Factor groups, semidirect product and quantum chemistry.

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Abstract

In this paper we prove some general theorems about representations of finite groups arising from the inner semidirect product of groups. We show how these results can be used for standard applications of group theory in quantum chemistry through the orthogonality relations for the characters of irreducible representations. In this context, conditions for transitions between energy levels, projection operators and basis functions were determined. This approach applies to composite systems and it is illustrated by the dihedral group related to glycolate oxidase enzyme.

Keywords: Representation theory, Semidirect product, Factor groups, Quantum chemistry.
1 Introduction

The concept of symmetry is ubiquitous in quantum mechanics. For example, the elementary particles can be classified using the irreducible representations of continuous symmetry groups. This approach begins at a seminal paper of Wigner [1] with systematic study of unitary representations of Poincaré group in relativistic quantum mechanics. Subsequently, a similar study was carried out in the scope of non-relativistic quantum mechanics through the invariance of the Schrödinger equation by Galilei group [2, 3, 4] and the theory of quarks, developed by Gell-Mann, [5, 6] may be understood with the flavour symmetries. Evidently, there are many other important findings related to applications of Lie groups and we do not pretend to cover them all.

In the context of finite groups, representation theory plays a fundamental role in quantum chemistry [7, 8, 9]. The quantum numbers are indices characterizing irreducible representations of finite groups [10] and the numbers and kinds of energy levels are determined by symmetry of molecule. As stressed by Wigner [11], the recognition that almost all rules of spectroscopy from the symmetry of the systems is a remarkable result. In fact, group theoretical techniques are important in determining the rules selection for optical process such as infrared and Raman activity. Transitions of lower symmetry may lead to mode splittings. These mode splittings and the changes in the infrared and Raman spectra can be predict using group theoretical techniques [12].

Despite success in quantum chemistry, applications of finite groups in many other fields were obtained. In the modern theory of quantum computation many formalisms for quantum error correction uses finite groups [13, 14]. Nice error bases are characterized in terms of the existence of certain characters in a group [13] and the characterization of decoherence-free subspaces for multiple-qubits errors can be determined by one-dimensional representation of the Pauli group [15, 16]. It was shown how to perform universal and fault tolerant quantum computation on decoherence-free subspaces. The quantum teleportation and the quantum dense coding in a finite-dimensional Hilbert space can be formulated in terms of an irreducible unitary representation of finite group [17]. Quantum logic gates capable of preserving quantum entanglement may be obtained of representations of braid group through quasitriangular Hopf algebras derived from a cyclic group [18]. Anyonic models based on finite groups have been proposed in the scope of topological quan-
The computation \[19, 20\] and topological quantum field theories associated to finite groups have been constructed \[21, 22\]. These examples show that the group-theoretical methods remain a powerful tool in the analysis of new quantum-mechanical problems.

In the quantum chemistry, after seminal works, new methods have also been developed. Unconventional approaches to obtain irreducible representations through regular projection matrices \[23\], new algorithms for point group symmetries \[24, 25\] and schemes for adapted symmetry functions of point groups \[26\] are some interesting examples. A beautiful application of the actions of finite groups was performed by Torres \[27\]. It is present a new procedure for the attainment of the number and isotropy group of the vibrational force constants for a given molecule. This approach is useful in the case of high symmetry because it does not require the use of the matrix representation generated by the set of internal coordinates.

An interesting algebraic structure that has been investigated in physics is the semidirect product of groups. In crystallography, the space group is called symmorphic group if it is a semidirect product of its point group with its translation group. Crystals whose space groups are of semidirect product type are called simple crystals and the point group of this type of crystal leaves not only the lattice invariant but also the crystal \[28\]. There are 73 symmorphic space groups and every other space group is isomorphic to a subgroup of one of semidirect product space groups. The determination of irreducible representations of symmorphic space groups using the semidirect product was performed by Bradley and Kammel \[29\] based on the seminal works of Mackey \[30\] and McIntosh \[31\]. These results are useful in calculating the electron energy bands in crystalline solids. In this line, Chen \[32\] presented a factorization lemma for the irreducible symmetry operators of semidirect product of two abelian groups so that symmetry adapted functions and algebraic solutions for the double-valued representation of the tetrahedral group were derived. Nevertheless, many interesting works related to this topic can be found in others fields. The Poincaré group, the asymptotic group in general relativity and invariance group of electrodynamics are examples of the semidirect product applied to certain group representations \[33\]. The symmetries of time-dependent Schrödinger equations related to semidirect product were examined by Okubo \[34\] and in the quantum computation theory, efficient algorithms have been found for several groups that be written as semidirect product of abelian groups \[35, 36\].

In this work, we present some general results about representations asso-
ciated to the inner semidirect product of finite groups and we show how these results can be useful in a spectroscopy analysis. The structure of this paper is as follows. In section 2 we present the mathematical results as well as possible applications in quantum chemistry. In section 3, an example using a dihedral group related to glycolate oxidase enzyme is performed. Conclusions are presented in section 4.

