Symmetry projection, geometry and choice of the basis

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A geometrical point of view of symmetry adapted projection to irreducible subspaces is presented. The projection is applied in two stages. The first step consists in projecting over subspaces spanning irreducible representations (irreps) of the symmetry group, while the second projection is carried out over the irreps of a subgroup defined through a suitable group chain. It is shown that choosing different chains is equivalent to propose alternative bases (passive point of view), while changing the projected function corresponds to the active point of view where the vector to be projected is rotated. Because of the importance of choosing the appropriate basis, an approach based on the concept of invariant operators to obtain the basis for discrete groups is presented. We show that this approach is analogue to the case of continuum groups and it is closely related to the definition of quantum numbers. The importance of these concepts is illustrated through the effect of symmetry breaking. Because of the deep insight into the group theory concepts, we believe the presented viewpoint helps to understand the main ingredients involved in group representation theory using the latest advances in the subject for discrete groups.

Keywords: Symmetry projection; quantum numbers; discrete groups; eigenfunction approach; symmetry breaking

Se presenta un punto de vista geométrico de la proyección a subepacios que portan representaciones irreducibles. La proyección se lleva a cabo en dos pasos. Primero se efectúa la proyección sobre subespacios que portan representaciones irreducibles del grupo de simetría, para posteriormente efectuar la proyección con respecto a un subgrupo definido a través de una cadena apropiada de subgrupos. Se muestra que la selección de diferentes cadenas es equivalente a proponer bases alternativas (punto de vista pasivo), mientras que el cambio de la función a proyectar equivale al punto de vista activo, donde el vector a proyectar es rotado. Debido a la importancia de seleccionar una base apropiada, se presenta un método de proyección basado en el concepto de operadores invariantes en el caso de grupos discretos. Se muestra que este método es análogo al caso de grupos continuos e intimamente relacionado con el mismo concepto de número cuántico. La importancia de estos conceptos es ilustrada mediante el concepto de rompimiento de simetría. Creemos que dada la profundidad del marco teórico presentado,este material será de gran ayuda en la comprensión de los conceptos de teroría de representaciones de grupos, en donde se ha incluido la esencia de los últimos métodos de proyección desarrollados para grupos discretos.

Descriptores: Proyección de simetría; números cuánticos; grupos discretos; método de funciones propias; rompimiento de simetría.

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1. Introduction

Symmetry plays a pervasive role in chemistry and physics. In chemistry the application of symmetry to molecular orbital theory, valence bond theory, crystal field theory, molecular chemical reactions, and ro-vibrational spectroscopy; for instance, represents the classical applications of group representation theory to this field [1–9]. In physics, on the other hand, group theory is the basic language in elementary particle physics, nuclear, molecular, atomic and space-time physics, for instance. It is not possible to conceive modern physics without group representation theory [10–16].

The advantage of approaching the systems from the symmetry point of view is twofold. On one hand it provides a way for a deep understanding of the concept of quantum numbers, but on the other hand it also allows a remarkable simplification in solving the Schrödinger equation as well as in establishing the selection rules. The basic idea to incorporate the systems symmetry consists in identifying invariant subspaces of minimum dimension labeled with irreducible representations (irreps) of the symmetry group. This goal is achieved on the basis of the orthogonality theorems, derived from the Schur's lemmas [14]. However, although the fundamental concepts involved in group representation theory are widely discussed in textbooks, recent advances related with projection techniques in discrete groups together with a geometrical point of view have not been considered as it should be. Here we take advantage of a geometrical analogy emphasizing the importance of using a subgroup to label the states, a standard approach in establishing the basis in continuous groups but not weighted up properly concerning discrete groups. The group theoretical concepts presented in this work are concerned with discrete finite groups, which emerge in natural form in the study of molecules, crystals and identical particles. The geometrical viewpoint however is also valid for continuous groups since in both cases the projection can be carried out by diagonalizing the matrix representation of invariant operators. The search for invariant operators is closely related to the establishment of a set of commuting operators to provide a complete labeling scheme for the states. In this contribution we show that the concept of quantum numbers leads to a projection technique known as the eigenfunction method in discrete groups developed by Chen [17]. This approach turns out to be the most efficient approach to carry out a projection and consequently to establish a basis since it forms part of a well established machinery in quantum mechanics consisting in diagonalizing matrices.

Symmetry may be considered from a geometrical point of view (obvious symmetry), but also from a dynamical perspective. In the latter case the concept of dynamical group emerges as an algebraic structure suitable to model the interactions [22]. In this way every dynamical variable is expanded in terms of the generators of the dynamical algebra. In particular the Hamiltonian belongs to this case and the basis to obtain its representation matrix is crucial. Several basis may be proposed, which may be suitable to be interpreted geometrically. In this contribution we emphasize this point of view taking discrete groups as a tool to achieve this goal.

This paper is organized as follows. A summary of the basic concepts of representation theory is presented in §2, emphasizing the geometrical interpretation of the projection of symmetry adapted functions. §3 is devoted to work out a simple example in order to illustrate the concepts of active and passive viewpoint. §4 is devoted to present the connection between the quantum numbers and the irreducible representations of a group. In addition it is shown that the eigenfunction approach emerges in natural form from this concept. In §5 we present the importance of choosing the appropriate basis in symmetry breaking phenomena. Finally, in §6 the summary and conclusions are presented.

2. Fundamental concepts of group representation theory

A general quantum mechanical problem consists in solving the Schrödinger equation. In particular for a time-independent Hamiltonian, a basis is expected to be proposed to obtain the Hamiltonian representation matrix and, in this way, proceed to its diagonalization. The basis can be rearranged in a special way in order to carry suitable labels known as *good* quantum numbers. This is precisely the role of group representation theory as we next explain.

We first identify the symmetry group G of the system, which is defined as the maximum set of transformations that leaves the Hamiltonian $\hat{H}$ invariant [11]:

$$[\hat{O}_R, \hat{H}] = 0; \quad \forall R \in G. \tag{1}$$

We then proceed to identify an invariant n-dimensional subspace of functions $\mathcal{L}_n = \{|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_n\rangle\}$, which transforms into itself under any operator $\hat{\mathcal{O}}_R$ associated with the element R in the symmetry group G. The maximum dimension n corresponds to the order $|G|$ of the symmetry group and is less than the dimension of the total space carrying the physical manifold of the system. In this contribution we shall consider scalar functions only. In a precise mathematical language we have [14]

$$\hat{\mathcal{O}}_R |\phi_i\rangle = \sum_{i=1}^{n} \Delta^{(\text{red})}_{ji}(R) \ |\phi_j\rangle ; \quad R \in G, \tag{2}$$

where the set of matrices $\Delta^{(\text{red})}(R), \forall R \in G$, constitutes a reducible matrix representation of G. Group representation theory provides the way to identify invariant subspaces $\mathcal{L}_{n_\Gamma}$, with $n_\Gamma < n$ which transforms into themselves. The new functions belonging to $\mathcal{L}_{n_\Gamma}$ satisfy the invariance condition

$$\hat{\mathcal{O}}_R \left|{}_q\psi^{(\Gamma)}_\gamma\right\rangle = \sum_{i=1}^{n_\Gamma} D^{(\Gamma)}_{\gamma'\gamma}(R) \left|{}_q\psi^{(\Gamma)}_{\gamma'}\right\rangle ; \quad R \in G, \tag{3}$$

where $\mathbf{D}^{(\Gamma)}(R)$ is a matrix irreducible representation of G and $q = 1, \ldots a_\Gamma$ is a multiplicity index that takes into account the repetition of irreps. The new kets $|{}_q\psi^{(\Gamma)}_\gamma\rangle$ are given in terms of linear combinations of the original ones

$$\left|{}_q\psi^{(\Gamma)}_{\gamma'}\right\rangle = \sum_{i}^{n} S_{i;q\Gamma\gamma} \, |\phi_i\rangle \, , \tag{4}$$

where the matrix $\mathbf{S} = ||S_{i;q\Gamma\gamma}|| = ||\langle\phi_i|{}_q\psi^{(\Gamma)}_{\gamma'}\rangle||$ defines the change of basis that reduces the original representation $\mathbf{\Delta}^{(\text{red})}(R)$ into a block diagonal form expressed as a direct sum of irreps

$$\mathbf{S}^{-1}\mathbf{\Delta}^{(\text{red})}(R)\mathbf{S} = \sum_{\Gamma} \oplus \, a_\Gamma \, \mathbf{D}^{(\Gamma)}(R), \tag{5}$$

where the symbol $\oplus$ means direct sum of matrices [14], and a_Γ is a multiplicity factor that indicates the number of times that the Γ-th irrep appears in the reduction. In Eq. (5) the matrix $\Delta^{(\text{red})}(R)$ is the only known variable, the rest of the terms have to be determined. The integer numbers a_Γ are calculated through the well known formula involving the characters $\chi(R)$ [14]:

$$a_\Gamma = \frac{1}{|G|} \sum_{R \in G}^{|G|} \chi^{(\Gamma)*}(R) \, \chi^{(\text{red})}(R), \tag{6}$$

while the matrix $\mathbf{S}$ is obtained by projecting one or more kets $|\phi_i\rangle$ as we shortly explain. But before proceeding with this task, we should remark that any vector $|\Psi\rangle$ can be expanded in terms of the basis $\mathcal{L}_n = \{\left|{}_q\psi^{(\Gamma)}_{\gamma'}\right\rangle\}$, which means that [11]

$$|\Psi\rangle = \sum_{\Gamma}^{|K|} \sum_{\gamma=1}^{n_\Gamma} \sum_{q}^{a_\Gamma} C_{q\Gamma\gamma} \left|{}_q\psi^{(\Gamma)}_{\gamma'}\right\rangle . \tag{7}$$

This equation corresponds to the expansion of a vector $|\Psi\rangle$ in terms of the basis $\{\left|{}_q\psi^{(\Gamma)}_{\gamma'}\right\rangle\}$, with coordinates $C_{q\Gamma\gamma}$ given by de internal product

$$C_{q\Gamma\gamma} \equiv \left\langle {}_q\psi^{(\Gamma)}_{\gamma} \,\middle|\, \Psi \right\rangle , \tag{8}$$

where we have assumed the orthonormality property

$$\left\langle {}_{q'}\psi^{(\Gamma')}_{\gamma'} \,\middle|\, {}_q\psi^{(\Gamma)}_{\gamma} \right\rangle = \delta_{qq'}\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'}. \tag{9}$$

If, in addition, the vector $|\Psi\rangle$ to be projected has been normalized, then $\sum_{\Gamma,\gamma,q} |C_{q\Gamma\gamma}|^2 = 1$. The expansion (7) justifies to depict the projection as in Fig. 1. In general, we have an hyper-space without the possibility of being represented

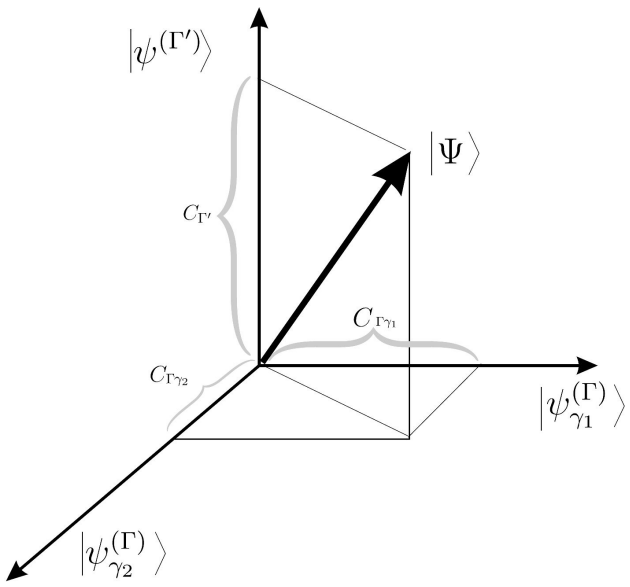

FIGURE 1. Graphical representation of the expansion (7).

in graphical form. To avoid this problem we shall discuss cases involving, at most, three irreps.

