Eur. Phys. J. D **5**, 257–265 (1999)

THE EUROPEAN PHYSICAL JOURNAL D

EDP Sciences

Algebraic time-reversal operation

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Received: 20 April 1998 / Revised: 12 October 1998 / Accepted: 30 October 1998

Abstract. We analyze the implementation of the time-reversal (TR) transformation in the algebraic approach to tetrahedral local molecules through the chain of groups $U(5) \supset U(4) \supset K(4) = A(4) \wedge S(4) \supset S(4) \approx T_d$. We determine the general form of the TR operation using a purely algebraic realization, based exclusively on the requirement that the irreducible representations must not be changed under the time inversion symmetry. As a result we can determine the TR behavior of purely algebraic operators.

PACS. 03.65.Fd Algebraic methods – 31.15.Hz Group theory

1 Introduction

Dynamical noninvariance groups in Quantum Mechanics provide a tool that has found a wide range of applications in nuclear and molecular systems [1–5].

Since under the TR operation, the Hermitian operators $\mathbf{r}$ and $\mathbf{p}$ become $\mathbf{r}$ and $-\mathbf{p}$, developments based on an expansion in powers of these canonical variables present the advantage that we know exactly the behavior of the usual quantum operators (Hamiltonian, transition operators, ...) with respect to the operations of Hermitian conjugation and time inversion. Moreover, if the studied system exhibits some geometrical invariance under the symmetry operations of a group, then the connection of the quantities $\mathbf{r}$ and $\mathbf{p}$ to the different elements of the system (bonds, nuclei, atoms, ...), enables the quantum operators in the symmetry group of this system to be easily symmetrized.

In the algebraic approach developed in [1–7], the basic operators are introduced abstractly, and they do not have a direct interpretation in terms of $\mathbf{r}$ and $\mathbf{p}$. Their TR properties must therefore be established by other intrinsic arguments.

In what follows, we shall restrict our study to tetrahedral molecular systems XY_4. It has been previously shown that $U(5)$ is an appropriate dynamic noninvariance group [6], the degeneracy group of this 4-equivalent oscillators system is $U(4)$. For a molecular system exhibiting a local mode spectrum, such as SiH_4, SnH_4, GeH_4, ..., the group $K(4) = A(4) \wedge S(4)$ gives a good description of the levels [7]. Finally $S(4) \approx T_d$ constitutes the symmetry group of these four equivalent bonds.

From [1,13], we know that all the physical states associated with the vibrational stretching modes of tetrahedral molecules can be obtained within the irreducible representation (irrep) $[N,0,0,0,0]$ of $U(5)$ as symmetrized Gel'fand-Zetlin's kets [7,12] in the group chain

$$U(5) \supset U(4) \supset K(4) \supset S(4) \approx T_d \tag{1}$$

and are obtained by means of [7]

$$|n_1 n_2 n_3 n_4 n_5, rC\sigma\rangle = P^{(C)}_{\sigma} |n_1 n_2 n_3 n_4 n_5\rangle \tag{2}$$

$$= \frac{1}{\sqrt{n_1! n_2! n_3! n_4! n_5!}}$$

$$\times P^{(C)}_{\sigma} (\mathbf{b}_1^{+n_1} \mathbf{b}_2^{+n_2} \mathbf{b}_3^{+n_3} \mathbf{b}_4^{+n_4} \mathbf{b}_5^{+n_5} |00000\rangle) \tag{3}$$

where

$$P^{(C)}_{\sigma} = \frac{[C]}{4!} \sum_{R \in T_d \approx S(4)} \mathcal{D}^{(C)*}_{\sigma\sigma}(R) \mathcal{O}_R \tag{4}$$

denotes the projection operator. The letter r, in relation (2) distinguishes the different irreps C of T_d group whose multiplicity is greater than 1. $K(4)$ provides labels which identify the different local states.

From all the possible realizations of the $U(5)$ generators [14,15], one of the most practical consists in writing them as Bosonic operators:

$$\mathbf{E}_{ij} = \mathbf{b}_i^{\dagger} \mathbf{b}_j \quad i,j = 1,...,5 \tag{5}$$

with the usual Bose relations $[\mathbf{b}_i, \mathbf{b}_j] = [\mathbf{b}_i^{\dagger}, \mathbf{b}_j^{\dagger}] = 0$ and $[\mathbf{b}_i, \mathbf{b}_j^{\dagger}] = \boldsymbol{\delta}_{ij}$.

The generators transform under the Hermitian conjugation as:

$$(\mathbf{E}_{ij})^{\dagger} = \mathbf{E}_{ji} \quad i,j = 1,...,5. \tag{6}$$

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The Hamiltonian of this four-bond system can be written as an expansion in power series of the generators:

$$\mathbf{H} = \alpha^{(0)}\,\mathbb{1} + \sum_{i,j=1}^{5} \alpha_{i,j}^{(1)} \mathbf{E}_{ij} + \sum_{i,j,k,l=1}^{5} \alpha_{i,j,k,l}^{(2)} \mathbf{E}_{ij}\mathbf{E}_{kl} + ... \tag{7}$$

Moreover, if we attribute the operators $\mathbf{b}_i$ and $\mathbf{b}_i^\dagger$ $(i = 1, ..., 4)$ as being annihilation and creation of one quantum of energy associated with the ith bond in the molecule [6], we can easily symmetrize the operators with respect to the symmetry group of the system [7]. This allows us to build a totally symmetric Hamiltonian with respect to $S(4)$.

However, the generators of $U(5)$ are not directly expressed as functions of the canonical variables position and momentum. Following the works of Zhang *et al.* [8,9] or Perelomov [10,11], one can define coherent states associated with $U(5)/U(4) \otimes U(1)$ isomorphic to $CP(4)$. A phase space representation of the generators of $U(5)$ is then obtained by evaluating the mean value of the generators in this coherent state basis. However this construction depends on the particular choice of the canonical coordinates of $U(5)/U(4) \otimes U(1)$ and their TR properties are not determined. They are obtained by analyzing the semi-classical limit of the model.

In the present approach the TR properties can be deduced without invoking a semi-classical limit, by taking into account the chain of groups (1), which gives a physical interpretation to the generators relating them to the bonds. We have thus to establish the representation of the TR transformation for the operators of an algebraic Hamiltonian by arguments that are not based on position and momentum operators. We will use properties based exclusively on the symmetries of the system; in particular the fact that the space of states associated with the irrep $[N, 0, 0, 0, 0]$ of $U(5)$ is stable under time inversion.

We shall assume that the irreps in the chain (1) give good quantum numbers for local tetrahedral molecules as shown in previous papers [7,16].

The main steps involved in this paper are:

- representation of the TR transformation on the algebra of the Boson operators as linear, antiunitary transformations;
- invariance of the operator $\mathbf{N} = \sum_{i=1}^{5} \mathbf{N}_i$ under the associated transformations;
- twice the TR operation applied on the Boson operators leads to the initial operators;
- TR operation commutes with the T_d group transformations;
- invariance under the TR symmetry of the algebraic invariant operators of $U(4)$ and $K(4)$.