2 Mathematical results

A theorem concerning to reduction of finite solvable was given by Schur \cite{37}. If we have a finite solvable group with a chain of subgroups

\[ G_1 \supset G_2 \supset \ldots \supset G_n \]  

(1)

where \( G_n \) is the unit element, the irreducible representations of \( G_i \) may be obtained from the irreducible representations of \( G_{i+1} \). Later developments for the space group were obtained by Seitz \cite{38}. As mentioned above, a scheme for determining the irreducible representations of space groups using the semidirect product was developed by Bradley and Kammel \cite{29} through induced representations and little groups. In this section we present some theorems about representations of semidirect product of groups. Here, we use the orthogonality relations for the characters, the isomorphism theorems of groups and the correspondence theorem. Also, we discuss applications to quantum chemistry involving composite systems. The following lemma gives a characterization of the irreducible representations for a subgroup of a group that is semidirect product of two subgroups, one of which is analyzed subgroup.

**Lemma 1** Let \( G_1 = N_1 \rtimes H_1, G_2 = N_2 \rtimes H_2, \ldots, G_n = N_n \rtimes H_n \) be finite groups. Then every irreducible representation of \( H_1 \times H_2 \times \ldots \times H_n \) corresponds to an unique irreducible representation of \( G_1 \times G_2 \times \ldots \times G_n \).

**Proof.** Since we have the semidirect product of groups, \( H_1 \simeq G_1/N_1, H_2 \simeq G_2/N_2, \ldots, H_n \simeq G_n/N_n \), and consequently \( H_1 \times H_2 \times \ldots \times H_n \simeq G_1/N_1 \times G_2/N_2 \times \ldots \times G_n/N_n \simeq (G_1 \times G_2 \times \ldots \times G_n)/(N_1 \times N_2 \times \ldots \times N_n) \) by first isomorphism theorem of groups. Then the orthogonality relations for the characters of irreducible representations of the \( (G_1 \times G_2 \times \ldots \times G_n)/(N_1 \times \)


\(N_2 \times \ldots \times N_n\) must satisfy
\[
\sum_{S_1 \times S_2 \times \ldots \times S_n} \chi^{(\mu_1 \otimes \mu_2 \otimes \ldots \otimes \mu_n)}(S_1 \times S_2 \times \ldots \times S_n)
= \frac{g_1 g_2 \ldots g_n}{n_1 n_2 \ldots n_n} \delta_{\mu_1 \mu_2 \ldots \mu_n, \nu_1 \nu_2 \ldots \nu_n};
\]
(2)
where \(S_i\) is an element of \(H_i\) and \(g_i = |G_i|, \ n_i = |N_i|\). As each coset \(R_i G_i\), with \(R_i \in G_i\), has \(n_i\) elements and every representation of the \(G_i/N_i\) corresponds to an unique representation of \(H_i\), we have for the last relation
\[
\sum_{S_1 \times S_2 \times \ldots \times S_n} \chi^{(\mu_1 \otimes \mu_2 \otimes \ldots \otimes \mu_n)}(S_1 \times S_2 \times \ldots \times S_n)
= \sum_{R_1 \times R_2 \times \ldots \times R_n} \chi^{(\mu_1 \otimes \mu_2 \otimes \ldots \otimes \mu_n)}(R_1 \times R_2 \times \ldots \times R_n)
= g_1 g_2 \ldots g_n \delta_{\mu_1 \mu_2 \ldots \mu_n, \nu_1 \nu_2 \ldots \nu_n}
= g_1 g_2 \ldots g_n \delta_{\mu_1, \nu_1} \delta_{\mu_2, \nu_2} \ldots \delta_{\mu_n, \nu_n}.
\]
(3)
Hence we have the orthogonality relations for the characters of irreducible representations of \(G_1 \times G_2 \times \ldots \times G_n\) and so the result follows.

**Lemma 2** Suppose \(\Gamma\) and \(\Gamma'\) reducible representations of finite groups \(G_1 \times G_2 \times \ldots \times G_n\) and \((G_1 \times G_2 \times \ldots \times G_n)/(N_1 \times N_2 \times \ldots \times N_n)\), respectively. If \(\chi(R_1^1) = p_1 \chi(S_1), \chi(R_1^2) = p_2 \chi(S_2), \ldots, \chi(R_n^1) = p_n \chi(S_n)\) for \(R_1^1 \in G_1, R_2^2 \in G_2, \ldots, R_n^m \in G_n, S_1 \in G_1/N_1, S_2 \in G_2/N_2, \ldots, S_n \in G_n/N_n\) where \(R_1^1, R_2^2, \ldots, R_n^m\) are elements of cosets \(R_1 N_1, R_2 N_2, \ldots R_n N_n\) and they are mapped by a homomorphism into elements \(S_1, S_2, \ldots, S_n\), respectively, then \(\Gamma\) contains \(p = p_1 p_2 \ldots p_n\) times the representation \(\Gamma'\).