The question which arises is concerned with the projection approach to satisfy (9). Here we shall consider $a_\Gamma = 0, 1$ in (5), because in such cases only the group characters are needed. Otherwise more advanced methods would be necessary [17–20], as will be discussed in Section 4. Hence, from now on we shall take $q = 0, 1$ and consequently this index will be omitted. We should stress however that the basic ideas and the analysis we present are equally valid to the general case $a_\Gamma \geq 2$.

The projection operator, involving characters only, is given by [11, 14]

$$\hat{\mathcal{P}}^{(\Gamma)} = \frac{n_\Gamma}{|G|} \sum_{R\in G}^{|G|} \chi^{(\Gamma)*}(R)\, \hat{\mathcal{O}}_R, \tag{10}$$

whose action over any vector $|\Psi\rangle$ leads to a vector spanning the Γ-th irrep

$$\hat{\mathcal{P}}^{(\Gamma)}\,|\Psi\rangle \propto \left|\zeta^{(\Gamma)}\right\rangle, \tag{11}$$

where we consider normalized projected functions, which explains the proportionality sign. As we note this projection does not distinguish components of the Γ-th irrep. Hence it is compulsory to obtain both components in order to have a complete description. This goal may be achieved with the projection operator involving an explicit matrix representations [14]. However it is possible, as an alternative, to extract the components using the characters of a subgroup $H \subset G$. The first step consists in choosing an appropriate group H as we next explain.

Given an irrep $\mathbf{D}^{(\Gamma)}(G)$ of the group G, the set of matrices $\{\mathbf{D}^{(\Gamma)}(h);\ h \in H\}$ constitutes a representation space of H. This representation is in general reducible and consequently it can be reduced in similar form to (5):

$$\mathbf{Q}^{-1}\mathbf{D}^{(\Gamma)}(h)\mathbf{Q} = \sum_\gamma \oplus\, a_\gamma\, \mathbf{D}^{(\gamma)}(h); \quad h \in H, \tag{12}$$

where we have denoted with γ the irreps of the subgroup H. It is said that if $a_\gamma = 0, 1$ then the subgroup is appropriate (canonical reduction), for in this case the components of the irrep Γ can be distinguished. In Eq. (12) we only need to calculate a_γ. For our purposes it is not necessary to obtain the $\mathbf{Q}$ matrix defining the change of basis. Associated with H we have the projection operator

$$\hat{\mathcal{P}}^{(\gamma)} = \frac{n_\gamma}{|H|} \sum_{h\in H}^{|H|} \chi^{(\gamma)*}(h)\, \hat{\mathcal{O}}_h. \tag{13}$$

The symmetry adapted functions $\psi^{(\Gamma)}_\gamma(\mathbf{x})$ are then obtained through the double projection

$$\hat{\mathcal{P}}^{(\gamma)}\hat{\mathcal{P}}^{(\Gamma)}\,|\Psi\rangle \propto \left|\psi^{(\Gamma)}_{\gamma'}\right\rangle, \tag{14}$$

where again the proportionality sign means that after the projection the functions are understood to be normalized. Here we should stress, as it can be proved, that the operators involved in (14) commute:

$$[\hat{\mathcal{P}}^{(\gamma)}, \hat{\mathcal{P}}^{(\Gamma)}] = 0; \tag{15}$$

and consequently, from the algebraic point of view, the order of these operators may be inverted. However the order stated in expression (14) is more convenient from the efficiency point of view as well as from a geometrical perspective, as it is next explained.

From the geometrical point of view, the first projection in (14) is equivalent to consider the expansion of the vector $|\Psi\rangle$ in the basis $\{|\psi^\Gamma\rangle\}$:

$$|\Psi\rangle = \sum_\Gamma B_\Gamma \left|\psi^\Gamma\right\rangle, \tag{16}$$

with normalized kets given by

$$\left|\psi^\Gamma\right\rangle = \sum_\gamma N_{\Gamma\gamma} \left|\psi^{(\Gamma)}_\gamma\right\rangle. \tag{17}$$

In this way the basis involved in the expansion is orthonormal

$$\langle\psi^{(\Gamma')}, \psi^{(\Gamma)}\rangle = \delta_{\Gamma\Gamma'}. \tag{18}$$

Equation (17) provides the second expansion of $|\psi^\Gamma\rangle$ in terms of the basis $|\psi^{(\Gamma)}_\gamma\rangle$, whose components are obtained through

$$\langle\psi^{(\Gamma)}_\gamma, \psi^{(\Gamma)}\rangle = N_{\Gamma\gamma}. \tag{19}$$

These successive projections are illustrated in Fig. 2. The relation between the coefficients $C_{\Gamma\gamma}$ in (7), for $q = 1$, is obtained by the substitution of (17) into (16), yielding the following result

$$C_{\Gamma\gamma} = B_\Gamma N_{\Gamma\gamma};\ \ \langle\Psi^\Gamma_\gamma|\Psi\rangle = \langle\Psi^\Gamma_\gamma|\Psi^\Gamma\rangle\langle\Psi^\Gamma|\Psi\rangle, \tag{20}$$

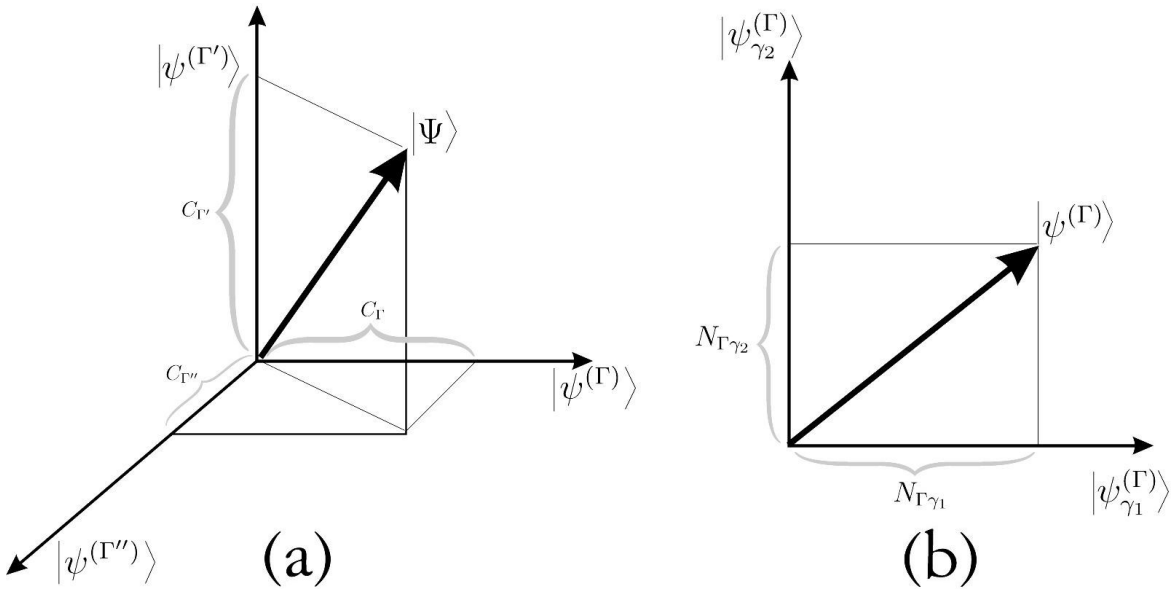

FIGURE 2. (a) Projection of the state $|\Psi\rangle$ over the space of kets $|\psi^{\Gamma}\rangle$ spanning irreps of the group G, (b) Projection of the component $|\psi^{\Gamma}\rangle$ over the space of kets $|\psi^{\Gamma}_{\gamma}\rangle$ carrying irreps of the subgroup H

provided the normalization constraints

$$\sum_{\Gamma}|B_{\Gamma}|^2=\sum_{\Gamma\gamma}|C_{\Gamma\gamma}|^2=\sum_{\gamma}|N_{\Gamma\gamma}|^2=1. \tag{21}$$

The selection of the subgroup H is not unique. In general several possibilities $G\supset H_\alpha$ are available, and each chain defines a reference frame, as we illustrate in Fig. 3. To point out the idea, let $G\supset K$ be a second group chain, besides $G\supset H$, which in turn defines the new expansion

$$|\psi^{\Gamma}\rangle=\sum_{\beta}A_{\Gamma\beta}\left|\zeta^{(\Gamma)}_{\beta}\right\rangle, \tag{22}$$

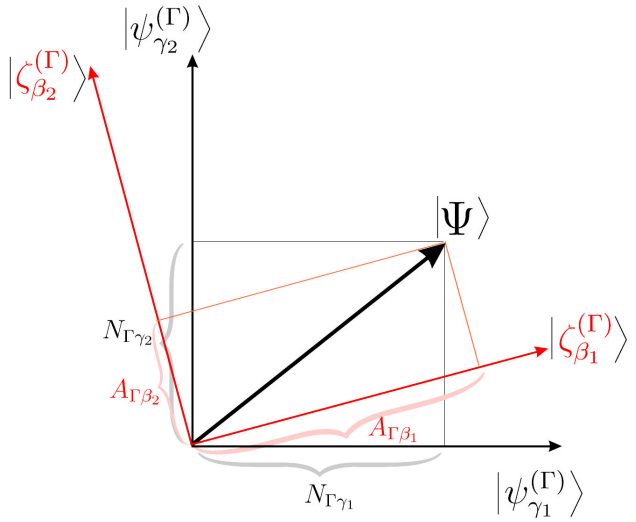

FIGURE 3. Each chain $G\supset H_\alpha$ defines a reference frame in the passive picture in such a way that the bases are connected through a rotation.

where now β labels the K subgroup irreps. From this expression and (17), we obtain the connection between the coordinates $N_{\Gamma\gamma}$ and $A_{\beta\Gamma}$

$$\sum_{\gamma}N_{\Gamma\gamma}M^{\Gamma}_{\beta\gamma}=A_{\Gamma\beta}, \tag{23}$$

where $M^{\Gamma}_{\beta\gamma}$ is the overlap matrix between the bases:

$$M^{\Gamma}_{\beta\gamma}=\langle\zeta^{\Gamma}_{\beta},\psi^{\Gamma}_{\alpha}\rangle. \tag{24}$$

Geometrically this is the rotation matrix that establishes the connection between the bases. We now proceed to show an example involving every concept before presenting an advanced projection method.

3. An illustrative example: H_3^+

To illustrate the concepts previously presented, we next consider as an example the projection of the s-orbitals of the hydrogen atoms in the molecule H_3^+. Here our representation space is $\mathcal{L}_3=\{|s_1\rangle,|s_2\rangle,|s_3\rangle\}$, which will be considered to satisfy the ortho-normality condition $\langle s_i\mid s_j\rangle=\delta_{ij}$. This assumption is chosen in order to simplify the discussion, but in any case it is possible to construct a set of localized orthonormal functions isomorphic to the s-orbitals with the property that both sets coincide in the null overlap limit [21].