As a result, these conditions allow us to determine the TR behavior of purely algebraic operators. For the Boson operators, we obtain the following general form of the transformation:

$$\tilde{\mathbf{b}_k^\dagger} = e^{i\omega}\mathbf{b}_k^\dagger, \qquad \tilde{\mathbf{b}_k} = e^{-i\omega}\mathbf{b}_k$$

$$\tilde{\mathbf{b}_5^\dagger} = e^{i\omega''}\mathbf{b}_5^\dagger, \quad \tilde{\mathbf{b}_5} = e^{-i\omega''}\mathbf{b}_5 \ (k = 1, ..., 4).$$

where ω and ω'' are two free parameters.

From which we deduce the action of the TR operation for the $U(5)$ generators:

$$\widetilde{\mathbf{b}_i^\dagger\mathbf{b}_j} = \mathbf{b}_i^\dagger\mathbf{b}_j, \qquad \widetilde{\mathbf{b}_5^\dagger\mathbf{b}_5} = \mathbf{b}_5^\dagger\mathbf{b}_5$$

$$\widetilde{\mathbf{b}_k^\dagger\mathbf{b}_5} = e^{i(\omega-\omega'')}\mathbf{b}_k^\dagger\mathbf{b}_5, \quad \widetilde{\mathbf{b}_5^\dagger\mathbf{b}_k} = e^{i(\omega''-\omega)}\mathbf{b}_5^\dagger\mathbf{b}_k \quad (i, j, k = 1, ..., 4).$$

1.1 Properties of the TR operation: Discussion of simple cases

Before we derive the transformation of the $U(5)$ generators, we want to illustrate using a simple case that such a transformation is not trivial. First, we recall some properties of TR operation. For further details, we refer to [17].

The TR transformation is an antiunitary operation which can be written as:

$$\boldsymbol{\theta} = \mathbf{U}\mathbf{K} \tag{8}$$

where $\mathbf{U}$ is unitary and $\mathbf{K}\Psi = \Psi^*$ is the transition to the complex conjugate. It verifies $\mathbf{K}^2 = \mathbb{1}$ or $\mathbf{K} = \mathbf{K}^{-1}$.

Furthermore $\boldsymbol{\theta}^2 = \pm\mathbb{1}$, the lower sign applies in the case of a Fermionic system. For the problem dealt with here, we need only to keep the case:

$$\boldsymbol{\theta}^2 = \mathbb{1} \quad \text{or} \quad \boldsymbol{\theta} = \boldsymbol{\theta}^{-1}. \tag{9}$$

The TR transformation acts on the Boson operators as $\mathbf{b}_i^\dagger \to \tilde{\mathbf{b}_i^\dagger} = \boldsymbol{\theta}\mathbf{b}_i^\dagger\boldsymbol{\theta}^{-1}$.

We immediately deduce the transformation of a generator:

$$\begin{aligned}\widetilde{\mathbf{b}_i^\dagger\mathbf{b}_j} &= \boldsymbol{\theta}\mathbf{b}_i^\dagger\mathbf{b}_j\boldsymbol{\theta}^{-1} \\ &= \boldsymbol{\theta}\mathbf{b}_i^\dagger\boldsymbol{\theta}^{-1}\boldsymbol{\theta}\mathbf{b}_j\boldsymbol{\theta}^{-1} \\ &= \tilde{\mathbf{b}_i^\dagger}\tilde{\mathbf{b}_j}\end{aligned}$$

and

$$(\tilde{\mathbf{b}_i^\dagger})^\dagger = (\boldsymbol{\theta}^{-1})^\dagger\mathbf{b}_i\boldsymbol{\theta}^\dagger = \boldsymbol{\theta}\mathbf{b}_i\boldsymbol{\theta}^{-1} = \tilde{\mathbf{b}_i} \tag{10}$$

(*i.e.* one can deduce the action of the TR operation on the $\mathbf{b}_i$ knowing the action on the $\mathbf{b}_i^\dagger$).

Finally, from [17], we recall that the operation of time inversion commutes with all symmetry operations of the rotation group $O(3)$:

$$[\boldsymbol{\theta}, \mathbf{P}_\mathbf{R}] = 0 \quad \forall\, \mathbf{R} \in O(3). \tag{11}$$

This relation holds necessarily for T_d as a subgroup of $O(3)$.

We start by discussing a simple case. Let us choose the following chain of groups:

$$U(3) \supset U(2). \tag{12}$$

Among the generators of $U(3)$, we separate those that generate the subgroup $U(2)$:

$$\underbrace{\underbrace{\mathbf{b}_1^\dagger\mathbf{b}_3 \qquad \mathbf{b}_1^\dagger\mathbf{b}_1 = \mathbf{N}_1}_{\mathbf{b}_3^\dagger\mathbf{b}_1 \qquad \mathbf{b}_1^\dagger\mathbf{b}_2}}_{\mathbf{b}_2^\dagger\mathbf{b}_3 \qquad \mathbf{b}_2^\dagger\mathbf{b}_1} \underbrace{\underbrace{\mathbf{b}_3^\dagger\mathbf{b}_2 \qquad \mathbf{b}_2^\dagger\mathbf{b}_2 = \mathbf{N}_2}_{\mathbf{b}_3^\dagger\mathbf{b}_3 = \mathbf{N}_3}}_{U(2)}}_{U(3)}$$

if we assume the physical system to be well-described by the chain (12), then the Hamiltonian can be written in a first approximation as a sum of the Casimir operators $\mathcal{C}_j$ of (12). Up to the second order in the generators, it reads:

$$\begin{aligned}\mathbf{H} &= \alpha_1\,\mathcal{C}_1(U(3)) + \alpha_2\,\mathcal{C}_2(U(3)) \\ &\quad + \beta_1\,\mathcal{C}_1(U(2)) + \beta_2\,\mathcal{C}_2(U(2)) \\ &= \alpha_1\mathbf{N} + \alpha_2\mathbf{N}^2 + \beta_1\mathbf{n} + \beta_2\mathbf{n}^2\end{aligned} \tag{13}$$

where we have denoted $\mathbf{N} = \mathbf{N}_1 + \mathbf{N}_2 + \mathbf{N}_3$ and $\mathbf{n} = \mathbf{N}_1 + \mathbf{N}_2$. As

$$(\mathbf{b}_i^\dagger\mathbf{b}_j)^\dagger = \mathbf{b}_j^\dagger\mathbf{b}_i \tag{14}$$

the Hamiltonian is Hermitian (with $\alpha_1, \alpha_2, \beta_1, \beta_2 \in \mathbb{R}$). Moreover, it has to be invariant under the TR operation: $\tilde{\mathbf{H}} = \mathbf{H}$. This could be realized by postulating one of the three following transformation rules:

R1: invariance of the Boson operators ($i = 1, 2, 3$)

$$\tilde{\mathbf{b}_i^\dagger} = \mathbf{b}_i^\dagger \quad (\text{or equivalently } \tilde{\mathbf{b}_i} = \mathbf{b}_i) \tag{15}$$

R2: invariance of the weight generators ($i = 1, 2, 3$)

$$\widetilde{\mathbf{b}_i^\dagger\mathbf{b}_i} = \mathbf{b}_i^\dagger\mathbf{b}_i \tag{16}$$

R3: invariance of the Casimir operators

$$\tilde{\mathbf{N}} = \mathbf{N} \tag{17}$$

$$\tilde{\mathbf{n}} = \mathbf{n} \tag{18}$$

Each of them implies that $\tilde{\mathbf{H}} = \mathbf{H}$.