**Proof.** The number of times that a given irreducible representation \(\Gamma^{(\mu)}\) is contained in a representation \(\Gamma'\) is given by:
\[
\alpha_{\mu}' = \frac{n_1 n_2 \ldots n_n}{g_1 g_2 \ldots g_n} \sum_{S_1, S_2, \ldots, S_n} \chi^{(\mu_1)}(S_1) \chi^{(\mu_2)}(S_2) \ldots \chi^{(\mu_n)}(S_n) \chi_{\Gamma_1'}(S_1) \chi_{\Gamma_2'}(S_2) \ldots \chi_{\Gamma_n'}(S_n),
\]
...
where $\mu_1, \mu_2, \ldots, \mu_n$ are irreducible representations of groups $G_1, G_2, \ldots, G_n$, respectively. Note that the tensor product of irreducible representations of groups $G_1, G_2, \ldots, G_n$ corresponds to an irreducible representation of group $G_1 \times G_2 \times \ldots \times G_n$. As each coset $RN_i$ has $|N_i| = n_i$ elements, we have

$$a'_\mu = \frac{1}{g_1g_2\ldots g_np_1p_2\ldots p_n} \sum_{S_1, S_2, \ldots, S_n} [\chi^{(\mu_1)^*}(R_1)\chi^{(\mu_2)^*}(R_2)\ldots\chi^{(\mu_n)^*}(R_n)\chi^{\Gamma_1'}(R_1)$$

$$\chi^{\Gamma_2'}(R_2)\ldots\chi^{\Gamma_n'}(R_n)].$$

On the other hand, the number of times that $\Gamma$ contains $\Gamma^\mu$ is

$$a_\mu = \frac{1}{g_1g_2\ldots g_n} \sum_{R_1R_2\ldots R_n} \chi^{(\mu)^*}(R_1 \times R_2 \times \ldots \times R_n)\chi^{\Gamma}(R_1 \times R_2 \times \ldots \times R_n)$$

$$= \frac{1}{g_1g_2\ldots g_n} \sum_{R_1R_2\ldots R_n} [\chi^{(\mu_1)^*}(R_1)\chi^{(\mu_2)^*}(R_2)\ldots\chi^{(\mu_n)^*}(R_n)\chi^{\Gamma_1'}(R_1)\chi^{\Gamma_2}(R_2)$$

$$\ldots\chi^{\Gamma_n}(R_n)].$$

Therefore

$$a_\mu = p_1p_2\ldots p_na'_\mu.$$ (4)

Thus $\Gamma$ contains $p$ times a representation $\Gamma'$. 

A first application in quantum chemistry can be obtained from the next theorem.

**Theorem 1** Let be $G = G_1 \times G_2 \times \ldots \times G_n = (N_1 \times N_2 \times \ldots \times N_n) \rtimes (H_1 \times H_2 \times \ldots \times H_n)$ a finite group. Then every representation of $H_1 \times H_2 \times \ldots \times H_n$ obtained from a irreducible representation of $G$ contains at most once a given irreducible representation of $H_1 \times H_2 \times \ldots \times H_n$.

**Proof.** The number of times that a given representation $\Gamma = \Gamma_1 \otimes \Gamma_2 \otimes \ldots \otimes \Gamma_n$ of $H = H_1 \times H_2 \times \ldots \times H_n$ which also corresponds to an unique irreducible representation of $G$ contains a given irreducible representation $\nu = \nu_1 \otimes \nu_2 \otimes \ldots \otimes \nu_n$ of the $H$ and $G$ is given by

$$a_\nu = \frac{n_1n_2\ldots n_n}{g_1g_2\ldots g_n} \sum_{S_1, S_2, \ldots, S_n} [\chi^{(\nu_1\otimes\nu_2\otimes\ldots\otimes\nu_n)^*}(S_1 \times S_2 \times \ldots \times S_n)$$

$$\chi^{\Gamma}(S_1 \times S_2 \times \ldots \times S_n)].$$
as $H = H_1 \times H_2 \times ... \times H_n \simeq (G_1 \times G_2 \times ... \times G_n)/(N_1 \times N_2 \times ... \times N_n)$. By lemma 1, every irreducible representation of $G$ corresponds to a unique the representation of $H$, which is an irreducible representation of $H$. Indeed if we consider the inverse of lemma 1 with the restriction that the irreducible representation of $G_1 \times G_2 \times ... \times G_n$ also corresponds to an unique representation of $(G_1 \times G_2 \times ... \times G_n)/(N_1 \times N_2 \times ... \times N_n)$, we have:

$$g_1 g_2 ... g_n \delta_{\nu_1 \nu_2 ... \nu_n} \Gamma_1 \Gamma_2 ... \Gamma_n$$

$$= \sum_{R_1 \times R_2 \times ... \times R_n} \left[ \chi^{(\nu_1 \otimes \nu_2 \otimes ... \otimes \nu_n)}(R_1 \times R_2 \times ... \times R_n) \right] \chi^{(\Gamma_1 \otimes \Gamma_2 \otimes ... \otimes \Gamma_n)}(R_1 \times R_2 \times ... \times R_n)$$

$$= n_1 n_2 ... n_n \sum_{S_1 \times S_2 \times ... \times S_n} \left[ \chi^{(\nu_1 \otimes \nu_2 \otimes ... \otimes \nu_n)}(S_1 \times S_2 \times ... \times S_n) \right] \chi^{(\Gamma_1 \otimes \Gamma_2 \otimes ... \otimes \Gamma_n)}(S_1 \times S_2 \times ... \times S_n).$$