This molecule is invariant under the $\mathcal{D}_{3h}$ group. However, since the s-orbitals are invariant under the horizontal reflection we can consider the subgroup $\mathcal{D}_3$ as the symmetry group of the system. In Fig. 4 we present the diagram of symmetry elements embedded in the reference frame of the molecule, while in Table 1 the $\mathcal{D}_3$ character table is given. In this table we have included the characters associated with

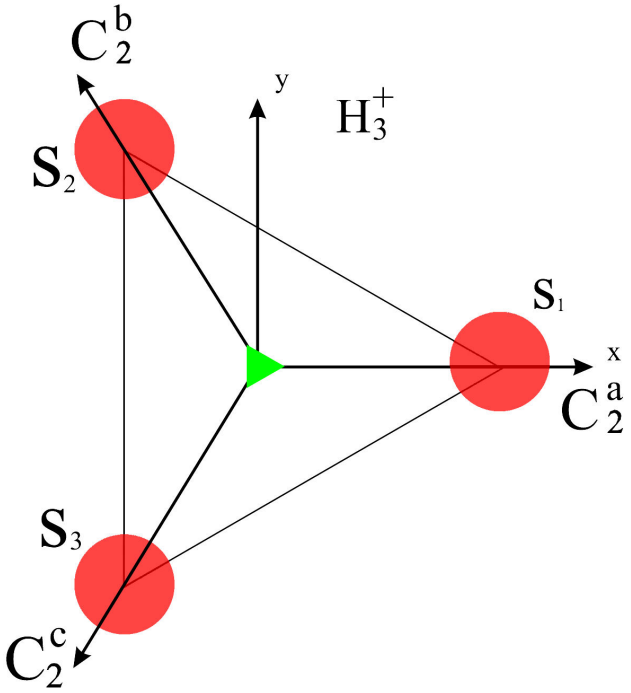

FIGURE 4. Molecular system H_3^+ embedded in the $\mathcal{D}_3$ diagram of symmetry elements.

TABLE I. Character table of the $\mathcal{D}_3$ group, as well as the characters of the reducible representation generated by the $\mathcal{L}_3$ space of s-orbitals.

D_3	E;	C_3, C_3^2;	C_2^a, C_2^b, C_2^c
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$\Gamma^{(\text{red})}$	3	0	1

the reducible representation generated by the space $\mathcal{L}_3$. Using (6) we find

$$\Gamma^{(\text{red})} = A_1 \oplus E. \tag{25}$$

The projection operator (10) may be applied to any function of the set $\mathcal{L}_3$, s_1-orbital for instance, and the action of the operator can be interpreted as the dot product of vectors in the $|G|$ dimensional space (this explains the action of projection)

$$\mathcal{P}^{(\Gamma)} s_1 = \frac{n_\Gamma}{|G|} \mathbf{c}_\Gamma \cdot \mathbf{f}_1, \tag{26}$$

where

$$\mathbf{c}_\Gamma = \Big(\chi^{(\Gamma)*}(E), \chi^{(\Gamma)*}(C_3), \chi^{(\Gamma)*}(C_3^2), \chi^{(\Gamma)*}(C_2^a), \chi^{(\Gamma)*}(C_2^b), \chi^{(\Gamma)*}(C_2^c)\Big), \tag{27}$$

$$\mathbf{f}_1 = \Big(\hat{\mathcal{O}}_E |s_1\rangle, \hat{\mathcal{O}}_{C_3} |s_1\rangle, \hat{\mathcal{O}}_{C_3^2} |s_1\rangle, \hat{\mathcal{O}}_{C_2^a} |s_1\rangle, \hat{\mathcal{O}}_{C_2^b} |s_1\rangle, \hat{\mathcal{O}}_{C_2^c} |s_1\rangle\Big) = \Big(|s_1\rangle, |s_2\rangle, |s_3\rangle, |s_1\rangle, |s_3\rangle, |s_2\rangle\Big). \tag{28}$$

TABLE II. Vectors involved in the projection (26), considering the three s-functions.

	$\mathbf{c}_{A_1}$	$\mathbf{c}_E$	$\mathbf{f}_1$	$\mathbf{f}_2$	$\mathbf{f}_3$
R	$\chi^{A_1*}(R)$	$\chi^{E*}(R)$	$\hat{\mathcal{O}}_R \|s_1\rangle$	$\hat{\mathcal{O}}_R \|s_2\rangle$	$\hat{\mathcal{O}}_R \|s_3\rangle$
E	1	2	$\|s_1\rangle$	$\|s_2\rangle$	$\|s_3\rangle$
C_3	1	-1	$\|s_2\rangle$	$\|s_3\rangle$	$\|s_1\rangle$
C_3^2	1	-1	$\|s_3\rangle$	$\|s_1\rangle$	$\|s_2\rangle$
C_2^a	1	0	$\|s_1\rangle$	$\|s_3\rangle$	$\|s_2\rangle$
C_2^b	1	0	$\|s_3\rangle$	$\|s_2\rangle$	$\|s_1\rangle$
C_2^c	1	0	$\|s_2\rangle$	$\|s_1\rangle$	$\|s_3\rangle$

Because of the linear dependence of the functions, the projected space turns out to be three-dimensional. Only for the regular representation the $|G|$-dimension corresponds to the space involved in the projection [14]. A convenient manner to carry out the projection is through the construction of Table II. Columns 2 and 3 correspond to the possible vectors $\mathbf{c}_\Gamma$, while the last three columns are associated with the kets $|s_i\rangle$, represented by the vectors $\mathbf{f}_i$. The projection of the ket $|s_1\rangle$ is obtained in a straightforward way

$$\hat{\mathcal{P}}^{(A_1)} |s_1\rangle \approx \left|\psi^{(A_1)}\right\rangle = \frac{1}{\sqrt{3}}(|s_1\rangle + |s_2\rangle + |s_3\rangle), \tag{29}$$

$$\hat{\mathcal{P}}^{(E)} |s_1\rangle \approx \left|\psi^{(E)}\right\rangle = \frac{1}{\sqrt{6}}(2|s_1\rangle - |s_2\rangle - |s_3\rangle). \tag{30}$$

In our geometric picture, this means that the vector $|s_1\rangle$ in the basis $\{|\psi^{(A_1)}\rangle, |\psi^{(E)}\rangle\}$ takes the form

$$|s_1\rangle = B_{A_1} \left|\psi^{(A_1)}\right\rangle + B_E \left|\psi^{(E)}\right\rangle, \tag{31}$$

with coordinates

$$B_{A_1} = \left\langle \psi^{(A_1)} \,\middle|\, s_1 \right\rangle = \frac{1}{\sqrt{3}};$$
$$B_E = \left\langle \psi^{(E)} \,\middle|\, s_1 \right\rangle = \frac{2}{\sqrt{6}}. \tag{32}$$

This result is illustrated in Fig. 5. We now have to establish a chain of groups to carry out the second projection. This fixes the reference frame for the components of the two-dimensional irrep. We propose the chain

$$\mathcal{D}_3 \supset \mathcal{C}_2^a; \quad \text{with } \mathcal{C}_2^a = \{E, C_2^a\}. \tag{33}$$

In Table III it is shown that the chain (33) is indeed canonical.

TABLE III. Reduction of the irreps of $\mathcal{D}_3$ to the $\mathcal{C}_2^a$ subgroup.

$\mathcal{C}_2^a$	E	C_2^a	
A	1	1	
B	1	-1	
A_1	1	1	A
A_2	1	-1	A
E	2	0	$A \oplus B$

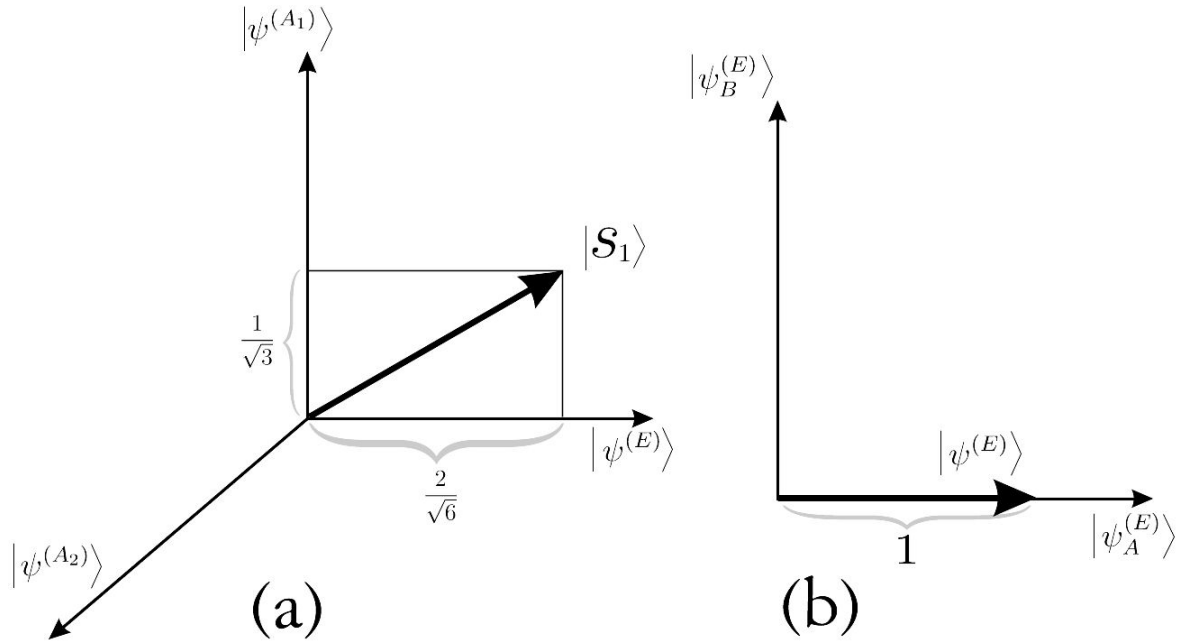

FIGURE 5. Graphical representation of: (a) the expansion (31) over the group and (b) the expansion (34) over the subgroup.

We now proceed to project the function $|\psi^{(E)}\rangle$ to the irreps A and B of the subgroup $\mathcal{C}_2^a$. The result is

$$\hat{\mathcal{P}}^{(A)}\left|\psi^{(E)}\right\rangle \approx \left|\psi^{(E)}\right\rangle + \hat{\mathcal{O}}_{C_2^a}\left|\psi^{(E)}\right\rangle \approx \left|\psi^{(E)}\right\rangle \equiv \left|\psi_A^{(E)}\right\rangle \quad (34)$$

$$\hat{\mathcal{P}}^{(B)}\left|\psi^{(E)}\right\rangle \approx \left|\psi^{(E)}\right\rangle - \hat{\mathcal{O}}_{C_2^a}\left|\psi^{(E)}\right\rangle = 0, \quad (35)$$

which means that the vector $|\psi^{(E)}\rangle$ is located along the $|\psi_A^{(E)}\rangle$ axis, as it is shown in Fig. 5. This result represents an incomplete task since we are unable to obtain the complete set of functions. To overcome this problem we may either rotate the vector or the reference frame. The former is achieved by selecting another function to be projected. The latter by selecting another chain. We next consider both possibilities.