The point we want to make is that the physical conditions that are involved in the construction of the algebraic model, lead directly to R3, but not necessarily to R1 or R2.

We have that R1 $\Rightarrow$ R2 $\Rightarrow$ R3.

We note that relations (17, 18) imply that $\widetilde{\mathbf{N}}_3 = \mathbf{N}_3$.

With R3, the operator $\mathbf{N}_3$ plays a particular role. In fact R3 is well-adapted to the chain of groups (12).

Studying a system for which a suitable chain of groups consists only of $U(3)$, R1 and R2 could be left unchanged, while R3 reduces to (17).

The rules R1 and R2 cannot be imposed *a priori*. In order to see that, we consider the following operators:

$$\begin{aligned}&\mathbf{B}_1 = \frac{1}{\sqrt{2}}(\mathbf{b}_1 - i\mathbf{b}_2), \quad \mathbf{B}_2 = \frac{1}{\sqrt{2}}(\mathbf{b}_1 + i\mathbf{b}_2), \quad \mathbf{B}_3 = \mathbf{b}_3 \\ &\mathbf{B}_1^\dagger = \frac{1}{\sqrt{2}}(\mathbf{b}_1^\dagger + i\mathbf{b}_2^\dagger), \quad \mathbf{B}_2^\dagger = \frac{1}{\sqrt{2}}(\mathbf{b}_1^\dagger - i\mathbf{b}_2^\dagger), \quad \mathbf{B}_3^\dagger = \mathbf{b}_3^\dagger.\end{aligned} \tag{19}$$

They satisfy the same commutation relations $[\mathbf{B}_i, \mathbf{B}_j^\dagger] = \boldsymbol{\delta}_{ij}$, $(i, j = 1, 2, 3)$. We can now interpret the operators $\mathbf{B}_i^\dagger\mathbf{B}_j$ as generators of a $U(3)$ group. We could invert (19) and from the $\mathbf{B}_i^\dagger$, $\mathbf{B}_j$ postulate the same transformation rules as we did for $\mathbf{b}_i^\dagger$, $\mathbf{b}_j$. In this way, we can build a Hamiltonian adapted to the chain $U(3) \supset U(2)$. On the other hand, from the expression (13) and reversing the relations (19), it is possible to deduce the transformed Hamiltonian, which can be written as:

$$\mathbf{H}' = \alpha_1\mathbf{N}' + \alpha_2\mathbf{N}'^2 + \beta_1\mathbf{n}' + \beta_2\mathbf{n}'^2 \tag{20}$$

where $\mathbf{N}' = \mathbf{B}_1^\dagger\mathbf{B}_1 + \mathbf{B}_2^\dagger\mathbf{B}_2 + \mathbf{B}_3^\dagger\mathbf{B}_3$ and $\mathbf{n}' = \mathbf{B}_1^\dagger\mathbf{B}_1 + \mathbf{B}_2^\dagger\mathbf{B}_2$.

$\mathbf{H}'$ is Hermitian and satisfies $\widetilde{\mathbf{H}}' = \mathbf{H}'$. However, from R1, one does not get similar relations for the $\mathbf{B}_i^\dagger$, $\mathbf{B}_j$:

$$\widetilde{\mathbf{B}}_1 = \mathbf{B}_2, \quad \widetilde{\mathbf{B}}_2 = \mathbf{B}_1, \quad \widetilde{\mathbf{B}}_3 = \mathbf{B}_3 \tag{21}$$

(and the related Hermitian conjugate expressions).

It follows that the Hamiltonian $\mathbf{H}'$ is invariant without verifying a rule of type R1.

Now from R2, we obtain for the new weight generators:

$$\widetilde{\mathbf{B}_1^\dagger\mathbf{B}_1} = \mathbf{B}_2^\dagger\mathbf{B}_2, \quad \widetilde{\mathbf{B}_2^\dagger\mathbf{B}_2} = \mathbf{B}_1^\dagger\mathbf{B}_1, \quad \widetilde{\mathbf{B}_3^\dagger\mathbf{B}_3} = \mathbf{B}_3^\dagger\mathbf{B}_3. \tag{22}$$

Once again, $\mathbf{H}'$ is invariant without verifying a rule of type R2.

In conclusion, it is only with the rule R3 that the two Hamiltonians verify the same property of invariance of the Casimir operators under the TR symmetry.

Having shown that R1 $\Rightarrow$ R2 $\Rightarrow$ R3, and taking into account the necessity of invariance of the Casimir operators, we can conclude that we have to define a more general expression than R1 for the transformation of the Boson operators $\mathbf{b}_i^\dagger$, $\mathbf{b}_j$. This will give us the expression of the transformed generators under the TR operation.

Another, even simpler example that shows that the rules R1, R2 or R3 cannot be imposed *a priori* without a physical interpretation is given by the chains

$$(\mathrm{I}): \qquad U(2) \supset U(1)$$

and

$$(\mathrm{II}): \qquad U(2) \supset SU(2) \supset SO(2).$$

The first one (I) is chosen to describe a one-dimensional vibrational degree of freedom (*e.g.* vibration of a diatomic molecule), while the second one (II) is taken to describe a rotational degree of freedom (orbital angular momentum). The generators of $U(2)$ can be represented by

$$\begin{aligned}
\mathbf{E}_{12} &= \mathbf{b}_1^\dagger \mathbf{b}_2 \\
\mathbf{E}_{11} &= \mathbf{b}_1^\dagger \mathbf{b}_1 \equiv \mathbf{N}_1 \equiv \mathbf{n} \\
\mathbf{E}_{21} &= \mathbf{b}_2^\dagger \mathbf{b}_1 \\
\mathbf{E}_{22} &= \mathbf{b}_2^\dagger \mathbf{b}_2 \equiv \mathbf{N}_2 \equiv \mathbf{N} - \mathbf{n}.
\end{aligned}$$

To describe angular momentum, the generators of $U(2)$ can be represented by

$$\begin{aligned}
\mathbf{N} &= \mathbf{E}_{22} + \mathbf{E}_{11} \\
\mathbf{J}_z &= (\mathbf{E}_{22} - \mathbf{E}_{11})/2 = \mathbf{N}/2 - \mathbf{n} \\
\mathbf{J}_- &= \mathbf{E}_{12} \\
\mathbf{J}_+ &= \mathbf{E}_{21}.
\end{aligned}$$

Thus, if we impose R3, which is well adapted for the vibrational chain (I) we would obtain

$$\widetilde{\mathcal{C}_1(U(2))} = \tilde{\mathbf{N}} = \mathcal{C}_1(U(2)) = \mathbf{N}$$

and

$$\widetilde{\mathcal{C}_1(U(1))} = \tilde{\mathbf{n}} = \mathcal{C}_1(U(1)) = \mathbf{n}$$

that is:

$$\widetilde{\mathbf{J}_z} = \mathbf{J}_z.$$

For the second chain, in order to obtain the TR transformation adapted to angular momentum, we require:

$$\widetilde{\mathbf{J}_z} = -\mathbf{J}_z,$$

$$\widetilde{\mathbf{J}_+} = -\mathbf{J}_-.$$

This can be obtained by choosing

$$\tilde{\mathbf{b}_1} = -\mathbf{b}_2, \qquad \tilde{\mathbf{b}_2} = \mathbf{b}_1.$$

We notice that this transformation satisfies $\boldsymbol{\theta}^2 = -\mathbb{1}$ when acting upon the boson operators ($\tilde{\tilde{\mathbf{b}_j}} = -\mathbf{b}_j$), but $\boldsymbol{\theta}^2 = \mathbb{1}$ acting on the generators ($\widetilde{\widetilde{\mathbf{E}_{ij}}} = \mathbf{E}_{ij}$), which are the actual physical observables. The conclusion from these examples is that the realization of the TR transformation cannot be defined only from the abstract algebraic properties of the chain. One needs to use the physical interpretation attributed to the operators.

