Review

Didactic interpretation of group theory applied in crystals
Interpretación didáctica de la teoría de grupos aplicada en cristales

V. H. Sierra[a], Cristhian Aguirre[b], José Barba-Ortega[b]

[a] *Grupo de Física Teórica y Desarrollo de Software, Universidad Distrital Francisco José de Caldas, Bogotá D.C, Colombia. orcid.org/0000-0002-4137-9702*
[b*] *Grupo de Física Mesoscópica, Departamento de Física, Universidad Nacional de Colombia, Bogotá D.C, Colombia. orcid.org/0000-0003-3415-1811*

ABSTRACT

Keywords:
Group Theory
Hamiltonian
Symmetry

The determination of the Hamiltonian in a molecule or a crystal can become a very complicated problem. However, symmetrical considerations of the problem may significantly simplify it. Therefore it is important to find the greatest number of crystal symmetries. This point highlights the importance of group theory as a calculation tool which synthesizes all crystal properties such as rotations, inversions and reflections. However, the study completed in many books concerning this subject is rather confusing and complicated for graduate students of Physics to understand due to the abstract nature of theoretical method and its relationship with the Hamiltonian. This paper encourages the execution of a didactic study, as well as the inclusion of detailed principles governing the use of the method. It is further illustrated through a detailed example of an orthorhombic crystal, subsequently establishing the isomorphism between the algebra used in group theory and the corresponding matrix representation, leading to a reduction in the Hamiltonian and its calculations.

RESUMEN

Palabras Clave:
Simetría
Hamiltoniano
Teoría de grupos.

La determinación del Hamiltoniano de una molécula o un cristal puede llegar a ser un problema muy complicado; sin embargo, las consideraciones de simetría sobre el problema pueden llegar a simplificarlo de manera sustancial. Razón por la cual, es pertinente buscar el mayor número de simetrías de un cristal. En este punto, se realza la importancia de la teoría de grupos como herramienta de cálculo, pues a través de ésta, se sintetizan todas las propiedades del cristal: las rotaciones, las inversiones y las reflexiones. Empero, el estudio realizado por muchos libros acerca de esta temática es demasiado confuso y complicado para los estudiantes de Licenciatura en Física, debido a la naturaleza abstracta del método de la teoría, y las relaciones que éste tiene con el Hamiltoniano. Lo anterior, motiva la realización de un estudio didáctico, así como detallado de los principios que rigen el uso del método. Además, se ilustra a través de un ejemplo detallado para el caso de un cristal ortorrómbico, procediendo a establecer los isomorfismos entre el álgebra utilizada en la teoría de grupos y la correspondiente representación de matrices, que permita efectuar la reducción del Hamiltoniano y los cálculos correspondientes.

Introduction

This paper shows an application of group theory to the solid state, studying the Hamiltonian in an atomic perspective. In order to realize this method, the main characteristics of an orthorhombic crystal (OC) are shown in section 2. In section 3, the symmetry operations of the crystal, how they make a group and the operation table of the group are analyzed and displayed.

The following paragraph provides some important mathematical detail, relating to the concept of classification and isomorphisms with linear algebra. In the final section, the concept of reduced representation is discussed, and how it establishes conditions that help in the considerable simplification of the Hamiltonian because of its close relationship with the system's symmetry.

The orthorhombic crystal (O. C.) When analyzing the main characteristic that separates a matter's solid state from the other states, the spacing and organization of the substance's atom is taken into account. Therefore, information on this organization should clarify the explanation of the material's behaviors and properties. Due to the small spaces between the atoms, electrostatic forces prove significant by reducing the system's disorder.