Rotating the vector: active picture

Let us now select the ket $|s_2\rangle$ to be projected. Following the previous approach, from Table II we obtain the projected states

$$\hat{\mathcal{P}}^{(A_1)}|s_2\rangle \approx \left|\psi^{(A_1)}\right\rangle = \frac{1}{\sqrt{3}}(|s_1\rangle + |s_2\rangle + |s_3\rangle), \quad (36)$$

$$\hat{\mathcal{P}}^{(E)}|s_2\rangle \approx \left|\zeta^{(E)}\right\rangle = \frac{1}{\sqrt{6}}(2|s_2\rangle - |s_3\rangle - |s_1\rangle). \quad (37)$$

Now we proceed with the projection over the subgroup irreps to obtain

$$\hat{\mathcal{P}}^{(A)}\left|\zeta^{(E)}\right\rangle \approx \left|\zeta^{(E)}\right\rangle + \hat{\mathcal{O}}_{C_2^a}\left|\zeta^{(E)}\right\rangle \approx \left|\psi_A^{(E)}\right\rangle = \frac{1}{\sqrt{6}}(2|s_1\rangle - |s_2\rangle - |s_3\rangle) \quad (38)$$

$$\hat{\mathcal{P}}^{(B)}\left|\zeta^{(E)}\right\rangle \approx \left|\zeta^{(E)}\right\rangle - \hat{\mathcal{O}}_{C_2^a}\left|\zeta^{(E)}\right\rangle \approx \left|\psi_B^{(E)}\right\rangle = \frac{1}{\sqrt{2}}(|s_2\rangle - |s_3\rangle). \quad (39)$$

Here we have selected the following phase

$$\left\langle\psi_B^{(E)}\right|\widehat{C}_3\left|\psi_A^{(E)}\right\rangle = \frac{\sqrt{3}}{2} \quad (40)$$

for the E irrep . The components for the expansion

$$|s_2\rangle = B_{A_1}\left|\psi^{(A_1)}\right\rangle + B_E\left|\zeta^{(E)}\right\rangle, \quad (41)$$

are again given by

$$B_{A_1} = \left\langle\psi^{(A_1)}\,\middle|\,s_2\right\rangle = \frac{1}{\sqrt{3}};$$
$$B_E = \left\langle\zeta^{(E)}\,\middle|\,s_2\right\rangle = \frac{2}{\sqrt{6}}, \quad (42)$$

while for the projected function

$$\left|\zeta^{(E)}\right\rangle = N_{EA}\left|\psi_A^{(E)}\right\rangle + N_{EB}\left|\psi_B^{(E)}\right\rangle, \quad (43)$$

we have

$$N_{EA} = \left\langle\psi_A^{(E)}\,\middle|\,\zeta^{(E)}\right\rangle = -\frac{1}{2};$$
$$N_{EB} = \left\langle\psi_B^{(E)}\,\middle|\,\zeta^{(E)}\right\rangle = \frac{\sqrt{3}}{2}. \quad (44)$$

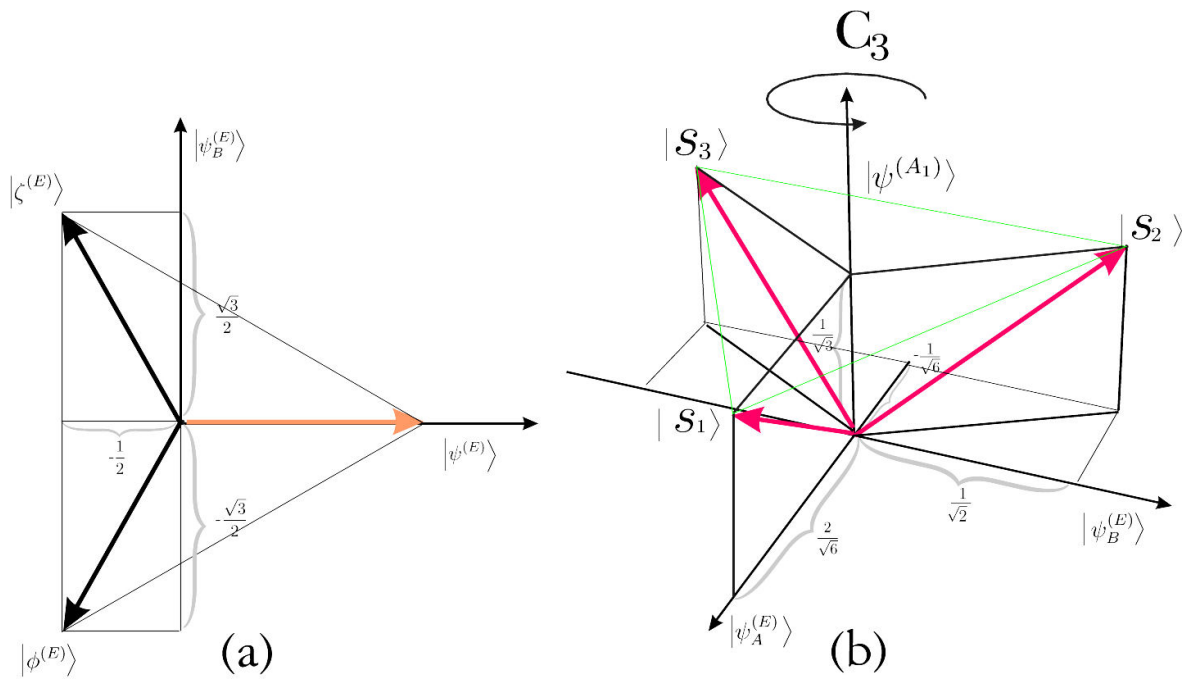

FIGURE 6. Graphical representation of the different choices for the projected vector. In (a) the three projected functions vectors over the E irrep are projected over the $\mathcal{C}_2^a$ irreps. In (b) the projection is over viewed in a three dimensional scheme.

These numbers are the components of the new vector $\left|\zeta^{(E)}\right\rangle$ in the same reference system. The vector has been rotated. The angle is obtained through the internal product

$$(\zeta^{(E)}, \psi^{(E)}) = -\frac{1}{2} = \cos\theta; \quad \theta = \frac{2\pi}{3}, \tag{45}$$

This situation is depicted in Fig. 6.

We may have been chosen $|s_3\rangle$ as the alternative vector. In that case the result for the expansion (16) is

$$|s_3\rangle = \frac{1}{\sqrt{3}}\left|\psi^{(A_1)}\right\rangle + \frac{2}{\sqrt{6}}\left|\phi^{(E)}\right\rangle, \tag{46}$$

where

$$\left|\phi^{(E)}\right\rangle = \frac{1}{\sqrt{6}}(2\,|s_3\rangle - |s_2\rangle - |s_1\rangle). \tag{47}$$

The second projection over $\left|\phi^{(E)}\right\rangle$ provides the full projected states

$$\left|\phi^{(E)}\right\rangle = -\frac{1}{\sqrt{2}}\left|\psi_A^{(E)}\right\rangle - \frac{\sqrt{3}}{2}\left|\psi_B^{(E)}\right\rangle. \tag{48}$$

We may now represent the projection in the 3-dimensional space $A \oplus E_A \oplus E_B$ through the relation (20). The states turn out to have the following components in the basis $\{|\psi_A^{(E)}\rangle, |\psi_B^{(E)}\rangle, |\psi_A^{(A_1)}\rangle\}$:

$$|s_1\rangle : \left(\frac{2}{\sqrt{6}}, 0, \frac{1}{\sqrt{3}}\right), \tag{49}$$

$$|s_2\rangle : \left(-\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{3}}\right), \tag{50}$$

$$|s_2\rangle : \left(-\frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{3}}\right). \tag{51}$$

These three possible projections are depicted in Fig. 6. We remark that these vectors are connected through a rotation C_3 in both Fig. 4 and Fig. 6b. While in the former we have the physical Euclidean space with the rotation axis located along the z-direction, in the latter we have a space of functions with the corresponding rotation axis located along the $\left|\psi^{(A_1)}\right\rangle$ direction, as it should be since this axis is invariant.

The presented analysis corresponds when the projected vectors are varied, but another possibility consists in changing the basis vectors as we next describe. In this way we are also able to obtain the complete projected basis.

Rotating the reference frame: passive picture

As previously mentioned, an alternative way to obtain the needed component of the E irrep is by rotating the reference frame. In such case we obtain another functions $\left|\eta_{A'}^{(E)}\right\rangle$ and $\left|\eta_{B'}^{(E)}\right\rangle$ spanning irreps of the new subgroup. Consider for instance the new chain

$$\mathcal{D}_3 \supset \mathcal{C}_2^b; \;\text{ with }\; \mathcal{C}_2^b = \{E, C_2^b\}, \tag{52}$$

keeping the ket $|s_1\rangle$ as the original vector $|\Psi\rangle$. The first expansion (16) takes the same form (31) with the same components (32). The difference appears when the new subgroup is considered. In this case the projected function $\left|\psi^{(E)}\right\rangle$ takes the form

$$\left|\psi^{(E)}\right\rangle = D_{EA'}\left|\eta_{A'}^{(E)}\right\rangle + D_{EB'}\left|\eta_{B'}^{(E)}\right\rangle, \tag{53}$$

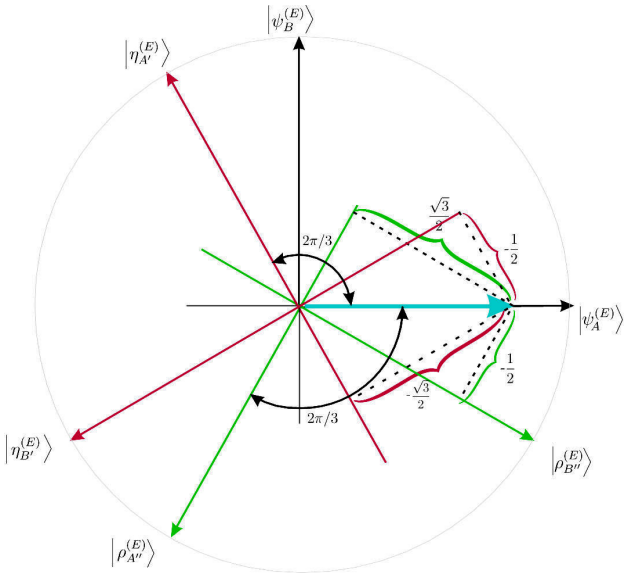

FIGURE 7. Passive picture corresponding the selection of the chains (52) and (58).

where the new functions are obtained by the projection over the irreps of the new subgroup $\mathcal{C}_2^b$:

$$\hat{\mathcal{P}}^{(A')}\left|\psi^{(E)}\right\rangle \approx \left|\psi^{(E)}\right\rangle + \hat{\mathcal{O}}_{C_2^b}\left|\psi^{(E)}\right\rangle \approx \left|\eta_{A'}^{(E)}\right\rangle = \frac{1}{\sqrt{6}}(2\,|s_2\rangle - |s_3\rangle - |s_1\rangle), \tag{54}$$

$$\hat{\mathcal{P}}^{(B')}\left|\psi^{(E)}\right\rangle \approx \left|\psi^{(E)}\right\rangle - \hat{\mathcal{O}}_{C_2^b}\left|\psi^{(E)}\right\rangle \approx \left|\eta_{B'}^{(E)}\right\rangle = \frac{1}{\sqrt{2}}(|s_3\rangle - |s_1\rangle). \tag{55}$$

Note that for convenience we denoted as A' and B' the irreps of the group $\mathcal{C}_2^b$. The components involved in the expansion (53) are given by

$$D_{EA'} = \left\langle \eta_{A'}^{(E)} \,\middle|\, \psi^{(E)} \right\rangle = -\frac{1}{2};$$

$$D_{EB'} = \left\langle \eta_{B'}^{(E)} \,\middle|\, \psi^{(E)} \right\rangle = -\frac{\sqrt{3}}{2}. \tag{56}$$

The geometrical representation is depicted in Fig. 7. We have thus changed the reference frame (the basis states) in order to obtain a non vanishing contribution for both components.

A point to remark is concerned with the phases involved in the two-dimensional representation E. The relative phases between (54) and (55) were fixed in accordance with the convention (40). This correlation must be carried out in order to have consistence with the reference frames. More specifically, a change in sign is equivalent to move from a right handed to left handed reference frame.

The connection between the reference frames in Fig. 7 is given by the rotation matrix (24). Explicitly the matrix is given by

$$\mathbf{M} = \left|\left|(\eta_{\beta'}^{(E)}, \psi_{\gamma}^{(E)})\right|\right| = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}. \end{pmatrix}, \tag{57}$$

which corresponds to a rotation of $-2\pi/3$ rad.