In this paper we will discuss the case of vibrational modes described by $U(5)$. We will attribute the physical interpretation of the operators through geometrical symmetry properties of the molecule.

2 Hypothesis and conditions on basic operators

We consider representations of the TR operation, on the algebra of Boson operators, as linear antiunitary transformations. A creation operator can be transformed into a linear combination of all other annihilation and creation operators of the unitary group $U(5)$, namely ($i = 1, ..., 5$):

$$\tilde{\mathbf{b}_i^\dagger} = \sum_{j=1}^{5} A_{ij} \mathbf{b}_j + \sum_{k=1}^{5} B_{ik} \mathbf{b}_k^\dagger. \tag{23}$$

From the relation (10) we can derive ($l = 1, ..., 5$):

$$\tilde{\mathbf{b}_l} = \sum_{p=1}^{5} A_{lp}^* \mathbf{b}_p^\dagger + \sum_{q=1}^{5} B_{lq}^* \mathbf{b}_q. \tag{24}$$

Taking into account the invariance condition on the irreps in the chain (1), this relation can be further reduced as follows.

2.1 First condition

We start by examining the operator $\mathbf{N} = \sum_{i=1}^{5} \mathbf{N}_i$. This operator is diagonal in the initial basis and consequently in the symmetrized basis too, with eigenvalue N. This eigenvalue is nothing but the label denoting the irrep $[N, 0, 0, 0, 0]$ of $U(5)$. It can be related to the number of bound states (given by the well-known Weyl formula [18]) associated with our vibrational problem. Under the TR symmetry, we must stay within the irrep containing all the physical states of our system, that is:

$$\tilde{\mathbf{N}} \equiv \mathbf{N}.$$

With the help of equations (23, 24), the latter expression becomes:

$$\begin{aligned}
\tilde{\mathbf{N}} &= \sum_{i=1}^{5} \widetilde{\mathbf{b}_i^\dagger \mathbf{b}_i} = \sum_{i=1}^{5} \tilde{\mathbf{b}_i^\dagger} \tilde{\mathbf{b}_i} \\
&= \sum_{i=1}^{5} \left\{ \left(\sum_{j=1}^{5} A_{ij} \mathbf{b}_j + \sum_{k=1}^{5} B_{ik} \mathbf{b}_k^\dagger \right) \left(\sum_{p=1}^{5} A_{ip}^* \mathbf{b}_p^\dagger + \sum_{q=1}^{5} B_{iq}^* \mathbf{b}_q \right) \right\} \\
&= \sum_{ijp} \Big\{ (A_{ij} A_{ip}^* + B_{ip} B_{ij}^*) \mathbf{b}_p^\dagger \mathbf{b}_j + A_{ij} A_{ip}^* \boldsymbol{\delta}_{jp} \\
&\quad + A_{ij} B_{ip}^* \mathbf{b}_j \mathbf{b}_p + B_{ij} A_{ip}^* \mathbf{b}_j^\dagger \mathbf{b}_p^\dagger \Big\} \\
&\equiv \sum_{i=1}^{5} \mathbf{b}_i^\dagger \mathbf{b}_i.
\end{aligned} \tag{25}$$

We can deduce that:

$$\sum_{ijp} A_{ij} A_{ip}^* \boldsymbol{\delta}_{jp} = 0 \ \text{ that is } \ A_{ij} = 0 \ \ \forall\, i, j. \tag{26}$$

Thus, relation (25) is reduced to:

$$\tilde{\mathbf{N}} = \sum_{i=1}^{5} \tilde{\mathbf{b}_i^\dagger} \tilde{\mathbf{b}_i} = \sum_{ijp} B_{ip} B_{ij}^* \ \mathbf{b}_p^\dagger \mathbf{b}_j \equiv \sum_{i=1}^{5} \mathbf{b}_i^\dagger \mathbf{b}_i.$$

It follows that the matrix B is a (5×5) unitary matrix.

2.2 Second condition

The second condition is given by relation (9), applied to a creation (or annihilation) operator:

$$\tilde{\tilde{\mathbf{b}}}_i^\dagger \equiv \mathbf{b}_i^\dagger \quad (\text{or} \quad \tilde{\tilde{\mathbf{b}}}_i \equiv \mathbf{b}_i). \tag{27}$$

From equations (23, 26), we have that:

$$\tilde{\mathbf{b}}_i^\dagger = \sum_{k=1}^{5} B_{ik}\mathbf{b}_k^\dagger \quad \text{which means that} \quad \tilde{\tilde{\mathbf{b}}}_i^\dagger = \sum_{k=1}^{5} B_{ik}^* \tilde{\mathbf{b}}_k^\dagger.$$

So equation (27) can now be expressed as:

$$\tilde{\tilde{\mathbf{b}}}_i^\dagger = \sum_{kj} B_{ik}^* B_{kj} \mathbf{b}_j^\dagger \equiv \mathbf{b}_i^\dagger.$$

This implies that $\sum_k B_{ik}^* B_{kj} = \delta_{ij}$, hence B is a (5×5) symmetric unitary matrix.

2.3 Third condition

For tetrahedral molecules, the molecular symmetry group T_d is isomorphic to the permutation group $S(4)$.

In other words, each symmetry $\mathbf{R}$ of T_d produces a permutation of the indices $i = 1, ..., 4$ numbering the four bonds. As a generator $\mathbf{b}_i^\dagger \mathbf{b}_j$ $(i, j = 1, ..., 4)$ is interpreted as the operator transferring one quantum from bond j to bond i, one can easily determine how such an operator transforms under $\mathbf{R} \in S(4) \approx T_d \subset O(3)$. With this condition, we only need to examine the relations imposed on the B_{ij} for any symmetry operation of $S(4)$. The reference configuration chosen for our XY_4 system is given in Figure 1 of [19], where the bond i corresponds to the atom Y_i labeled by the index i. In order to illustrate the results obtained, we give hereafter an example in a particular case.

Under the $C_3(1, 1, 1)$ rotation, the four bonds transform as: (4) (132). In this case, we get the following relations: $B_{11} = B_{33}$, $B_{12} = B_{13} = B_{23}$, $B_{14} = B_{34}$, $B_{15} = B_{35}$. Repeating the same procedure for all symmetry operations of $S(4)$, we deduce that:

$$B_{ii} = \alpha \ (i = 1, ..., 4); \quad B_{ij} = \beta \ (i \neq j = 1, ..., 4) \tag{28}$$

$$B_{i5} = \delta \ (i = 1, ..., 4). \tag{29}$$

We will denote $B_{55} = \gamma$.