Thus

$$\sum_{S_1 \times S_2 \times ... \times S_n} \left[ \chi^{(\nu_1 \otimes \nu_2 \otimes ... \otimes \nu_n)}(S_1 \times S_2 \times ... \times S_n) \right] \chi^{(\Gamma_1 \otimes \Gamma_2 \otimes ... \otimes \Gamma_n)}(S_1 \times S_2 \times ... \times S_n)$$

$$= \frac{g_1 g_2 ... g_n}{n_1 n_2 ... n_n} \delta_{\nu_1 \nu_2 ... \nu_n} \delta_{\Gamma_1 \Gamma_2 ... \Gamma_n}.$$  

(5)

Therefore:

$$a_\nu = \frac{n_1 n_2 ... n_n}{g_1 g_2 ... g_n} \delta_{\nu_1 \Gamma_1} \delta_{\nu_2 \Gamma_2} ... \delta_{\nu_n \Gamma_n} h_1 h_2 ... h_n;$$

(6)

by using the orthogonality relations for the characters of irreducible representations. Thus $a_\nu = 0$ or $a_\nu = 1$.

This theorem has an immediate physical implications. It indicates in perturbation theory that if the symmetry group of perturbed Hamiltonian is a subgroup $H$ of the group $G$ related to unperturbed Hamiltonian, with $G = N \times H$, the energy levels do not divide itself, since $a_\nu = 0$ or $a_\nu = 1$. The following theorem is useful for the determination of the electronic transitions.

**Theorem 2** Suppose $G = G_1 \times G_2 \times ... \times G_n = (N_1 \times N_2 \times ... \times N_n) \times (H_1 \times H_2 \times ... \times H_n)$ a finite group, $\Gamma^{(\theta)}$ a reducible representation of $G$ which corresponds to an unique representations of $G/N = (G_1 \times G_2 \times ... \times G_n)/(N_1 \times N_2 \times ... \times N_n)$ and $\Gamma^{(\mu)}$ and $\Gamma^{(\nu)}$ irreducible representations of $G$ and $G/N$, respectively.
Then \( \Gamma^{(\nu)} \) corresponds to an unique reducible representation of \( G/N \) and the number of times that \( \Gamma^{(\rho)} \otimes \Gamma^{(\mu)} \) contains the representation \( \Gamma^{(\nu)} \) is given by:

\[
a_{\nu} = \frac{1}{h} \sum_{s_1, s_2, \ldots, s_n} \left[ \chi^{(\mu_1)}(s_1)\chi^{(\rho_1)}(s_1)\chi^{(\nu_1)}(s_1)\chi^{(\mu_2)}(s_2)\chi^{(\rho_2)}(s_2)\chi^{(\nu_2)}(s_2) \right. \\
\left. \quad \ldots \chi^{(\mu_n)}(s_n)\chi^{(\rho_n)}(s_n)\chi^{(\nu_n)}(s_n) \right],
\]

where \( h = |H| = h_1h_2\ldots h_n, s_i \) is an element of the subgroup \( H_i \) and \( \chi^{(\mu_i)}, \chi^{(\rho_i)}, \chi^{(\nu_i)} \) are characters associated to representations \( \Gamma^{(\mu_i)}, \Gamma^{(\rho_i)}, \Gamma^{(\nu_i)} \), respectively, of the groups \( G_i \) and \( G_i/N_i \). In particular if \( \Gamma^{(\rho)} \) is a representation that satisfies the conditions of the lemma 2, the number of times \( a_{\nu} \) that \( \Gamma^{(\rho)} \otimes \Gamma^{(\mu)} \) contains the representation \( \Gamma^{(\nu)} \) is given by \( a_{\nu} = pa_{\nu} \).

**Proof.** Since \( \Gamma^{(\rho)} \) is a representation of \((G_1 \times G_2 \times \ldots \times G_n)/(N_1 \times N_2 \times \ldots \times N_n)\) and \( G \) is a semidirect product of groups, then \( \Gamma^{(\rho)} \) corresponds to an unique representation of \( H_1 \times H_2 \times \ldots H_n \), as \( H_1 \times H_2 \times \ldots H_n \simeq (G_1 \times G_2 \times \ldots \times G_n)/(N_1 \times N_2 \times \ldots \times N_n) \). Besides, \( \Gamma^{(\rho)} \) corresponds to an unique reducible representation of the \( G/N \), because if \( \Gamma^{(\rho)} \) were irreducible representation, we would have a contradiction by lemma 1. Similarly, \( \Gamma^{(\mu)} \) and \( \Gamma^{(\nu)} \) are also irreducible representations of the \((G_1 \times G_2 \times \ldots \times G_n)/(N_1 \times N_2 \times \ldots \times N_n)\). Furthermore the tensor product of irreducible representations is also an irreducible representation. Thus