A third selection of reference frame is provided by the chain

$$\mathcal{D}_3 \supset \mathcal{C}_2^c; \;\; \text{with} \;\; \mathcal{C}_2^c = \{E, C_2^c\}. \tag{58}$$

Again, keeping the ket $|s_1\rangle$ as the original vector $|\Psi\rangle$ the first expansion (16) takes the same form (31) with the same components (32). Now the projected function $\left|\psi^{(E)}\right\rangle$ takes the form

$$\left|\psi^{(E)}\right\rangle = D_{EA''}\,\left|\rho_{A''}^{(E)}\right\rangle + D_{EB''}\left|\rho_{B''}^{(E)}\right\rangle. \tag{59}$$

In the second projection the new projected functions are:

$$\hat{\mathcal{P}}^{(A'')}\left|\psi^{(E)}\right\rangle \approx \left|\psi^{(E)}\right\rangle + \hat{\mathcal{O}}_{C_2^c}\left|\psi^{(E)}\right\rangle \approx \left|\rho_{A''}^{(E)}\right\rangle = \frac{1}{\sqrt{6}}(2\,|s_3\rangle - |s_1\rangle - |s_2\rangle), \tag{60}$$

$$\hat{\mathcal{P}}^{(B')}\left|\psi^{(E)}\right\rangle \approx \left|\psi^{(E)}\right\rangle - \hat{\mathcal{O}}_{C_2^c}\left|\psi^{(E)}\right\rangle \approx \left|\rho_{B''}^{(E)}\right\rangle = \frac{1}{\sqrt{2}}(|s_1\rangle - |s_2\rangle). \tag{61}$$

The components involved in the expansion (59) are then given by

$$D_{EA'} = \left\langle \rho_{A''}^{(E)} \,\middle|\, \psi^{(E)} \right\rangle = -\frac{1}{2};$$

$$D_{EB'} = \left\langle \rho_{B''}^{(E)} \,\middle|\, \psi^{(E)} \right\rangle = \frac{\sqrt{3}}{2}. \tag{62}$$

The geometrical representation is depicted in Figure 7. Here, the rotation matrix takes the form

$$\mathbf{M} = \left|\left|(\rho_{\beta''}^{(E)}, \psi_{\gamma}^{(E)})\right|\right| = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2}. \end{pmatrix}, \tag{63}$$

corresponding to a rotation of $2\pi/3$ radians. The geometrical interpretation is displayed also in Fig. 7. He have thus shown that a new choice of basis is equivalent to rotate the reference frame, and we have as many choices as allowed group chains. The same interpretation can be used for the general case when multiplicity of irreps appears. The projection however must be made following a different approach called the eigenfunction approach [17–20].

Finally, given our example, it should be appreciated the advantage of the order $\hat{\mathcal{P}}^{(\gamma)}\hat{\mathcal{P}}^{(\Gamma)}$ followed in the projection in (14) in accordance with a group chain $G \supset H$. This is the natural approach to see the projection in successive steps. Otherwise the projection should be viewed as an induction process where the irreps of H are induced to irreps of G [8]. In a purely algebraic approach, however, both approaches are equivalent. In Table IV we depicted a summary of the projections and expansions in the different basis.

TABLE IV. The results of the expansion for the three alternative vectors, for the active and the passive picture. Only the components of the E contribution change.

Vector	$\|s_1\rangle$	$\|s_2\rangle$	$\|s_3\rangle$
	$\frac{1}{\sqrt{3}}\left\|\psi^{(A_1)}\right\rangle + \frac{2}{\sqrt{6}}\left\|\psi^{(E)}\right\rangle$	$\frac{1}{\sqrt{3}}\left\|\psi^{(A_1)}\right\rangle + \frac{2}{\sqrt{6}}\left\|\zeta^{(E)}\right\rangle$	$\frac{1}{\sqrt{3}}\left\|\psi^{(A_1)}\right\rangle + \frac{2}{\sqrt{6}}\left\|\phi^{(E)}\right\rangle$
Basis	$\left\|\psi^{(E)}\right\rangle$	$\left\|\zeta^{(E)}\right\rangle$	$\left\|\phi^{(E)}\right\rangle$
C_2^a	$\left\|\psi_A^{(E)}\right\rangle$	$-\frac{1}{2}\left\|\psi_A^{(E)}\right\rangle + \frac{\sqrt{3}}{2}\left\|\psi_B^{(E)}\right\rangle$	$-\frac{1}{2}\left\|\psi_A^{(E)}\right\rangle - \frac{\sqrt{3}}{2}\left\|\psi_B^{(E)}\right\rangle$
C_2^b	$-\frac{1}{2}\left\|\eta_{A'}^{(E)}\right\rangle - \frac{\sqrt{3}}{2}\left\|\eta_{B'}^{(E)}\right\rangle$	$\left\|\eta_{A'}^{(E)}\right\rangle$	$-\frac{1}{2}\left\|\eta_{A'}^{(E)}\right\rangle + \frac{\sqrt{3}}{2}\left\|\eta_{B'}^{(E)}\right\rangle$
C_2^c	$-\frac{1}{2}\left\|\rho_{A''}^{(E)}\right\rangle + \frac{\sqrt{3}}{2}\left\|\rho_{B''}^{(E)}\right\rangle$	$-\frac{1}{2}\left\|\rho_{A''}^{(E)}\right\rangle - \frac{\sqrt{3}}{2}\left\|\rho_{B''}^{(E)}\right\rangle$	$\left\|\rho_{A''}^{(E)}\right\rangle$

4. Choice of the basis: quantum numbers and eigenfunction approach

In this section we shall discuss the procedure to obtain a basis. Instead of using the traditional approach based on the projection operators we shall present an approach based on the definition of quantum numbers.

One of the fundamental concepts in quantum mechanics is the complete set of commuting operators (CSCO). The essence of this concept lies on the necessity of labeling without ambiguity the eigenstates of the Schrödinger equation for stationary states

$$\hat{\mathcal{H}}|\Psi\rangle = E|\Psi\rangle. \tag{64}$$

It should be clear that the Hamiltonian itself can be considered as part of the set of the CSCO, since the energy E provides a label for the eigenstates $|\Psi\rangle$ through (64). If α stands for an index introduced to distinguish different energies, a more precise form of expressing the Eq. (64) is

$$\hat{\mathcal{H}}|\Psi_i^\alpha\rangle = E_\alpha|\Psi_i^\alpha\rangle; \quad i = 1, \ldots, g_\alpha, \tag{65}$$

where the subindex i accounts for the possibility of having several functions (in this case g_α functions) associated with the same energy. In practice, since the exact solutions $|\Psi_i^\alpha\rangle$ cannot be found, they are expanded in terms of a set of n known orthonormal kets $|\phi_j\rangle$

$$|\Psi_i^\alpha\rangle = \sum_{j=1}^{n} s_{j;\alpha,i}|\phi_j\rangle. \tag{66}$$

The substitution of this equation into (65) leads to the system of eigenvalues

$$\sum_{j=1}^{n}(h_{kj} - E_\alpha\delta_{kj})s_{j;\alpha,i} = 0, \tag{67}$$

where

$$h_{kj} = \langle\phi_k|\hat{\mathcal{H}}|\phi_j\rangle \tag{68}$$

are the matrix elements of the Hamiltonian in the basis $\mathcal{L}_n = \{|\phi_i\rangle, i = 1, \ldots, n\}$. The homogeneous linear set of Eqs. (67) is equivalent to the diagonalization of the matrix $\mathbf{H} \equiv ||h_{kj}||$, *e.g*

$$\mathbf{S^{-1}HS} = \Lambda, \tag{69}$$

where Λ is a diagonal matrix with elements given by the eigenvalues E_α, and $\mathbf{S} \equiv ||s_{j;\alpha,i}||$. The CSCO is concerned with the procedure to distinguish (adding labels corresponding to eigenvalues of additional operators) the set of kets $\{|\Psi_i^\alpha\rangle, i = 1, \ldots, g_\alpha\}$. The criterion to establish the CSCO is based on symmetry concepts, where the machinery of group representation theory emerges as a fundamental tool.

By definition the maximum set of transformations that leaves the Hamiltonian invariant corresponds to the *symmetry group* G, as previously pointed out through (1). We may think that the set of operators $\{\hat{\mathcal{H}}, \mathcal{O}_{R_i};\ i = 1, \ldots, |G|\}$ is useful to define a CSCO, but in general $[\mathcal{O}_{R_i}, \mathcal{O}_{R_j}] \neq 0$, unless the group is Abelian. This problem is solved by selecting subsets of G,corresponding to the conjugate classes of the group. A *conjugate class* K_i with number of elements $|K_i|$ is defined by the set of elements $\{g_j^{(i)};\ j = 1, \ldots |K_i|\}$, which are connected by at least one element $u \in G$ through

$$g_j^{(i)} = u\ g_k^{(i)}\ u^{-1}. \tag{70}$$

The class operator for the i-th class is defined by

$$\hat{K}_i = \sum_{\beta=1}^{|K_i|} \hat{\mathcal{O}} g_\beta^{(i)}. \tag{71}$$

From (1), it is clear that

$$[\hat{H}, \hat{K}_i] = 0, \quad \forall \hat{K}_i \tag{72}$$

and since every class K_i commute with any element $u \in G$, we have that $[K_i, u] = 0$, a property followed from (70). As a consequence we also have the remarkable property

$$[K_j, K_i] = 0, \quad \forall i, j. \tag{73}$$

Hence the Hamiltonian together with the classes of the group constitute a set of commuting operators and they can be di-

agonalized simultaneously in any space of independent functions. Let $\mathcal{L}_n = \{|\phi_i\rangle, i = 1, \ldots, n\}$ the space to be chosen, which may be given by atomic orbitals or internal coordinates. The set $\{|\Psi_i^\alpha\rangle,\ i = 1, \ldots, g_\alpha\}$ given by (66) are eigenvectors of $\hat{H}$. We may now construct the representation matrix of the class K_p in this basis

$$||\langle\Psi_j^\alpha|\hat{K}_p|\Psi_i^\alpha\rangle||; \quad i, j = 1, \ldots g_\alpha. \tag{74}$$

The diagonalization of this matrix provides eigenvectors of type $\{|\Psi_k^{\alpha,\lambda_p}\rangle,\ k = 1, \ldots, g_{\alpha,\lambda_p}\}$, with the property

$$\hat{\mathcal{H}}|\Psi_l^{\alpha,\lambda_p}\rangle = E_\alpha|\Psi_l^{\alpha,\lambda_p}\rangle, \quad \hat{K}_p|\Psi_l^{\alpha,\lambda_p}\rangle = \lambda_p|\Psi_l^{\alpha,\lambda_p}\rangle, \tag{75}$$

where λ_p is the label that distinguishes the different eigenvalues of the class operator $\hat{K}_p$, and l accounts for the degeneracy. We may now proceed to obtain the matrix representation of the next class $\hat{K}_q$ in the new basis $|\Psi_l^{\alpha,\lambda_p}\rangle$, to obtain eigenvectors with the additional label λ_q. We may follow this procedure with the rest of the classes to obtain a set of states $\{|\Psi_l^{\alpha,\lambda_1,\ldots,\lambda_{|K|}}\}$ characterized by the eigenvalues $\{\alpha, \lambda_1, \ldots, \lambda_{|K|}\}$. This set of labels is not complete, a degeneracy still remains. To see why this is the case we should note that the classes $\{K_i; i = 1, \ldots, |K|\}$ are linearly independent and consequently there are as many different sets $\{\lambda_1, \ldots, \lambda_{|K|}\}$ as number of classes. But we know that the number of irreps is equal to the number of classes and consequently the set of labels $\{\lambda_1, \ldots, \lambda_{|K|}\}$ is expected to specify an irrep. Introducing the label ν for the possible solutions (irreps), a more precise labeling would be