Furthermore, it should be noted that not all substances have the same chemical components; their organizations may vary considerably, however, almost all solids have a particular molecular organization, or crystal, which to this effect is determined as:

"[A crystal is] composed of atoms arranged in a pattern that is repeated periodically in three dimensions" [1]

As the crystal's structure appears identical throughout the whole material, we may consider the crystal as a "brick" with which a material is constructed. This concept is also often referred to as a crystalline network [2], which can be made up of different shapes and sizes of the "bricks". In general, the differences do not lie in the components of the network, but in the length and angles that form the side edges, which are called primitive axes a1, a2 y a3 [3]. One of these crystals is the O. C. in which, despite the fact that all the angles formed by their sides are at 900, their sides are all different.

The symmetries of a O. C. Concerning symmetry, it is established that:

"An object or figure is said to have symmetry if some movement of the figure or operation on the figure leaves it in a position indistinguishable from its original position" [4]
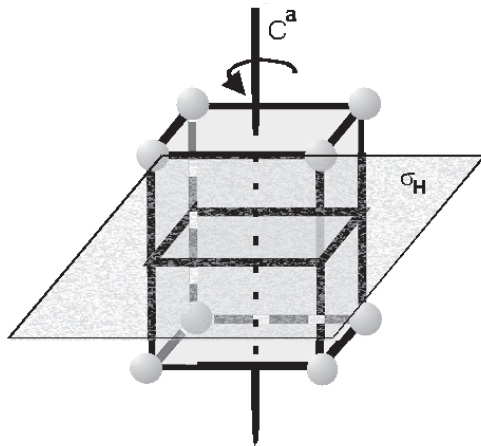
Below, an O. C. is shown:

Figure 1. An orthorhombic crystal formed by the same atoms in each corner, with three axes of rotation Ca and three planes of reflection σ.

The O. C. presents the following types of symmetry:
Identity operation [5]: where the crystal remains in its initial position.

Symmetry rotation axis of order n: For the O. C. there are three C2, perpendicular to the faces of the crystal and denoted in the figure by C_2^a, C_2^b and C_2^c. The order 2 means that it only supports the rotation of 00 and 1800.

Plane of symmetry: The O. C. has three planes of symmetry, two verticals σv and one horizontal σh, all of them parallel to two crystal faces.

Center of symmetry: The center of the crystal coincides with a center of symmetry.

Alternating axis of symmetry of order n [6]: The O. C. has three of such axes, each one associated to an axis and a perpendicular symmetry plane. They are denoted as S_2^a, S_2^b and S_2^c respectively.

However, two of these alternating axes S_2^b and S_2^c (those related to C^a and C^b), generate a configuration that can be retrieved through other symmetry operations. These operations have some special properties. For example, suppose the operation of center of symmetry ***i***. For the O. C. this operation is equal to the alternating axis symmetry operation with respect to C^a, and can be obtained by applying two symmetry operations consecutively, in the following way:
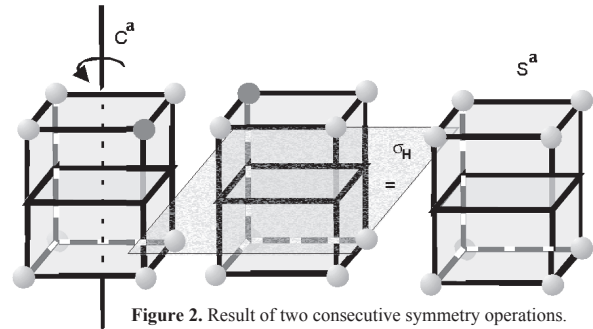
$$C_2^a \otimes \sigma_h = S_2^a \qquad (1)$$

Figure 2. Result of two consecutive symmetry operations.

Where $\otimes$ is used to specify a binary operation, because the mathematical meaning of performing a symmetry operation followed by the other (it could be a sum or a multiplication) is actually unknown. To that effect, many of the symmetry operations can be obtained by applying two symmetry operations consecutively.

The *Cayley table* for the symmetry operations of the O. C. is shown below.

Table I Cayley table of the O. C.