\[
a_{\nu} = \frac{1}{h} \sum_{s_1, s_2, \ldots, s_n} \left[ \chi^{(\mu_1 \otimes \mu_2 \otimes \ldots \otimes \mu_n)}(s_1 \times s_2 \times \ldots \times s_n) \chi^{(\rho_1 \otimes \rho_2 \otimes \ldots \otimes \rho_n)}(s_1 \times s_2 \times \ldots \times s_n) \chi^{(\nu_1 \otimes \nu_2 \otimes \ldots \otimes \nu_n)}(s_1 \times s_2 \times \ldots \times s_n) \right] \\
= \frac{1}{h} \sum_{s_1, s_2, \ldots, s_n} \left[ \chi^{(\mu_1)}(s_1)\chi^{(\rho_1)}(s_1)\chi^{(\nu_1)}(s_1)\chi^{(\mu_2)}(s_2)\chi^{(\rho_2)}(s_2)\chi^{(\nu_2)}(s_2) \right. \\
\left. \ldots \chi^{(\mu_n)}(s_n)\chi^{(\rho_n)}(s_n)\chi^{(\nu_n)}(s_n) \right].
\]

If \( \Gamma^{(\rho)} \) satisfies the conditions of the lemma 2,

\[
a'_{\nu} = \frac{1}{h} \sum_{s_1, s_2, \ldots, s_n} \left[ \chi^{(\mu_1)}(s_1)p_1\chi^{(\rho_1)}(s_1)\chi^{(\nu_1)}(s_1)\chi^{(\mu_2)}(s_2)p_2\chi^{(\rho_2)}(s_2)\chi^{(\nu_2)}(s_2) \right. \\
\left. \ldots \chi^{(\mu_n)}(s_n)p_n\chi^{(\rho_n)}(s_n)\chi^{(\nu_n)}(s_n) \right] \\
= p_1p_2\ldots p_na_{\nu}.
\]
Hence the theorem is proved. ■

This theorem can be useful for the selection rules. If \( \theta_k^{(\rho)}, \psi_i^{(\mu)} \) and \( \phi_j^{(\nu)} \) are basis function for the representations \( \Gamma^{(\rho)}, \Gamma^{(\mu)} \) and \( \Gamma^{(\nu)} \), respectively, we can determine whether the products or linear combinations of these products belong to \( \nu \)-th representation through characters of the subgroup \( H_1 \times H_2 \times \ldots \times H_n \) of \( G \). If \( a_\nu \neq 0 \) transitions occurs between energy levels \( \mu \) and \( \nu \). We now show how to obtain projection operators in this context according to the Van Vleck procedure with the basis function generating machine [7].

**Theorem 3** Let \( \Gamma^{(\rho)} = \Gamma^{(\rho_1)} \otimes \Gamma^{(\rho_2)} \otimes \ldots \otimes \Gamma^{(\rho_n)} \) be an irreducible representation of \( (G_1 \times G_2 \times \ldots \times G_n)/(N_1 \times N_2 \times \ldots \times N_n) \) of dimension \( d_\rho \), \( G = G_1 \times G_2 \times \ldots \times G_n = (N_1 \times H_1) \times (N_2 \times H_2) \times \ldots (N_n \times H_n) \) a finite group that has \( m \) non-equivalent irreducible representations and \( O_{R_i} \) an operator associated to element \( R_i \in G_i \). Thus

(i) the action of the operator

\[
P^{(\rho)}_{\lambda_1 \lambda_2 \ldots \lambda_n k_1 k_2 \ldots k_n} = \frac{d_{\rho_1} d_{\rho_2} \ldots d_{\rho_n}}{h_1 h_2 \ldots h_n} \sum_{(R_1 R_2 \ldots R_n) \in H \leq G} \Gamma^{(\rho_1)}_{\lambda_1 k_1} \Gamma^{(\rho_2)}_{\lambda_2 k_2} \ldots \Gamma^{(\rho_n)}_{\lambda_n k_n} O_{R_1} O_{R_2} \ldots O_{R_n}
\]

(9)
on a basis-function of the representation space results in 0 unless it belongs to the \( k_1 k_2 \ldots k_n \)-th row of the irreducible representation \( \Gamma^{(\rho)} \) which also corresponds to an unique irreducible representation of \( H_1 \times H_2 \times \ldots \times H_n \), where \( |H_i| = h_i \).

(ii) the operator \( P^{(\rho)}_{k_1 k_2 \ldots k_n k_1 k_2 \ldots k_n} \) projects only part of the function

\[
\Phi = \sum_{\rho_1=1}^{m_1} \sum_{\rho_2=1}^{m_2} \ldots \sum_{\rho_n=1}^{m_n} \sum_{k_1=1}^{d_{\rho_1}} \sum_{k_2=1}^{d_{\rho_2}} \ldots \sum_{k_n=1}^{d_{\rho_n}} \phi^{(\rho_1)}_{k_1} \phi^{(\rho_2)}_{k_2} \ldots \phi^{(\rho_n)}_{k_n}
\]

(10)
that belongs to the \( k_1 k_2 \ldots k_n \)-th row of the irreducible representation \( \Gamma^{(\rho)} \).