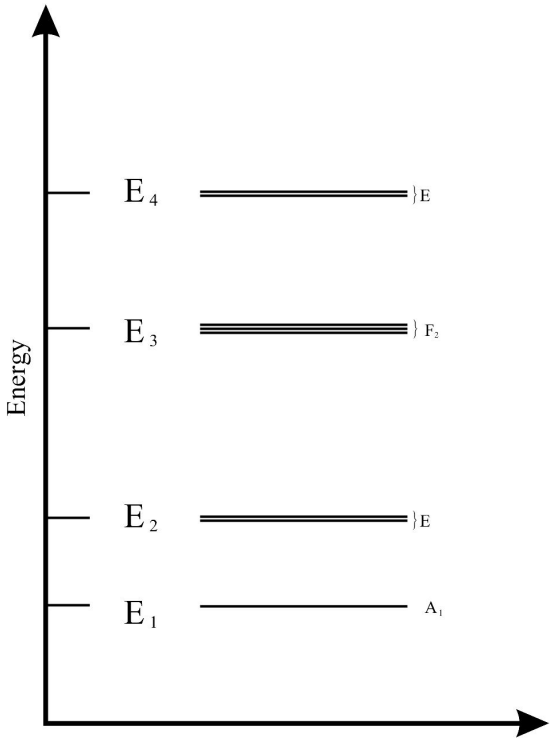

FIGURE 8. Eigenstates labeled with the energy and the irreps. A degeneracy still remains due to the degeneracy of the irreps.

$$\{\lambda_1^\nu, \lambda_2^\nu, \ldots, \lambda_{|K|}^\nu\}. \tag{76}$$

This is a formal way to name an irrep. For two and three dimensional irreps (E and F), for instance, a degeneracy still remains, which by the way is not broken by the Hamiltonian since the energy E_α only distinguish different sets with the same irrep. This situation is illustrated in Fig. 8.

The question which arises is concerned with the identification of the new set of operators capable to distinguish the states associated with the degeneracy of the irreps. The answer is given by the classes of a subgroup.

Let H be a subgroup of G: $H \subset G$. Suppose that H has $|k|$ classes $\{k_1, \ldots, k_{|k|}\}$ which clearly satisfy

$$[k_p, k_q] = 0. \tag{77}$$

But the classes $\{K_i,\ i = 1, \ldots, |K|\}$ of the group G commute with any element of the group, and consequently commute also with the classes of the subgroup

$$[K_i, k_p] = 0, \quad \forall i, p. \tag{78}$$

This fact suggests to diagonalize the operators $\hat{k}_p$ in the basis $\{|\Psi_l^{\alpha,\lambda_1,\ldots,\lambda_{|K|}}\rangle\}$ to obtain a complete labeling for the components of the irreps. Indeed, this is the case as long as a suitable subgroup forming a canonical chain is chosen. After this procedure of diagonalization the matrix representation of the classes of the subgroup H, we arrive to the complete labeling scheme

$$\left|\Psi^{\alpha,\lambda_1^\nu,\ldots,\lambda_{|K|}^\nu}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle, \tag{79}$$

where the subindices λ_p^μ are defined by

$$\hat{k}_p\left|\Psi^{\alpha,\lambda_1^\nu,\ldots,\lambda_{|K|}^\nu}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle = \lambda_p^\mu\left|\Psi^{\alpha,\lambda_1^\nu,\ldots,\lambda_{|K|}^\nu}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle, \tag{80}$$

considering that μ labels the irreps of the subgroup H. This process of labeling is very simple and we will see that it is not necessary to use all the classes to establish an unambiguous labeling scheme. In fact, the relevant involved classes are intended to contain the generators of the group and subgroup, a resulting set with cardinality less than the total number of classes $|K|$.

Let us now turn our attention to the identification of the labels involved in (79) as quantum numbers. The time evolution of the expectation value of an operator $\hat{A}$ is given by [24]

$$\frac{d}{dt}\langle\Psi|\hat{A}|\Psi\rangle = \langle\Psi|[\hat{H}, \hat{A}]|\Psi\rangle + \langle\Psi|\frac{\partial\hat{A}}{\partial t}|\Psi\rangle, \tag{81}$$

where $[\hat{H}, \hat{A}]$ is the commutator of the Hamiltonian with the operator $\hat{A}$. Hence, a remarkable consequence is that if the operator $\hat{A}$ does not depend explicitly on time and commute with the Hamiltonian, then the expected value is constant in time:

$$\frac{d}{dt}\langle\Psi|\hat{A}|\Psi\rangle = 0; \quad [\hat{H}, \hat{A}] = 0, \ \frac{\partial\hat{A}}{\partial t} = 0. \tag{82}$$

Suppose now that the states are chosen to be eigenstates of the Hamiltonian together with the classes of the group G and subgroup H. Then

$$|\Psi\rangle \;\rightarrow\; \left|\Psi^{\alpha,\lambda_1^\nu,\ldots,\lambda_{|K|}^\nu}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle, \tag{83}$$

and the set of Eqs. (82) translates into

$$\begin{aligned}&\frac{d}{dt}E_\alpha = 0; \quad \frac{d}{dt}\lambda_i^\nu = 0;\\ &\frac{d}{dt}\lambda_p^\mu = 0; \quad i = 1,\ldots,|K|; \quad p = 1,\ldots,|k|,\end{aligned} \tag{84}$$

when $\hat{A}$ is substituted by $\hat{\mathcal{H}}$, $\hat{K}_i$ and $\hat{k}_p$. Hence the eigenvalues of the set of operators $\{\hat{\mathcal{H}}; \hat{K}_1,\ldots,K_{|K|}; \hat{k}_1,\ldots,k_{|k|}\}$ are independent of time and consequently are *quantum numbers*.

For a given energy eigenvalue α there is a set of λ_i^ν values characterizing the ν-th irrep in accordance with (76). As mentioned before this fact suggests a connection between the λ_i^ν values and the characters $\chi_i^{(\nu)}$ of the group as we show next. For a given irrep ν the representation of a class K_i is given by

$$\mathbf{D}^{(\nu)}(K_i) = \sum_{\beta=1}^{|K_i|} \mathbf{D}^{(\nu)}(g_\beta^{(i)}). \tag{85}$$

But since

$$[\mathbf{D}^{(\nu)}(K_i), \mathbf{D}^{(\nu)}(R)] = 0; \quad \forall R \in G, \tag{86}$$

it follows by Schur's Lema II [14], that $\mathbf{D}^{(\nu)}(K_i)$ must be proportional to the unit matrix. In fact, we have [14]

$$\mathbf{D}^{(\nu)}(K_i) = \frac{|K_i|\chi_i^{(\nu)}}{n_\nu}\mathbf{1}. \tag{87}$$

But the eigenvalues of the classes are given by

$$\mathbf{D}^{(\mu)}(K_i) = \lambda_i^\nu \mathbf{1}, \tag{88}$$

and consequently

$$\lambda_i^\nu = \frac{|K_i|}{n_\nu}\chi_i^{(\nu)}; \quad i = 1,\ldots,|K|, \tag{89}$$

where n_ν refers to the dimension of the ν-th irrep. A similar relation holds for λ_p^μ and the characters of the subgroup H. Note that the expression (89) basically tells us that a character table constitutes a tabulation of quantum numbers, a remarkable feature not mentioned explicitly in textbooks. Indeed, the Eq. (89) leads to the most efficient projection technique, as we next explain.

The relation (89) itself suggests a projection method based on the diagonalization of class operators. This assertion may be appreciated because of the following: any set of symmetry adapted functions $\{|\psi_i^{(\nu)}\rangle,\ i = 1, n_\nu\}$ spanning the ν-th irrep of dimension n_ν satisfies [17]

$$\hat{K}_i|\psi_i^{(\nu)}\rangle = \lambda_i^\nu|\psi_i^{(\nu)}\rangle; \quad i = 1,\ldots,n_\nu, \tag{90}$$

which is a consequence of (88) and it means that the functions $|\psi_i^{(\nu)}\rangle$ are eigenvectors of the class operators with eigenvalue λ_i^ν. This remarkable result suggests to proceed in the other way around to obtain (79): we start diagonalizing the class operators and at the end the Hamiltonian is diagonalized taking advantage that its representation in such basis is block diagonal. This approach leads to the eigenfunction method of projecting functions [17].

Eigenfunction Method

Here it is convenient to point out the difference between the approach presented here and Chen's approach to the eigenfunction method. As the reader noticed, our approach is based on Wigner's theorem and the concept of CSCO to label the eigenstates. In this way the concept of quantum numbers is intrinsically connected with the eigenvalues of the class operators which in turn are related to irreps of the symmetry group. In contrast, in Chen's theory the main ingredient is that the eigenvectors in the class space are identified as projection operators, while Wigner's theorem is discussed separately. The whole representation theory is developed in detail but it seems disconnected with the fundamental Wigner's theorem.

We now introduce in more detail the eigenfunction approach. We start with an arbitrary set of orthonormal functions $\{|\phi_i\rangle,\ i = 1,\ldots,n\}$ with $\langle\phi_i|\phi_j\rangle = \delta_{ij}$. Then we choose a subset of classes of G as well as of H that allows their corresponding irreps to be distinguished [17–20]. A linear combination of the selected classes provides eigenvectors carrying the ν-th irrep. Let us consider an example to illustrate this idea. Suppose we want to obtain the symmetry projected functions from the same space previously considered: $\mathcal{L}_3 = \{|s_1\rangle, |s_2\rangle, |s_3\rangle\}$ corresponding to the atomic s-orbitals of the H_3^+ molecule. The character table is given by Table 1 with the classes $K_1 = \{E\}, K_2 = \{C_3, C_3^2\}$ and $K_3 = \{C_2^a, C_2^b, C_2^c\}$. Let us now construct a table of eigenvalues of the classes, which we call it the $\lambda's$ table, by using the expression (89). The result is given in Table 2, from which we notice that the class K_3 by itself distinguishes the irreps (it contains the generators of the group) and consequently the eigenvectors in (83) may be simplified to

$$\left|\Psi^{\alpha,\lambda_1^\nu,\ldots,\lambda_{|K|}^\nu}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle \rightarrow \left|\Psi^{\alpha,\lambda_3^\nu}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle, \tag{91}$$

TABLE V. λ's table for the group $\mathcal{D}_3$ obtained from the character table and the relation (89)

$\mathcal{D}_3$	λ_1^ν	λ_2^ν	λ_3^ν
A_1	1	2	3
A_2	1	2	-3
E	1	-1	0

where

$$\hat{K}_3\left|\Psi^{\alpha,\lambda_3^{A_1}}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle = \lambda_3^{A_1}\left|\Psi^{\alpha,\lambda_3^{A_1}}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle = +3\left|\Psi^{\alpha,\lambda_3^{A_1}}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle, \quad (92)$$

$$\hat{K}_3\left|\Psi^{\alpha,\lambda_3^{A_2}}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle = \lambda_3^{A_2}\left|\Psi^{\alpha,\lambda_3^{A_2}}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle = -3\left|\Psi^{\alpha,\lambda_3^{A_2}}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle, \quad (93)$$

$$\hat{K}_3\left|\Psi^{\alpha,\lambda_3^{E}}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle = \lambda_3^{E}\left|\Psi^{\alpha,\lambda_3^{E}}_{\lambda_1^\mu,\ldots,\lambda_{|k|}^\mu}\right\rangle = 0, \quad (94)$$

in accordance with Table V. This analysis suggests to deal with the representation of the class K_3 in the space $\mathcal{L}_3$ as a first step to obtain the projection. Consider now the element $C_2^a \in \mathcal{D}_3$. From Fig. 4 we obtain the transformation of the s-orbitals under the rotation C_2^a: $C_2^a|s_1\rangle \to |s_1\rangle, C_2^a|s_2\rangle \to |s_3\rangle, C_2^a|s_3\rangle \to |s_2\rangle$. In matrix form

$$\hat{C}_2^a(|s_1\rangle,|s_2\rangle,|s_3\rangle) = (|s_1\rangle,|s_2\rangle,|s_3\rangle)\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix} \equiv (|s_1\rangle,|s_2\rangle,|s_3\rangle)\Delta(C_2^a), \quad (95)$$

where we have introduced the definition for the representation $\Delta(C_2^a)$ associated with the operator C_2^a in the space $\mathcal{L}_3$. Following the same approach for the rotations C_2^b and C_2^c we obtain their corresponding matrix representations

$$\Delta(C_2^b) = \begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}, \quad \Delta(C_2^c) = \begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}. \quad (96)$$

These results allow the matrix representation of the class K_3 to be constructed in a straightforward way. In fact, the representation is given by

$$\Delta(K_3) = \Delta(C_2^a) + \Delta(C_2^b) + \Delta(C_2^c) = \begin{pmatrix}1&1&1\\1&1&1\\1&1&1\end{pmatrix}. \quad (97)$$

The diagonalization of this matrix provides the eigensystem given in Table VI.