2.4 Fourth condition

$U(4)$ is the degeneracy group for a system of 4 equivalent oscillators. The irreps $[n, 0, 0, 0]$ of $U(4)$ included in the irrep $[N, 0, 0, 0, 0]$ of $U(5)$ are given by the usual betweenness conditions [12,20]:

$$0 \leq n \leq N.$$

Moreover, we can verify that

$$\dim [n, 0, 0, 0] = \frac{(n+3)!}{n!\, 3!} = C_{n+4-1}^n$$

corresponds to the degeneracy of a 4-dimensional oscillator in the n-state. The number n is the eigenvalue of the operator $\mathbf{n} = \sum_{i=1}^{4} \mathbf{N}_i$, which is one of the building blocks of the Hamiltonian expansion (of type (13)), and can thus be interpreted as the energy of a 4-dimensional isotropic harmonic oscillator. As in Section 2.1, n can be seen as the label denoting the irrep $[n, 0, 0, 0]$ of $U(4)$. Consequently, we require that the TR transformation cannot transform a state n to another state n' with different energy. This gives:

$$\tilde{\mathbf{n}} \equiv \ \mathbf{n} \text{ that is } \tilde{\mathbf{N}} - \tilde{\mathbf{N}}_5 \equiv \mathbf{N} - \mathbf{N}_5 \text{ or } \tilde{\mathbf{N}}_5 \equiv \mathbf{N}_5.$$

Developing this expression, and taking into account the relations (29), we find that $\delta = 0$.

2.5 Diagonalization of matrix B

Up to now, we have not made explicit the unitarity of matrix B. The usual and simplest way to express this property consists in diagonalizing B, which gives:

$$P^{-1}BP = D = \begin{pmatrix} \alpha - \beta & & & & \\ & \alpha - \beta & & & 0 \\ & & \alpha - \beta & & \\ & 0 & & \alpha + 3\beta & \\ & & & & \gamma \end{pmatrix}$$

$$\text{with} \quad P = \frac{1}{2}\begin{pmatrix} 1 & -1 & 1 & 1 & 0 \\ -1 & 1 & 1 & 1 & 0 \\ 1 & 1 & -1 & 1 & 0 \\ -1 & -1 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 2 \end{pmatrix}.$$

P and B being two unitary matrices, this implies that D has the following form:

$$D = \begin{pmatrix} e^{i\omega} & & & & \\ & e^{i\omega} & & & 0 \\ & & e^{i\omega} & & \\ & 0 & & e^{i\omega'} & \\ & & & & e^{i\omega''} \end{pmatrix}$$

with $\omega, \omega', \omega'' \in \mathbb{R}$. From this we can easily deduce the matrix B:

$$B = PDP^{-1} =$$

$$\frac{1}{4}\begin{pmatrix} 3e^{i\omega} + e^{i\omega'} & e^{i\omega'} - e^{i\omega} & e^{i\omega'} - e^{i\omega} & e^{i\omega'} - e^{i\omega} & 0 \\ e^{i\omega'} - e^{i\omega} & 3e^{i\omega} + e^{i\omega'} & e^{i\omega'} - e^{i\omega} & e^{i\omega'} - e^{i\omega} & 0 \\ e^{i\omega'} - e^{i\omega} & e^{i\omega'} - e^{i\omega} & 3e^{i\omega} + e^{i\omega'} & e^{i\omega'} - e^{i\omega} & 0 \\ e^{i\omega'} - e^{i\omega} & e^{i\omega'} - e^{i\omega} & e^{i\omega'} - e^{i\omega} & 3e^{i\omega} + e^{i\omega'} & 0 \\ 0 & 0 & 0 & 0 & 4e^{i\omega''} \end{pmatrix}. \tag{30}$$

Table 1. Matrix representation of $K(4)$ for the generators (1 2); (2 3); (3 4) of $S(4)$ ($0 \leq \alpha_i < 2\pi \;\; i = 1, ..., 4$).

$D(R) \equiv D(R_1 R_2)(R \in K(4))$	$D(R_1)$ $(R_1 \in A(4))$	$\times$	$D(R_2)$ $(R_2 \in S(4))$
$\begin{pmatrix} e^{i\alpha_1} & 0 & 0 & 0 \\ 0 & 0 & e^{i\alpha_2} & 0 \\ 0 & e^{i\alpha_3} & 0 & 0 \\ 0 & 0 & 0 & e^{i\alpha_4} \end{pmatrix}$	$\begin{pmatrix} e^{i\alpha_1} & 0 & 0 & 0 \\ 0 & e^{i\alpha_2} & 0 & 0 \\ 0 & 0 & e^{i\alpha_3} & 0 \\ 0 & 0 & 0 & e^{i\alpha_4} \end{pmatrix}$	$\times$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$
$\begin{pmatrix} e^{i\alpha_1} & 0 & 0 & 0 \\ 0 & e^{i\alpha_2} & 0 & 0 \\ 0 & 0 & 0 & e^{i\alpha_3} \\ 0 & 0 & e^{i\alpha_4} & 0 \end{pmatrix}$	$\begin{pmatrix} e^{i\alpha_1} & 0 & 0 & 0 \\ 0 & e^{i\alpha_2} & 0 & 0 \\ 0 & 0 & e^{i\alpha_3} & 0 \\ 0 & 0 & 0 & e^{i\alpha_4} \end{pmatrix}$	$\times$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$
$\begin{pmatrix} 0 & e^{i\alpha_1} & 0 & 0 \\ e^{i\alpha_2} & 0 & 0 & 0 \\ 0 & 0 & e^{i\alpha_3} & 0 \\ 0 & 0 & 0 & e^{i\alpha_4} \end{pmatrix}$	$\begin{pmatrix} e^{i\alpha_1} & 0 & 0 & 0 \\ 0 & e^{i\alpha_2} & 0 & 0 \\ 0 & 0 & e^{i\alpha_3} & 0 \\ 0 & 0 & 0 & e^{i\alpha_4} \end{pmatrix}$	$\times$	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$

2.6 Fifth condition

We can now concentrate our attention on $K(4)$. Initially the group $K(n)$ ($n \in \mathbb{N}^*$) was introduced by Kramer and Moshinsky [21,22] in the study of a n-nucleon system. This group is obtained as the semi-direct product $A(n) \wedge S(n)$ where $A(n)$ is the group of the $n \times n$ unitary diagonal matrices and $S(n)$ the permutation group of n objects.

In our case, there is a convenient way [23] to write the operations $R = R_1 R_2$ of $K(4)$ in matrix form; $D(R)$ is the product $D(R_1)D(R_2)$ where $D(R_1)$ is a 4-dimensional diagonal matrix, function of 4 real parameters α_i, and $D(R_2)$ is a matrix in the natural representation of $S(4)$. An illustration of this matrix representation is given in Table 1. From this table, it appears clearly that $K(4)$ is a subgroup of $U(4)$.