(iii) the operator

\[
P^{(\rho)} = \sum_{k_1} \sum_{k_2} \ldots \sum_{k_n} P^{(\rho)}_{k_1 k_2 \ldots k_n k_1 k_2 \ldots k_n}
\]

\[
= \frac{d_{\rho_1} d_{\rho_2} \ldots d_{\rho_n}}{h_1 h_2 \ldots h_n} \sum_{R_1} \sum_{R_2} \ldots \sum_{R_n} \chi^{(\rho_1)}(R_1) \chi^{(\rho_2)}(R_2) \ldots \chi^{(\rho_n)}(R_n) O_{R_1 \times R_2 \times \ldots \times R_n}
\]

\[
= \frac{d_{\rho_1} d_{\rho_2} \ldots d_{\rho_n}}{h_1 h_2 \ldots h_n} \sum_{R_1} \sum_{R_2} \ldots \sum_{R_n} \chi^{(\rho_1)}(R_1) \chi^{(\rho_2)}(R_2) \ldots \chi^{(\rho_n)}(R_n) O_{R_1 \times R_2 \times \ldots \times R_n}
\]
projects the arbitrary function $\Phi$ defined above in a function $\phi^{(p)}$ belonging to the $p$-th irreducible representation of the groups $G_1 \times G_2 \times \ldots \times G_n$ and $H_1 \times H_2 \times \ldots \times H_n$.

**Proof.** For the item (i), we have that operator

$$P_{\lambda_k}^p = \frac{d_p}{h} \sum_R \Gamma_{\lambda_k}^{(p)} (R) O_R$$

(11)
can be written as

$$P_{\lambda_1 \lambda_2 \ldots \lambda_n}^{(p_1 \otimes p_2 \otimes \ldots \otimes p_n)} = \frac{d_{p_1} d_{p_2} \ldots d_{p_n}}{h_{12} \ldots h_n} \sum_{R_1 \times R_2 \times \ldots \times R_n} \left[ \Gamma_{\lambda_1 \lambda_2 \ldots \lambda_n}^{(p_1 \otimes p_2 \otimes \ldots \otimes p_n)} (R_1 \times R_2 \times \ldots \times R_n) \right] \sum_{R_1} \Gamma_{\lambda_1}^{(p_1)} (R_1) \Gamma_{\lambda_2}^{(p_2)} (R_2) \ldots \Gamma_{\lambda_n}^{(p_n)} (R_n) O_{R_1 R_2 \ldots R_n}.$$  

By lemma 1 we have that $\Gamma^{(p)}$ corresponds to an unique irreducible representation of $G_1 \times G_2 \times \ldots \times G_n$ and $H_1 \times H_2 \times \ldots \times H_n$. Then we can use the orthogonality theorem for the irreducible representations of the $H_1 \times H_2 \times \ldots \times H_n$, resulting in

$$P_{\lambda_1 \lambda_2 \ldots \lambda_n}^{(p_1 \otimes p_2 \otimes \ldots \otimes p_n)} \varphi_{l_1}^{(i_1)} \varphi_{l_2}^{(i_2)} \ldots \varphi_{l_n}^{(i_n)} = P_{\lambda_1}^{(p_1)} \varphi_{l_1}^{(i_1)} P_{\lambda_2}^{(p_2)} \varphi_{l_2}^{(i_2)} \ldots P_{\lambda_n}^{(p_n)} \varphi_{l_n}^{(i_n)} = \delta_{l_1 \lambda_1}^{(p_1)} \delta_{l_1 \lambda_1}^{(p_1)} \delta_{l_2 \lambda_2}^{(p_2)} \delta_{l_2 \lambda_2}^{(p_2)} \ldots \delta_{l_n \lambda_n}^{(p_n)} \delta_{l_n \lambda_n}^{(p_n)} \varphi_{l_1}^{(i_1)} \varphi_{l_2}^{(i_2)} \ldots \varphi_{l_n}^{(i_n)}$$

(12)

For the item (ii), taking $\lambda_1 = k_1, \lambda_2 = k_2, \ldots, \lambda_n = k_n$ in the eq. (12), we have

$$P_{k_1 k_2 \ldots k_n}^{(p_1 \otimes p_2 \otimes \ldots \otimes p_n)} \varphi_{l_1}^{(i_1)} \varphi_{l_2}^{(i_2)} \ldots \varphi_{l_n}^{(i_n)} = P_{k_1}^{(p_1)} \varphi_{l_1}^{(i_1)} P_{k_2}^{(p_2)} \varphi_{l_2}^{(i_2)} \ldots P_{k_n}^{(p_n)} \varphi_{l_n}^{(i_n)} = \delta_{k_1 \lambda_1}^{(p_1)} \delta_{k_2 \lambda_2}^{(p_2)} \ldots \delta_{k_n \lambda_n}^{(p_n)} \delta_{l_1 \lambda_1}^{(p_1)} \delta_{l_2 \lambda_2}^{(p_2)} \ldots \delta_{l_n \lambda_n}.$$  