TABLE VI. Eigensystem associated with the matrix representation of the class operator K_3.

Irrep	Eigenvalue	Eigenvector
A_1	3	(1,1,1)
E	0	(1,0,-1)
E	0	(1,-1,0)

We should note that the eigenvalues correspond to the values 3 and 0 of the λ's Table V. The eigenvectors of Table VI give rise to the following symmetry adapted functions

$$|\Psi^{+3}\rangle = \frac{1}{\sqrt{3}}(|s_1\rangle + |s_2\rangle + |s_3\rangle), \quad (98)$$

$$|_1\Psi^0\rangle = \frac{1}{\sqrt{3}}(|s_1\rangle - |s_3\rangle), \quad (99)$$

$$|_2\Psi^0\rangle = \frac{1}{\sqrt{3}}(|s_1\rangle - |s_2\rangle), \quad (100)$$

where we have temporarily introduced an arbitrary left subindex in order to distinguish the degenerate eigenvectors associated with the irrep E (eigenvalue 0 in accordance to Table V). We now proceed to introduce a suitable subgroup H in order to establish the labels λ_p^μ associated with the classes k_p in (91). Let us propose the subgroup $\mathcal{C}_2^a = \{E, C_2^a\}$, a selection that is usually expressed in the form of the chain of subgroups

$$\mathcal{D}_3 \supset \mathcal{C}_2^a. \quad (101)$$

To know whether this is a suitable chain to label the states we should obtain the irreps of the subgroup $\mathcal{C}_2^a$ contained in the irrep E. To this end it is convenient to present the character table of the subgroup $\mathcal{C}_2^a$, including the characters of the irreps of the group $\mathcal{D}_3$ (correlation table). This analysis is displayed in Table VII, where the last three rows correspond to the irreps of $\mathcal{D}_3$ and are obtained by taking the characters of Table I corresponding to each irrep, selecting the columns K_1 and K_3 where the elements of the subgroup $\mathcal{C}_2^a$ are located.

The last column corresponds to the reduction of the irreps of $\mathcal{D}_3$ into irreps of $\mathcal{C}_2^a$, and may be obtained either by inspection or using (6). We note that no repetition of irreps of $\mathcal{C}_2^a$ appears in the reduction of E and consequently the chain (117) is *canonical*. We may now identify the class that determines the irreps of the subgroup following the same approach that was used in the group. Since in the subgroup $\mathcal{C}_2^a$ all the irreps are one dimensional the λ's table coincide with the character table and consequently we can identify in a straightforward way the class $k_2 = C_2^a$ to distinguish the irreps. This means that if we diagonalize the matrix representation of the operator $\hat{C}_2^a$ in the basis (99-100), the corresponding eigenvalues

TABLE VII. Irreps of $\mathcal{C}_2^a$ contained in the irreps of the group $\mathcal{D}_3$.

$\mathcal{C}_2^a$	E	C_2^a	
A	1	1	
B	1	-1	
A_1	1	1	A
A_2	1	-1	B
E	2	0	$A \oplus B$

will be $+1, -1$, for irreps A and B respectively, in accordance with Table VII. Indeed, the representation of the operator C_2^a turns out to be

$$\begin{aligned}\hat{C}_2^a(|\Psi^{+3}\rangle,\ |_1\Psi^0\rangle,\ |_2\Psi^0\rangle) \\ = (|\Psi^{+3}\rangle,\ |_1\Psi^0\rangle,\ |_2\Psi^0\rangle)\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix} \\ \equiv (|\Psi^{+3}\rangle,\ |_1\Psi^0\rangle,\ |_2\Psi^0\rangle)\Delta(C_2^a),\end{aligned} \tag{102}$$

where we have used (95) and (96). The representation $\Delta(C_2^a)$ is a block diagonal matrix, an expected result since the operators $\hat{C}_2^a$ cannot mix functions of different irreps of the group $\mathcal{D}_3$. The diagonalization of the matrix $\Delta(C_2^a)$ provides the eigenvectors

$$\begin{aligned}|\Psi_1^0\rangle &= |_1\Psi^0\rangle + |_2\Psi^0\rangle \\ &= \frac{1}{\sqrt{6}}(2|s_1\rangle - |s_2\rangle - |s_3\rangle),\end{aligned} \tag{103}$$

$$|\Psi_{-1}^0\rangle = |_1\Psi^0\rangle - |_2\Psi^0\rangle = \frac{1}{\sqrt{2}}(|s_2\rangle - |s_3\rangle), \tag{104}$$

where the subindex appearing in the new functions corresponds to the eigenvalues of the operator $\hat{C}_2^a$. But from Tables V and VII we know the correspondence of the eigenvalues with the traditional labeling of the irreps. For the group $\mathcal{D}_3$

$$+3 \leftrightarrow A_1;\ \ 0 \leftrightarrow E, \tag{105}$$

while for the subgroup

$$+1 \leftrightarrow A;\ \ -1 \leftrightarrow B. \tag{106}$$

We may now identify the functions in the usual notation

$$|\Psi^{+3}\rangle \equiv |\Psi^{A_1}\rangle = \frac{1}{\sqrt{3}}(|s_1\rangle + |s_2\rangle + |s_3\rangle), \tag{107}$$

$$|\Psi_1^0\rangle \equiv |\Psi_A^E\rangle = \frac{1}{\sqrt{6}}(2|s_1\rangle - |s_2\rangle - |s_3\rangle), \tag{108}$$

$$|\Psi_{-1}^0\rangle \equiv |\Psi_B^E\rangle = \frac{1}{\sqrt{2}}(|s_2\rangle - |s_3\rangle). \tag{109}$$

To obtain these projected functions we have carried out two diagonalizations, corresponding to the operators $\hat{K}_3$ and $\hat{k}_2 = \hat{C}_2^a$. We may simplify this procedure by diagonalizing a unique operator obtained as a linear combination of the operators K_3 and $\hat{k}_2$. To obtain the appropriate combination we construct a table containing the possible eigenvalues according to the λ's table for $\mathcal{D}_3$ and $\mathcal{C}_2^a$, together with the reduction given in Table VII. The results are given the Table VIII.

TABLE VIII. Eigenvalues associated with the operators $\hat{K}_3$ and $\hat{k}_2 = \hat{C}_2^a$ corresponding to the chain of groups $\mathcal{D}_3 \supset \mathcal{C}_2^a$.

$\mathcal{D}_3$	λ_3^ν	$\mathcal{C}_2^a$	λ_2^μ	$\lambda_3^\nu + \lambda_2^\mu$
A_1	+3	A	+1	+4
A_2	-3	B	-1	-4
E	0	A	+1	+1
E	0	B	-1	-1

TABLE IX. Eigensystem associated with the matrix representation of the class operator $\hat{C}_{II}$.

Irreps	Eigenvalue	Eigenvector
A_1	+4	(1,1,1)
(E, A)	+1	(2,-1,-1)
(E, B)	-1	(0,1,-1)

In the last column we have included the sum of the eigenvalues. As noted all the numbers are different, a fact that implies that we can define the operator C_{II} as

$$C_{II} \equiv \hat{K}_3 + \hat{k}_2 = 2\hat{C}_2^a + \hat{C}_2^b + \hat{C}_2^c, \tag{110}$$

whose diagonalization provides the symmetry adapted functions in a straightforward way in one step. Proceeding in this manner we obtain the representation matrix

$$\Delta(C_{II}) = \begin{pmatrix}2&1&1\\1&1&2\\1&2&1\end{pmatrix}. \tag{111}$$

The diagonalization of this matrix provides the eigensystem presented in Table VI, from which we identify immediately the symmetry adapted functions in the form

$$|\Psi^{+4}\rangle \equiv |\Psi^{A_1}\rangle = \frac{1}{\sqrt{3}}(|s_1\rangle + |s_2\rangle + |s_3\rangle), \tag{112}$$

$$|\Psi^1\rangle \equiv |\Psi_A^E\rangle = \frac{1}{\sqrt{6}}(2|s_1\rangle - |s_2\rangle - |s_3\rangle), \tag{113}$$

$$|\Psi^{-1}\rangle \equiv |\Psi_B^E\rangle = \frac{1}{\sqrt{2}}(|s_2\rangle - |s_3\rangle). \tag{114}$$

This example allows us to establish the series of steps to obtain a basis according to a chain of groups for any molecular system:

Step 1. - From the character table of the symmetry group G, the λ's table is generated using (89).

Step 2. - We proceed to identify the column that distinguishes the irreps of the group G. In general more than one column is needed to achieve this goal. In such case a linear combination of columns are selected in such a way that the eigenvalues are all different. This process defines the linear combination of classes, which we shall identify with the operator $\hat{C}$.

Step 3.- A subgroup H is proposed in such a way that the irreps of G are not contained more than once in H.

Step 4.- From the character table of H, we construct the λ's table and identify the columns that distinguishes the irreps. The columns involved define a linear combination of classes of the subgroup which define the operator $\hat{C}(s)$. This operator is the equivalent of $\hat{C}$ in the group G.

Step 5.- A table of eigenvalues associated with G and H is constructed (Table V in our example). A linear combination of λ's is identified to define a new operator $\hat{C}_{II}$.

Step 6.- The representation of the operator $\hat{C}_{II}$ is generated using the space to be projected. The diagonalization of the matrix representation $\Delta(C_{II})$ provides the symmetry adapted functions.

We should stress that up to step 5, no dependence of the space appears. Given a molecular system, the first 4 steps are general and are useful to project any representation space; electronic functions, rotational functions, vibrational function or spin functions. Only the last step is a function of the space.

5. Symmetry Breaking

In this section we show one of the advantages of labeling the states according to a given chain of groups [17]. For example, by establishing an appropriate group chain the analysis of a perturbation on the system is simplified. Such perturbations can be associated, for example, with the application of an electric or magnetic field in the system surroundings [21].

