmatrix} 0&1&0&0 \\ 0&0&1&0 \\ 1&0&0&0 \\ 0&0&0&1 \end{pmatrix}, \chi_5 = \begin{pmatrix} 0&1&0&0 \\ 1&0&0&0 \\ 0&0&0&1 \\ 0&0&1&0 \end{pmatrix}, \chi_6 = \begin{pmatrix} 0&1&0&0 \\ 0&0&0&1 \\ 0&0&1&0 \\ 1&0&0&0 \end{pmatrix} \tag{11}$$

$$\chi_7 = \begin{pmatrix} 0&0&1&0 \\ 0&0&0&1 \\ 1&0&0&0 \\ 0&1&0&0 \end{pmatrix}, \chi_8 = \begin{pmatrix} 0&0&0&1 \\ 1&0&0&0 \\ 0&0&1&0 \\ 0&1&0&0 \end{pmatrix}, \chi_9 = \begin{pmatrix} 1&0&0&0 \\ 0&0&1&0 \\ 0&0&0&1 \\ 0&1&0&0 \end{pmatrix} \tag{12}$$

$$\chi_{10} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \chi_{11} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \ \chi_{12} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{13}$$

$$\bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \ \bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{14}$$

$$\bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \ \bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{15}$$

$$\bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \ \bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{16}$$

$$\bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \ \bar{\chi}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{17}$$

Appendix 2: 3 × 3 matrix representation for the group $\mathcal{T}_d$

In what follows we show the 24 3 × 3 matrix representations of the elements of the group $\mathcal{T}_d$ grouped into the corresponding classes. Their traces yield the characters of the irrep T_2 shown in Table 1. Although we do not show it explicitly, there is a one-to-one correspondence with the matrices of Appendix 1.

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{18}$$

$8C_3$

$$\begin{gathered} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} \end{gathered} \tag{19}$$

$3C_2$

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{20}$$

$6S_4$

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix},$$
$$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{21}$$

$6\sigma_d$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$
$$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \tag{22}$$

References

1. S. Capozziello, A. Lattanzi, Chirality **15**, 227 (2003)
2. S. Capozziello, A. Lattanzi, Chirality **15**, 466 (2003)
3. S. Capozziello, A. Lattanzi, Chirality **16**, 162 (2004)
4. S. Capozziello, A. Lattanzi, Adv. Quantum Chem. **49**, 227 (2005)
5. S. Capozziello, A. Lattanzi, Int. J. Quantum Chem. **104**, 885 (2005)
6. S. Capozziello, A. Lattanzi, Chirality **18**, 462 (2006)
7. F.A. Cotton, *Chemical Applications of Group Theory*, 3rd edn. (John Wiley & Sons, New York, 1990)
8. P. Amore, F. M. Fernández, and J. Garcia, Ann. Phys. **353**, 238 (2015)