Therefore

$$P_{k_1 k_2 \ldots k_n}^{(p_1 \otimes p_2 \otimes \ldots \otimes p_n)} = \phi_{\lambda_1}^{(p_1)} \phi_{\lambda_2}^{(p_2)} \ldots \phi_{\lambda_n}^{(p_n)}.$$  

9
In the item (iii), we have

\[ P^{(\rho)} \Phi = \sum_{k_1} \sum_{k_2} \cdots \sum_{k_n} P^{(\rho_1)}_{k_1 k_1} P^{(\rho_2)}_{k_2 k_2} \cdots P^{(\rho_n)}_{k_n k_n} \Phi \]

\[ = \frac{d_{\rho_1} d_{\rho_2} \cdots d_{\rho_n}}{h_1 h_2 \cdots h_n} \sum_{R_1 \in H_1 \leq G_1} \sum_{R_2 \in H_2 \leq G_2} \cdots \sum_{R_n \in H_n \leq G_n} \sum_{k_1 k_1 \cdots k_n} \left[ \Gamma^{(\rho_1)}_{k_1 k_1} (R_1) \Gamma^{(\rho_2)}_{k_2 k_2} (R_2) \Gamma^{(\rho_n)}_{k_n k_n} (R_n) \Phi \right] \]

\[ = \frac{d_{\rho_1}}{h_1} \sum_{R_1} \chi^{(\rho_1)} (R_1) \sum_{\rho_1 = 1} \phi^{(\rho_1)}_{1} O_{R_1} \frac{d_{\rho_2}}{h_2} \sum_{R_2} \chi^{(\rho_2)} (R_2) \sum_{\rho_2 = 1} \phi^{(\rho_2)}_{2} O_{R_2} \cdots \frac{d_{\rho_n}}{h_n} \sum_{R_n} \chi^{(\rho_n)} (R_n) \sum_{\rho_n = 1} \phi^{(\rho_n)}_{n} O_{R_n} \]

\[ = \phi^{(\rho_1)} \phi^{(\rho_2)} \cdots \phi^{(\rho_n)}, \]  

(13)

as claimed.

It is interesting to note that the item (i) provides a recipe for to generate all the patterns of a given function related to an irreducible representation of \( G_1 \times G_2 \times \cdots \times G_n \) and \( H_1 \times H_2 \times \cdots \times H_n \), simultaneously, in accordance with the Van Vleck scheme. The item (ii) shows how it is possible to obtain from an arbitrary function an element that belongs to the \( k_1 k_2 \cdots k_n \)-th row of the irreducible representation. In order to show how this approach can be extended we consider the next lemma.

**Lemma 3** Let \( G = G_1 \times G_2 \times \cdots \times G_n = (N_1 \times N_2 \times \cdots \times N_n) \times (H_1 \times H_2 \times \cdots \times H_n) \) be a finite group. Then every subgroup of \( H_1 \times H_2 \times \cdots \times H_n \) is of the form \( (G'_1 \times G'_2 \times \cdots \times G'_n)/(N_1 \times N_2 \times \cdots \times N_n) \) with \( N_1 \times N_2 \times \cdots \times N_n \leq G'_1 \times G'_2 \times \cdots \times G'_n \leq G_1 \times G_2 \times \cdots \times G_n \).

**Proof.** As \( G_1 \times G_2 \times \cdots \times G_n \) is a semidirect product of groups, we have:

\[ H_1 \times H_2 \times \cdots \times H_n \cong \frac{G_1 \times G_2 \times \cdots \times G_n}{N_1 \times N_2 \times \cdots \times N_n}. \]  

(14)

By using the correspondence theorem and first isomorphism theorem we have that every subgroup of the \( (G_1 \times G_2 \times \cdots \times G_n)/(N_1 \times N_2 \times \cdots \times N_n) \) is of the form \( (G'_1 \times G'_2 \times \cdots \times G'_n)/(N_1 \times N_2 \times \cdots \times N_n) \) where \( N_1 \times N_2 \times \cdots \times N_n \leq G'_1 \times G'_2 \times \cdots \times G'_n \leq G_1 \times G_2 \times \cdots \times G_n \), as desirable.

With this result the following theorem can be proved.
Theorem 4 Every irreducible representation of the a subgroup of the
\( H = H_1 \times H_2 \times \ldots \times H_n \) with \( G = (N_1 \times N_2 \times \ldots \times N_n) \times (H_1 \times H_2 \times \ldots \times H_n) \) corresponds to an unique irreducible representation of the a group \( G_1' \times G_2' \times \ldots \times G_n' \) with \( N_1 \times N_2 \times \ldots \times N_n \leq G_1' \times G_2' \times \ldots \times G_n' \leq G_1 \times G_2 \times \ldots \times G_n \).