Let us consider a time independent system with Hamiltonian, $\widehat{H}$, written as follows

$$\widehat{H} = \widehat{H}_0 + \widehat{V}, \tag{115}$$

where $\widehat{H}_0$ is the zeroth order Hamiltonian with eigenkets [24]

$$\widehat{H}_0 \left|\psi_{n(\Gamma),\gamma_1,\gamma_2}\right\rangle = E_n \left|\psi_{n(\Gamma),\gamma_1,\gamma_2}\right\rangle, \tag{116}$$

where n labels the energy eigenvalue and $\Gamma, \gamma_1, \gamma_2$, are irreps associated with the group chain [9]

$$G \supset K_1 \supset K_2. \tag{117}$$

Here $\widehat{H}_0$ is considered to be invariant under G group, which explain the labeling scheme. The subgroup K_2 was considered to account for the possibility that after the symmetry breaking a degeneracy still remains. The eigenkets $\left|\psi_{n(\Gamma),\gamma_1,\gamma_2}\right\rangle$ are orthonormal [14],

$$\langle\psi_{m(\Gamma'),\gamma_1',\gamma_2'}, \psi_{n(\Gamma),\gamma_1,\gamma_2}\rangle = \delta_{mn}\delta_{\Gamma'\Gamma}\delta_{\gamma_1',\gamma_1}, \delta_{\gamma_2',\gamma_2}. \tag{118}$$

When the perturbation $\widehat{V}$ is added the symmetry may be preserved or diminished. We shall consider the latter case with the new symmetry group given by K_1:

$$\left[\widehat{O}_S, \widehat{V}\right] = 0, \qquad \forall S \in K_1. \tag{119}$$

The potential is then invariant under K_1 but not anymore under G. The potential $\widehat{V}^{A_1}$ carries the totally symmetric representation A_1 of K_1.

Given that $\widehat{V}$ is not invariant under G the matrix elements take the form

$$\langle\psi_{m(\Gamma'),\gamma_1',\gamma_2'}|\widehat{V}^{A_1}|\psi_{n(\Gamma),\gamma_1,\gamma_2}\rangle = \mathcal{V}_{mn}\ \delta_{\gamma_1',\gamma_1}, \delta_{\gamma_2',\gamma_2}. \tag{120}$$

Note that in case V had the same symmetry G, the matrix elements would take the form

$$\begin{aligned}\langle\psi_{m(\Gamma'),\gamma_1',\gamma_2'}|\widehat{V}|\psi_{n(\Gamma),\gamma_1,\gamma_2}\rangle \\ = \mathcal{V}^{\Gamma}_{mn}\delta_{\Gamma'\Gamma}\delta_{\gamma_1',\gamma_1}, \delta_{\gamma_2',\gamma_2},\end{aligned} \tag{121}$$

and the matrix $\mathcal{V}^{\Gamma}_{mn}$ would involve kets spanning the same Γ irrep. In contrast, the matrix elements $\mathcal{V}_{mn}$ in (120) mix states of different Γ irrep. The kets $|\psi_{n(\Gamma),\gamma_1,\gamma_2}\rangle$ are then expected to be mixed since the label Γ is no longer a good quantum number.

The eigenvectors $|\Phi^{\alpha(\gamma_1)}_{\gamma_2}\rangle$ associated with the perturbed Hamiltonian (115) are defined through

$$\widehat{H}|\Phi^{\alpha(\gamma_1)}_{\gamma_2}\rangle = E_\alpha|\Phi^{\alpha(\gamma_1)}_{\gamma_2}\rangle, \tag{122}$$

where we assume that the degeneracy corresponds to the dimension of the γ_2 irrep. The new eigenkets take thus the general form

$$\left|\Phi^{\alpha(\gamma_1)}_{\gamma_2}\right\rangle = \sum_{n(\Gamma)} C^{\alpha;\gamma_1,\gamma_2}_{n(\Gamma)} \left|\psi_{n(\Gamma),\gamma_1,\gamma_2}\right\rangle. \tag{123}$$

Here we have two remarks. Firstly, the Kronecker deltas appearing in the matrix elements (120) are a consequence of having labeled the states in accordance with the chain (117), anticipating the symmetry reduction, and secondly, the dimensions of the blocks associated with the Hamiltonian matrix corresponds to the number of functions $\left|\psi_{n(\Gamma),\gamma_1,\gamma_2}\right\rangle$, characterized by the Γ irrep, containing the γ_1 irrep.

5.1. Example

As an example we next analyze the symmetry breaking of a particle in a cubic box. In this case the zeroth order Hamiltonian $\widehat{H}_0$ is given by

$$\widehat{H}_0 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right); \tag{124}$$

with the following boundary conditions:

$$\begin{cases} V(x,y,z) = 0; \ \ 0 \le x \le a; \ \ 0 \le y \le a; 0 \le z \le a \\ V(x,y,z) = \infty; \ \ x < 0; y < 0; z < 0 \\ V(x,y,z) = \infty; \ \ x > a; y > a; z > a \end{cases} \tag{125}$$

The eigenfunctions are given by

$$\langle \mathbf{r}|\Psi_{n_x n_y n_z}\rangle = \sqrt{\frac{2}{a}}\sin(\pi n_x x/a) \times \sqrt{\frac{2}{a}}\sin(\pi n_y y/a)\sqrt{\frac{2}{a}}\sin(\pi n_z z/a), \quad (126)$$

with eigenvalues [24]

$$E_{\mathbf{n}} = \frac{\hbar^2\pi^2}{2ma^2}(n_x^2+n_y^2+n_z^2). \quad (127)$$

To simplify the discussion we shall consider that the symmetry group of the system is O_h, which corresponds to the the geometrical symmetry (obvious symmetry) of the cubic box [23]. We now consider a perturbation of the form

$$\widehat{V} = ez\mathcal{E}_z, \quad (128)$$

which may correspond to the appearance of an electric field along the z axis. After this perturbation, the system's symmetry group is reduced to $\mathcal{C}_{4v}$, which is a subgroup of O_h, and $\widehat{V}$ is invariant under this group. In general the perturbation splits the levels but since the group $\mathcal{C}_{4v}$ contains a degenerate irrep, it is not expected that the electric field removes the degeneracy completely. In this case it is convenient to establish a labeling scheme of the original functions according to the group chain [17],

$$O_h \supset C_{4v} \supset C_{2v}, \quad (129)$$

The projection of the functions (126) in accordance with the chain (129) provides the symmetry adapted basis of the form

$$|\Psi_{\mathbf{n}(\Gamma)},\gamma_1,\gamma_2\rangle = \sum_{n_x,n_y,n_z} D^{\mathbf{n}}_{n_x,n_y,n_z}|\Psi_{n_x n_y n_z}\rangle, \quad (130)$$

where the sum involves states of the same energy characterized by $\mathbf{n}$.

The matrix elements of the interaction potential acquire the general form (120). In this case the dimension of the matrix representation of the interaction turns out to be infinite. However, using perturbation theory it is possible to estimate the effect of the symmetry reduction. Let us consider a 3-dimensional level with T_{1u} symmetry associated with the energy

$$E_0 = \frac{\hbar^2\pi^2}{2ma^2}\cdot 6, \quad (131)$$

with quantum numbers $(1,1,2)$ and permutations. The reduction of the representation involved is given by

$$T_{1u} = A_1 \oplus E, \quad (132)$$

while for the reduction of $\mathcal{C}_{4v}$ to $\mathcal{C}_{2v}$ we have

$$E = B_1 \oplus B_2. \quad (133)$$

The first order correction $E^{(1)}$ to the energy E_0 is given by the eigenvalues of a block diagonal matrix, with each block labeled with the γ_1 irrep, in this case $\gamma_1 = A_1, E$:

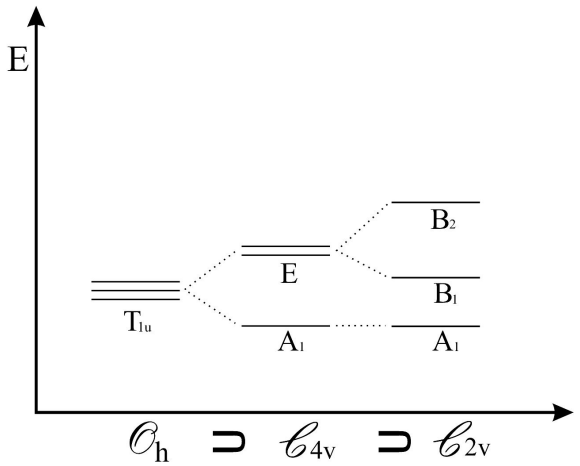

FIGURE 9. Level splitting according to the canonical group chain $O_h \supset C_{4v} \supset C_{2v}$.

$$V^{T_{1u}}_{E,\gamma_2} = \langle \Psi_{\mathbf{n}(T_{1u}),E;\gamma_2}|\widehat{V}^{A_1}|\Psi_{\mathbf{n}(T_{1u}),E,\gamma_2}\rangle; \quad \gamma_2 = B_1, B_2, \quad (134)$$

$$V^{T_{1u}}_{A_1} = \left\langle \Psi_{\mathbf{n}(T_{1u}),A_1,A_1}\right| \widehat{V}^{A_1} \left|\Psi_{\mathbf{n}(T_{1u}),A_1;A_1}\right\rangle, \quad (135)$$

where

$$V^{T_{1u}}_{E,B_1} = V^{T_{1u}}_{E,B_2} \quad (136)$$

as expected from Wigner-Eckart theorem [17]. The energies, up to first-order perturbation correction, are then given by

$$E = E_0 + V^{T_{1u}}_{E,\gamma_2}; \quad \gamma_2 = B_1, B_2, \quad (137)$$

$$E = E_0 + V^{T_{1u}}_{A_1,A_1}. \quad (138)$$

We should stress that the matrix elements are already diagonal and it is not necessary to proceed with a diagonalization of the 3×3 dimensional matrix. This simplification is a consequence of the appropriate labeling scheme in accordance with the chain (129).

We may consider the addition of a new perturbation. Now the Hamiltonian would be given by:

$$\widehat{H}_1 = \widehat{H} + \widehat{V}_2, \quad (139)$$

where $\widehat{V}_2$ is invariant under C_{2v} symmetry group. Again, the labeling scheme provides with energy corrections in diagonal form. In Fig. 9 we show the level splitting according to the previous analysis.

6. Conclusions

We have presented the basic concepts involved in group representation theory emphasizing the geometrical point of view. From a reducible representation space, a change of basis is carried out in order to reduce such space into a direct sum of irreducible spaces labeled with irreps (eigenvalues of the

class operators in discrete groups, and Casimir operators for continuous groups). A complete labeling scheme is obtained by establishing an appropriate (canonical) group chain. An additional chain is needed when multiplicity of irreps appears. Although the latter case is not discussed, the geometrical interpretation is not modified.

The concept of projection is illustrated with a simple although yet remarkable rich system. The process of obtaining symmetry adapted functions is analyzed through two steps projection. The result of the second projection depends not only on the projected function but also on the selected group chain. We have shown that the change of the projected functions is equivalent to carry out a rotation from an active point of view, while the passive perspective corresponds to choosing alternative group chains. The different basis associated with the group chains are connected with a rotation matrix.

It has been shown that the concept of quantum numbers in discrete groups is basically associated with the character tables of the groups. A remarkable consequence of looking for the invariants is that the eigenfunction method to project functions emerges in natural form. The projections reduce to diagonalize the representation matrix of a set of commuting operators. This method makes superfluous the use of the character tables in the symmetry projection process and provides in natural form a labeling scheme according to a chain of groups. The labeling scheme following a group chain is quite important in symmetry breaking situations, like the presence of electric or magnetic fields in the systems surroundings.

The present analysis illustrates many of the fundamental concepts used in group representation theory. In the more general framework of algebraic methods [22], where the concept of dynamical group emerges as the basic ingredient, each chain of groups defines a dynamical symmetry, which means that a Hamiltonian expanded in terms of Casimir operators associated with that chain is diagonal in the corresponding basis. A more general Hamiltonian involves Casimir operators of several chains and its matrix representation can be obtained by using the transformation brackets, which in our work are given by the overlap matrix (24). Hence a dynamical symmetry defines a reference frame which is connected through a multi dimensional rotation with the other possible dynamical symmetries.

We believe that the presented material shows a useful point of view to help in understanding group representation theory, providing the basic physical ingredients of advanced projection techniques.

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