The irreps of $K(4)$ are given in [7]. They can be denoted by

$$(n_1\, n_2\, n_3\, n_4, \{f_w\})$$

with n_1, n_2, n_3, $n_4 \in \mathbb{N}$. $w = (n_1\, n_2\, n_3\, n_4)$ represents an irrep of $A(4)$ and f_w a product of irreps of subgroups of $S(4)$ whose direct sum equals $S(4)$.

It must be noted that

$$(n_{\pi(1)} n_{\pi(2)} n_{\pi(3)} n_{\pi(4)}, \{f_w\}) = (n_1\, n_2\, n_3\, n_4, \{f_w\}), \quad \forall \pi \in S\,(4)$$

i.e., it does not matter in which order the quantum numbers $n_1\, n_2\, n_3\, n_4$ appear. From this, we can deduce that $K(4)$ admits an infinite number of irreps just as there is an infinite number of non-equivalent sets $\{n_i\}_{i=1,...,4}$.

For a given value $n = n_1 + n_2 + n_3 + n_4$ it is possible to classify the different types of irreps of $K(4)$. This is given in [7]. The irreps of $K(4)$ which can appear in the subduction of the irrep [n, 0, 0, 0] of $U(4)$ are:

$$\begin{aligned}
&(n_1\, n_1\, n_1\, n_1, \{4000\}),\\
&(n_1\, n_1\, n_1\, n_2, \{300\}\{1\}),\\
&(n_1\, n_1\, n_2\, n_2, \{20\}\{20\}),\\
&(n_1\, n_1\, n_2\, n_3, \{20\}\{1\}\{1\}),\\
&(n_1\, n_2\, n_3\, n_4, \{1\}\{1\}\{1\}\{1\}).
\end{aligned}$$

It was shown in [7] that these irreps are exactly those which identify the states of a local tetrahedral molecule.

Invariant operators are associated to these irreps. They enable the identification of the different local states. The way of constructing them is developed in [7]. Their expressions in terms of Bosonic operators are:

$$\begin{aligned}
\mathbf{J}_1(\mathbf{K}(4)) &= \mathbf{N}_1 + \mathbf{N}_2 + \mathbf{N}_3 + \mathbf{N}_4,\\
\mathbf{J}_2(\mathbf{K}(4)) &= {\mathbf{N}_1}^2 + {\mathbf{N}_2}^2 + {\mathbf{N}_3}^2 + {\mathbf{N}_4}^2,\\
\mathbf{J}_3(\mathbf{K}(4)) &= {\mathbf{N}_1}^3 + {\mathbf{N}_2}^3 + {\mathbf{N}_3}^3 + {\mathbf{N}_4}^3,\\
\mathbf{J}_4(\mathbf{K}(4)) &= {\mathbf{N}_1}^4 + {\mathbf{N}_2}^4 + {\mathbf{N}_3}^4 + {\mathbf{N}_4}^4.
\end{aligned}$$

These operators are functions of the weight operators $\mathbf{N}_i$ ($i = 1, ..., 4$) only and consequently diagonal in the symmetrized basis.

As $K(4)$ provides us with labels which identify the different local states, we now demand that these irreps remain invariant under the TR symmetry, or in other words, that one cannot go from a local state to another (for the same value of n) only by this time symmetry. This gives:

$$\widetilde{\mathbf{J}}_i(\mathbf{K}(4)) \equiv \mathbf{J}_i(\mathbf{K}(4)) \text{ with } i = 1, ..., 4. \qquad (31)$$

The operator $\mathbf{J}_1(\mathbf{K}(4))$ is the linear algebraic invariant of $U(4)$, which we already examined in Section 2.4. Under the

TR operation (30), the quadratic invariant $\mathbf{J}_2(\mathbf{K}(4)) = \mathbf{N}_1^2 + \mathbf{N}_2^2 + \mathbf{N}_3^2 + \mathbf{N}_4^2$ becomes:

$$\sum_{i=1}^{4} \widetilde{\mathbf{N}}_i^2 = (|\alpha|^4 + 3|\beta|^4) \sum_{i=1}^{4} \mathbf{N}_i^2 + \sum_{\substack{(i=j=p=q) \\ \text{excluded}}} C_{i,j,p,q}(\alpha,\beta)\ \mathbf{b}_i^\dagger \mathbf{b}_j \mathbf{b}_p^\dagger \mathbf{b}_q.$$

The condition (31), for $i = 2$, leads to two new relations:

$$(|\alpha|^4 + 3|\beta|^4) = 1 \tag{32}$$

$$C_{i,j,p,q}(\alpha,\beta) = 0 \tag{33}$$

$\forall\ i,j,p,q$ included in the sum mentioned above.

Equation (32) gives the unique solution

$$\omega' = \omega \mod[2\pi].$$

From this it is easy to verify that condition (33) is automatically fulfilled.

We can thus write:

$$B = \begin{pmatrix} e^{i\omega} & & & & \\ & e^{i\omega} & & 0 & \\ & & e^{i\omega} & & \\ & 0 & & e^{i\omega} & \\ & & & & e^{i\omega''} \end{pmatrix}.$$

The result of the TR operation can now be expressed for the $U(5)$ generators $(i,j,k = 1,...,4)$ as:

$$\begin{aligned} &\widetilde{\mathbf{b}_i^\dagger \mathbf{b}_j} = \mathbf{b}_i^\dagger \mathbf{b}_j, && \widetilde{\mathbf{b}_5^\dagger \mathbf{b}_5} = \mathbf{b}_5^\dagger \mathbf{b}_5, \\ &\widetilde{\mathbf{b}_k^\dagger \mathbf{b}_5} = e^{i(\omega-\omega'')} \mathbf{b}_k^\dagger \mathbf{b}_5, && \widetilde{\mathbf{b}_5^\dagger \mathbf{b}_k} = e^{i(\omega''-\omega)} \mathbf{b}_5^\dagger \mathbf{b}_k. \end{aligned} \tag{34}$$

As the invariants of $K(4)$ depend only on the generators of $U(4)$ (more precisely on the weight operators of $U(4)$), the first equality in relations (34) implies that all the algebraic invariants of $K(4)$ are invariant under the TR operation, that is, the conditions (31) are all fulfilled.

3 TR symmetry applied on a G-Z ket

3.1 Construction of a real basis

Naturally the question which arises now concerns the values of ω and ω''. More precisely, the Hamiltonian describing the four-bond system we are studying is not (and does not need to be) invariant under the symmetry operations of $U(5)$, (which is the dynamic noninvariance group of the chain of groups (1)).