3	**E**	**C^a**	**C^b**	**C^c**	**σ_h**	**σ^a**	**σ^b**	**S**
E	E	C^a	C^b	C^c	σ_h	σ^a	σ^b	S_a
C^a	C^a	E	C^c	C^b	S^a	σ^b	σ^a	σ_h
C^b	C^b	C^c	E	C^a	σ^b	S^a	σ_h	σ^a
C^c	C^c	C^b	C^a	E	σ^a	σ_h	S^a	σ^b
σ_h	σ_h	S^a	σ^b	σ^a	E	C^c	C^b	C^a
σ^a	σ^a	σ^b	S^a	σ_h	C^c	E	C^a	C^b
σ^b	σ^b	σ^a	σ_h	S^a	C^b	C^a	E	C^c
S^a	S^a	σ_h	σ^a	σ^b	C^a	C^b	C^c	E

C^a Rotation operation. σ_h Horizontal reflection operation.

σ^a Vertical reflection operation S^a Alternating rotation axis.

69

It is observed that by using these eight elements, all possible symmetry operations of the system are considered (remember that $S^a = i$). Therefore, this set of symmetry operations fulfills the properties of and thus forms a group, as explained below:

1. It is closed under the defined operation. In our example, all combination of operation results are included in the table.

2. It fulfills the associative property: It is clear to see that the elements of this table fulfill the property.

3. It has a neutral element: In the crystal in question, it is the identity operation.

4. Existence of the opposite element: in the case of the crystal, it is the same symmetry operation.
Moreover, due to the fact that the addition table is symmetric diagonally across, the group is commutative or Abelian [7].

Some additional mathematical elements To understand the relationship between the symmetry and the system's energy, it is necessary to transform the information obtained in the previous section into matrix form. To do this, two concepts must be taken into account, the first being related with class, which indicates that: P and Q are to be two members of a group. *They are said to be members of the same class if they are related by the equation.*

$$Q = X^{-1}PX \qquad (2)$$

Where X is any member of the group, including P and Q [5]. Since the group of an O. C. is commutative, the group has eight classes.

The next important concept is the concept of *irreducible representation of a group* [5]. It makes it possible to determine that some mathematical elements can behave in the same way as the elements of table 1.

An example of this concept would be the 3x3 diagonal matrices; their elements in the diagonal can only be 1 or -1; if the usual multiplication of matrices is done (that is, of rows by columns), a matrix that complies with the initial characteristics is again produced.

To illustrate, the matrices associated with the operation described in (1) are:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \times \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad (3)$$

However, this is not the only possible representation; there are other elements between which an isomorphism can be proposed [7], that is, a one-to-one correspondence between the elements in the Cayley table and other mathematical elements. In group theory, there are two types of representations: the reducible representations, which are the most compact, non-composite representations. In order to know how many reducible representations a group will have, the following theorem is used:

The number of irreducible representations of a finite group is equal to the number of p classes [8].

Therefore, this group has eight reducible representations. Aside from the usual inaccurate representation [5], we can propose the following representation :

$$E = C^a = C^b = C^c = 1 \qquad (4)$$

$$\sigma_h = \sigma^a = \sigma^b = S^a = 1 \qquad (5)$$

This complies with the Cayley table cannot be simplified further. On the other hand, the one presented in (3) can be written as:

$$\sigma_v = \begin{pmatrix} \Gamma_1(\sigma_v) & 0 & 0 \\ 0 & \Gamma_1(\sigma_v) & 0 \\ 0 & 0 & \Gamma_2(\sigma_v)1 \end{pmatrix} \qquad (6)$$

It is known that there are eight reducible representations in the system, but what do the dimensions of these representations look like? What will be the order of the matrix representations? In that vein, it was found that there are two representations of dimension 1: the inaccurate one, and the one shown in equations (5) and (6). If the following theorem is analyzed:

The sum of the squares of the dimensions dγ of the irreducible representations of a finite group is equal to the order of the group [8]:

$$\sum_{\gamma=1}^{p} d_\gamma^2 = g \qquad (7)$$

Since the order of the group is 8, there is no other option than for the dimensions of the *irreducible representations* to be one-dimensional.