Proof. As every irreducible representation of the \((G_1' \times G_2' \times \ldots \times G_n')/(N_1 \times N_2 \times \ldots \times N_n)\) corresponds to an unique irreducible representation of the \( G_1' \times G_2' \times \ldots \times G_n' \) by using the lemma 1, the theorem follows of the lemma 3.

This last theorem shown that the analysis developed previously can be continued for the subgroups of the subgroups of the semidirect product.

3 Applications

Functional roles played by structural symmetry in macromolecules has been investigated \[39\]. Symmetry is essential for allosteric regulation according to model proposed by Monod et al \[40\]. The association between protomers in an oligomer may be such as to confer an element of symmetry on the molecule is the first assumption of the model. Another assumption is that the symmetry of each set of stereospecific receptors is the same as the symmetry of the molecule. Besides, when the protein goes from one state to another state, its molecular symmetry is conserved. It is shown that symmetrical oligomeric complexes with two or more identical subunits are formed by most of the soluble and membrane-bound proteins found in living cells and nearly all structural proteins are symmetrical polymers of hundred to millions of subunits \[39\]. The glycolate oxidase enzyme is an example of such proteins.

In this section we consider the dihedral group \( D_4 \) corresponding to symmetry of the glycolate oxidase enzyme. The group \( G = D_4 \times D_4 \) is formed by elements

\[
G = \{ E \times E, E \times C_2(x), C_2(x) \times E, C_2(x) \times C_2(x), \\
E \times C_2(y), C_2(y) \times E, C_2(y) \times C_2(y), E \times C_2(z) \\
C_2(z) \times E, C_2(z) \times C_2(z), C_2(x) \times C_2(y), C_2(y) \times C_2(x) \\
C_2(x) \times C_2(z), C_2(z) \times C_2(x), C_2(y) \times C_2(z), C_2(z) \times C_2(y) \}.
\]
Consider the following subgroups
\[ N_1 \times N_2 = \{ E \times E, E \times C_2(x), C_2(x) \times E, C_2(x) \times C_2(x) \}, \]
\[ H_1 \times H_2 = \{ E \times E, E \times C_2(y), C_2(y) \times E, C_2(y) \times C_2(y) \}. \]
We have that
\[ G = D_4 \times D_4 = (N_1 \times N_2) \rtimes (H_1 \times H_2) \]
and therefore
\[ \frac{D_4 \times D_4}{N_1 \times N_2} \cong H_1 \times H_2. \]
The subgroup \( H_1 \times H_2 \) has four non-equivalent irreducible representations \( \Gamma^{(1)}, \Gamma^{(2)}, \Gamma^{(3)}, \Gamma^{(4)} \) with characters

|        | \( E \times E \) | \( E \times C_2(y) \) | \( C_2(y) \times E \) | \( C_2(y) \times C_2(y) \) |
|--------|------------------|------------------|------------------|------------------|
| \( \Gamma^{(1)} \) | 1                | -1               | 1                | 1                |
| \( \Gamma^{(2)} \) | 1                | -1               | 1                | -1               |
| \( \Gamma^{(3)} \) | 1                | 1                | -1               | -1               |
| \( \Gamma^{(4)} \) | 1                | -1               | -1               | 1                |

We can note that the cosets
\[ C_1 = \{ E \times E, E \times C_2(x), C_2(x) \times E, C_2(x) \times C_2(x) \} \]
\[ C_2 = \{ E \times C_2(y), E \times C_2(z), C_2(x) \times C_2(y), C_2(x) \times C_2(z) \} \]
\[ C_3 = \{ C_2(y) \times E, C_2(y) \times C_2(x), C_2(z) \times E, C_2(z) \times C_2(x) \} \]
\[ C_4 = \{ C_2(y) \times C_2(y), C_2(y) \times C_2(z), C_2(z) \times C_2(y), C_2(z) \times C_2(z) \} \]
are mapped by a homomorphism into elements \( E \times E, E \times C_2(y), C_2(y) \times E, C_2(y) \times C_2(y) \), respectively. It is easy to verify that these irreducible representations also corresponds to an unique irreducible representations of the \( D_4 \times D_4 \).

4 Conclusions

The concept of inner semidirect product can be explored in the context of the representations of finite groups and it is possible to derive results with a direct physical interpretation in quantum chemistry. In this approach, we
obtained some general theorems using the orthogonality relations, the isomorphism theorems and the correspondence theorem. In the scenario of the perturbation theory, we show that if the symmetry group of the Hamiltonian is a subgroup of the unperturbed Hamiltonian, the energy levels do not divided itself. Conditions for transitions between energy levels were determined as well as projection operators and basis functions. Importantly, our results are general and apply to composite systems since we consider the direct product of groups and therefore the tensor product of representations. Finally, we present an example using the dihedral group corresponding to symmetry of the glycolate oxidase enzyme. As perspectives, this study can be conducted using the outer semidirect product groups and its implications in quantum chemistry may be analyzed.

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