Under Hermitian conjugation and TR operation, the operators $\mathbf{b}_k^\dagger \mathbf{b}_5$ and $\mathbf{b}_5^\dagger \mathbf{b}_k$ $(k = 1,...,4)$ transform as:

$$\begin{aligned} &(\mathbf{b}_k^\dagger \mathbf{b}_5)^\dagger = \mathbf{b}_5^\dagger \mathbf{b}_k, && \widetilde{\mathbf{b}_k^\dagger \mathbf{b}_5} = e^{i(\omega-\omega'')} \mathbf{b}_k^\dagger \mathbf{b}_5, \\ &(\mathbf{b}_5^\dagger \mathbf{b}_k)^\dagger = \mathbf{b}_k^\dagger \mathbf{b}_5, && \widetilde{\mathbf{b}_5^\dagger \mathbf{b}_k} = e^{i(\omega''-\omega)} \mathbf{b}_5^\dagger \mathbf{b}_k. \end{aligned} \tag{35}$$

Thus, if we search a Hermitian and totally symmetric combination of $\mathbf{b}_5^\dagger \mathbf{b}_k$ and $\mathbf{b}_k^\dagger \mathbf{b}_5$ fulfilling the condition of TR invariance, that is an operator which can appear in the Hamiltonian, we find:

$$\mathbf{O} = \frac{1}{2} \sum_{k=1}^{4} (e^{i\frac{\omega-\omega''}{2}}\ \mathbf{b}_k^\dagger \mathbf{b}_5 + e^{-i\frac{\omega-\omega''}{2}}\ \mathbf{b}_5^\dagger \mathbf{b}_k).$$

As the parameters ω and ω'' are involved in the expression of the operator $\mathbf{O}$, it is necessary to calculate the matrix elements of this operator. We have to reformulate the basis of our system to obtain what is called a real basis [24,25]. Let us first examine the kets of our system. A basis adapted to the chain of groups (1) is given in [7]. It is built from:

$$|n_1\, n_2\, n_3\, n_4\, n_5\rangle = \frac{1}{\sqrt{n_1!\, n_2!\, n_3!\, n_4!\, n_5!}} \times \mathbf{b}_1^{+n_1}\, \mathbf{b}_2^{+n_2}\, \mathbf{b}_3^{+n_3}\, \mathbf{b}_4^{+n_4}\, \mathbf{b}_5^{+n_5} |0\,0\,0\,0\,0\rangle \tag{36}$$

with $N = \sum_{i=1}^{5} n_i$, through an orthogonal transformation (*i.e.* all coefficients are real). From [24,25], we can easily transform the ket (36) in order to obtain a real basis. We briefly recall how to obtain it.

If $|\psi\rangle$ is an element of the basis, then under TR symmetry, we may write:

$$\widetilde{|\psi\rangle} = \boldsymbol{\theta}|\psi\rangle.$$

Then, we can build:

$$|\psi\rangle_{\mathbb{R}} = \lambda|\psi\rangle + \lambda^* \widetilde{|\psi\rangle}$$

which is now invariant under the TR operation for all $\lambda \neq 0$. A convenient choice of λ enables us to normalize:

$${}_{\mathbb{R}}\langle\psi|\psi\rangle_{\mathbb{R}} = 1. \tag{37}$$

In our case, up to a phase factor common to all kets, the real basis is simply deduced from the initial basis as:

$$|n_1 n_2 n_3 n_4 n_5\rangle_{\mathbb{R}} = e^{i\frac{n(\omega-\omega'')}{2}} |n_1 n_2 n_3 n_4 n_5\rangle \tag{38}$$

with $n = n_1 + n_2 + n_3 + n_4$.

3.2 Matrix elements of reorganized generators

With respect to a real basis, the Hamiltonian matrix has real elements [24–26].

A proof can be sketched as follows:

$$\boldsymbol{\theta}|\psi\rangle_{\mathbb{R}} = |\psi\rangle_{\mathbb{R}} \text{ for every real ket } |\psi\rangle_{\mathbb{R}}, \tag{α}$$

$$\mathbb{1}\!\!\mathrm{I}\, |\psi\rangle_{\mathbb{R}} = \boldsymbol{\theta}^\dagger \boldsymbol{\theta} |\psi\rangle_{\mathbb{R}} \overset{(\alpha)}{=} \boldsymbol{\theta}^\dagger |\psi\rangle_{\mathbb{R}} = |\psi\rangle_{\mathbb{R}}, \tag{β}$$

$${}_{\mathbb{R}}\langle\varphi|\psi\rangle_{\mathbb{R}} = {}_{\mathbb{R}}\langle\varphi|(\boldsymbol{\theta}|\psi\rangle_{\mathbb{R}}) = {}_{\mathbb{R}}\langle\psi|(\boldsymbol{\theta}^\dagger|\varphi\rangle_{\mathbb{R}}) \overset{(\beta)}{=} {}_{\mathbb{R}}\langle\psi|\varphi\rangle_{\mathbb{R}} \in \mathbb{R}, \tag{γ}$$

$$\boldsymbol{\theta}(\mathbf{H}|\psi\rangle_{\mathbb{R}}) = \mathbf{H}(\boldsymbol{\theta}|\psi\rangle_{\mathbb{R}}) = \mathbf{H}|\psi\rangle_{\mathbb{R}},\ i.e.\ \mathbf{H}|\psi\rangle_{\mathbb{R}} = |\varphi\rangle_{\mathbb{R}}, \tag{δ}$$

$$H_{ij} = {}_{\mathbb{R}}\langle\psi_i|\mathbf{H}|\psi_j\rangle_{\mathbb{R}} \overset{(\delta)}{=} {}_{\mathbb{R}}\langle\psi_i|\varphi\rangle_{\mathbb{R}} \overset{(\gamma)}{\in} \mathbb{R}.$$

The matrix elements of all the operators built on the generators of the degeneracy group $U(4)$

$$\begin{aligned}&{}_{\mathbb{R}}\langle n_1...n'_i...n'_j...n_5|\mathbf{b}_i^\dagger\mathbf{b}_j|n_1...n_i...n_j...n_5\rangle_{\mathbb{R}}\\&\quad=\sqrt{n_i+1}\sqrt{n_j}\delta_{n'_i,n_i+1}\ \delta_{n'_j,n_j-1}\quad(i,j=1,...,4)\end{aligned}\tag{39}$$

are the same as those in the initial basis.

However, the matrix elements of the generators $\mathbf{b}_i\mathbf{b}_5^\dagger$ and $\mathbf{b}_5^\dagger\mathbf{b}_i$ $(i=1,...,4)$

$$\begin{aligned}&{}_{\mathbb{R}}\langle n_1...n'_i...n_5-1|\mathbf{b}_i^\dagger\mathbf{b}_5|n_1...n_i...n_5\rangle_{\mathbb{R}}\\&\quad=e^{-i\frac{n(\omega-\omega'')}{2}}\sqrt{n_i+1}\sqrt{n_5}\ \delta_{n'_i,n_i+1}\quad(i=1,...,4)\end{aligned}\tag{40}$$

$$\begin{aligned}&{}_{\mathbb{R}}\langle n_1...n'_i...n_5+1|\mathbf{b}_5^\dagger\mathbf{b}_i|n_1...n_i...n_5\rangle_{\mathbb{R}}\\&\quad=e^{i\frac{n(\omega-\omega'')}{2}}\sqrt{n_i}\sqrt{n_5+1}\ \delta_{n'_i,n_i-1}\quad(i=1,...,4)\end{aligned}\tag{41}$$

depend on the parameters ω and ω''.