At this point, one has all the mathematical information necessary to determine the shape of the Hamiltonian.

It is important to keep in mind that, although there are eight irreducible representations, (but only four distinct ones), a representation will be written in the following way:

$$\Gamma = 2\Gamma^1 + 2\Gamma^2 + 2\Gamma^3 + 2\Gamma^4 \qquad (8)$$

This equation is a useful result, extracted from group theory. Here Γ^1 is a type of irreducible representation. A way to find the Hamiltonian of the system when the matter is in solid state is through the **Ritz method** [8], which consists of proposing functions that allows one to discover the energy of the system. In doing so, the energy of the system can be defined by:
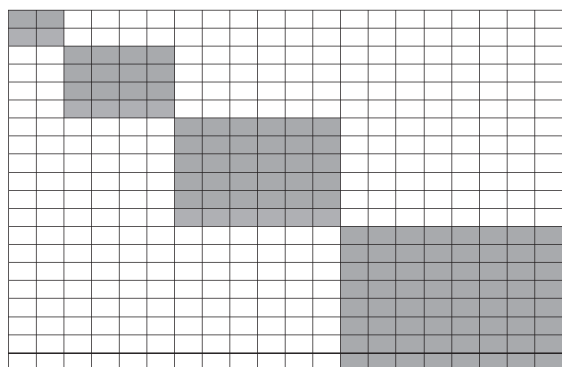
$$\det\left|H_{ij} - \lambda S_{ij}\right| = 0 \qquad (9)$$

Where Sij are *overlap integrals* [5] and the determinant is the secular determinant [8]. The Hamiltonian is a de facto symmetric operator if there are symmetries within the system, and its elements not in the diagonal line are made equal to the overlap integrals. To know which elements survive in the determinant (9), the representation (8) can be used, which demonstrates how the system is in degeneration, given the supra-indices of the equation.

Then, the determinant will consist of two non-degenerate functions, two that are two, three and four times degenerate, respectively. Thus, when defining the matrix of the determinant, it will have twenty rows and columns; the secular determinant will have the shape shown in equation (10), where the shaded spaces are the components of the matrix that are different from zero.

Conclusions

In the present work, an analysis of the symmetry operations of a O. C. was made; and with these symmetry operations a Cayley table was proposed and it was verified that the operations belonged to a group.

Later, isomorphisms were discovered, with the matrix algebra and the irreducible representations associated with the group were found. Finally, with these results, relationships were established with the functions that determine the energy of the system, and with this information a substantial simplification of the secular determinant of the system was made.

It is observed that there is a significant reduction in the degree of difficulty of the secular determinant, since 70% of its components are already eliminated, which demonstrates the usefulness of having the information of symmetry operations and all other information provided by the group theory. This demonstrates to the students the importance of group theory in relation to the physical aspects of the system

References

[1] C. S. Barret, *Structure of metals,* 2nd ed. New York: McGraw Hill, 1952.

[2] C. Kittel, *Introducción a la física del estado sólido,* 3ra ed., España: Editorial Reverte, 1997.

[3] C. Kittel, *Introducción a la física del estado sólido,* 3ra ed., España: Editorial Reverte, 1997, pp. 7.

[4] D. Sands, *Introducción a la cristalografía,* 1ra ed. España: Editorial Reverte, 1993.

[5] A. Nussbaum, *Teoría de grupos aplicada para químicos, físicos e ingenieros,* 1ra ed. España: Editorial Reverte, 1974.

[6] I. N. Levine, *Química Cuántica,* 5ta ed. Madrid: Pearson Educación S.A. 2001

[7] P. S. Alexandroff, *Introducción a la teoría de grupos,* 2da ed. Buenos Aires: Editorial Universitaria de Buenos Aires. 1965

[8] L. Mariot, *Group theory and solid state physics.* 1st ed. Englewood Cliffs: Prentice-Hall, 1962.

(10)