Thus we can build reorganized generators $(i=1,...,4)$

$$\mathfrak{b}_i^\dagger\mathfrak{b}_5=e^{i\frac{\omega-\omega''}{2}}\mathbf{b}_i^\dagger\mathbf{b}_5,\quad\mathfrak{b}_5^\dagger\mathfrak{b}_i=e^{-i\frac{\omega-\omega''}{2}}\mathbf{b}_5^\dagger\mathbf{b}_i$$

whose matrix elements in the real basis are independent of ω and ω'':

$$\begin{aligned}&{}_{\mathbb{R}}\langle n_1...n'_i...n_5-1|\mathfrak{b}_i^\dagger\mathfrak{b}_5|n_1...n_i...n_5\rangle_{\mathbb{R}}\\&\qquad=\sqrt{n_i+1}\sqrt{n_5}\ \delta_{n'_i,n_i+1}\quad(i=1,...,4)\end{aligned}\tag{42}$$

$$\begin{aligned}&{}_{\mathbb{R}}\langle n_1...n'_i...n_5+1|\mathfrak{b}_5^\dagger\mathfrak{b}_i|n_1...n_i...n_5\rangle_{\mathbb{R}}\\&\qquad=\sqrt{n_i}\sqrt{n_5+1}\ \delta_{n'_i,n_i-1}\quad(i=1,...,4)\end{aligned}\tag{43}$$

Moreover, these matrix elements are exactly the same as those of the generators $\mathbf{b}_i^\dagger\mathbf{b}_5$ and $\mathbf{b}_5^\dagger\mathbf{b}_i$ $(i=1,...,4)$ in the initial basis.

4 Discussion

The conclusion of this analysis is that no new condition appears for the values of ω and ω''. One could set $\omega''=\omega$ for simplicity, but there is no physical or mathematical argument to impose it.

Moreover, choosing $\omega''=\pi/2$ or $\omega''=2\pi$ leads (respectively) to $\tilde{\mathbf{b}}_5^\dagger=i\mathbf{b}_5^\dagger$ or $\tilde{\mathbf{b}}_5^\dagger=\mathbf{b}_5^\dagger$, thus the dynamical realization of that operator depends on the value of ω'' explicitly and can only be more specified by a significant new physical interpretation: $\mathbf{b}_5^\dagger$, $\mathbf{b}_5$ can be interpreted as interaction operators with other degrees of freedom of the molecular system (bending modes, Fermi interaction, rotation, ...), or as interaction operators with an external excitation (electrical field, ...) through the dipole operator [16,27] or even as effective operators taking into account all the interactions of the stretching modes with all other degrees of freedom.

Furthermore, as shown in the simple example ($U(3)\supset U(2)$) of the introduction, R3 is verified while R1 and R2 are not. However, $\omega''=\omega\neq2\pi$ would imply R2, $\omega''=\omega=2\pi$ would imply R1 (and R2) without changing the Hamiltonian matrix.

Finally, another interesting result can be deduced from this paper.

By means of the projection operator (4) $P_\sigma^{(C)}$, and with the physical association of the operators $\mathbf{b}_i$ and $\mathbf{b}_i^\dagger$ $(i=1,...,4)$ to the ith bond in the molecule, it is easy to symmetrize the generators

$$\mathbf{b}_i^\dagger\mathbf{b}_j,\mathfrak{b}_i^\dagger\mathfrak{b}_5,\mathfrak{b}_5^\dagger\mathfrak{b}_i\quad i,j=1,...,4\tag{44}$$

in the symmetry group of the molecule. We may note $\mathbf{Y}_\sigma^{r(C)}$ these symmetrized operators constructed with the reorganized operators (44), where the notation r, C, σ has been explained in the introduction (see equation (2)). It must be noticed that these symmetrized operators $\mathbf{Y}_\sigma^{r(C)}$ are not necessarily Hermitian or TR invariant, but their matrix elements are independent of ω and ω''. Now using the Wigner-Eckart theorem and knowing the matrix elements (39), (42), (43), we can deduce the matrix elements of the operators $\mathbf{Y}_\sigma^{r(C)}$

$$\begin{aligned}&{}_{\mathbb{R}}\langle n'_1n'_2n'_3n'_4n'_5,r'C'\sigma'|\mathbf{Y}_\sigma^{r(C)}|n''_1n''_2n''_3n''_4n''_5,r''C''\sigma''\rangle_{\mathbb{R}}\\&=[C']^{-1/2}F^{(CC'')\sigma'}_{\sigma\sigma''(C')}\\&\times{}_{\mathbb{R}}\langle n'_1n'_2n'_3n'_4n'_5,r'C'||\mathbf{Y}^{r(C)}||n''_1n''_2n''_3n''_4n''_5,r''C''\rangle_{\mathbb{R}}\end{aligned}\tag{45}$$

where ${}_{\mathbb{R}}\langle n'_1n'_2n'_3n'_4n'_5,r'C'||\mathbf{Y}^{r(C)}||n''_1n''_2n''_3n''_4n''_5,r''C''\rangle_{\mathbb{R}}$ denotes the reduced matrix element of $\mathbf{Y}_\sigma^{r(C)}$, and $F^{(CC'')\sigma'}_{\sigma\sigma''(C')}$ represents a tetrahedral coupling coefficient. Of course, this reduced matrix element does not depend on the parameters ω and ω''.

As all physical operators (Hamiltonian, dipole momentum, ...) can be expanded as a sum of product of symmetrized operators $\mathbf{Y}_\sigma^{r(C)}$, using the internal coupling relation, one can easily obtained the reduced matrix element of this product; namely in the case of a product of two operators

see equation (46) below

$$\begin{aligned}&{}_{\mathbb{R}}\langle n'_1n'_2n'_3n'_4n'_5,r'C'||(\mathbf{Y}^{n_1(C_1)}\times\mathbf{Y}^{n_2(C_2)})^{(C_3)}||n_1n_2n_3n_4n_5,rC\rangle_{\mathbb{R}}\\&\quad=\sqrt{[C_3]}(-1)^{C'+C+C_1+C_2}\sum_{n''_1,n''_2,n''_3,n''_4,n''_5,r'',C''}{}_{\mathbb{R}}\langle n'_1n'_2n'_3n'_4n'_5,r'C'||\mathbf{Y}^{n_1(C_1)}||n''_1n''_2n''_3n''_4n''_5,r''C''\rangle_{\mathbb{R}}\\&\qquad\times{}_{\mathbb{R}}\langle n''_1n''_2n''_3n''_4n''_5,r''C''||\mathbf{Y}^{n_2(C_2)}||n_1n_2n_3n_4n_5,rC\rangle_{\mathbb{R}}\begin{Bmatrix}C_1&C_2&C_3\\C&C'&C''\end{Bmatrix}\end{aligned}\tag{46}$$

with $\left\{ \begin{matrix} C_1 & C_2 & C_3 \\ C & C' & C'' \end{matrix} \right\}$ denoted a $6C$ symbol.

Consequently, not only for the Hamiltonian but the matrix elements of any operator built through this formalism do not depend on the parameters ω and ω''.

5 Conclusion

Within a purely algebraic frame, we have determined the general form of the TR operation which is compatible with symmetries of XY_4 molecules. We analyzed the action of TR operation on particular operators which are algebraic invariants of continuous and semi-continuous Lie groups. The basic constraint on the TR operation is the requirement that an irrep must stay stable under the transformation. We have deduced the TR behavior of all the quantities involved in our formalism, not only the generators of the dynamical group $U(5)$, but also of the Boson operators. The transformation laws depend on two parameters which may be fixed by the physical interpretation of each particular model.

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