A Numerical Method to Obtain a Symmetry-Adapted Basis from the Hamiltonian or a Similar Matrix

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A practical method is proposed which using the hamiltonian matrix, or some other matrix corresponding to any operator with identical symmetry properties, enables one to obtain the transformation matrix, from the given basis to a symmetry-adapted basis.

The method is very suitable for applications in the fields of molecular orbital and force constant calculations.

Introduction

In problems of molecular orbital calculation and force constant determination it is extremely useful to work with symmetry adapted basis vectors [3, 5]. These vectors belong to the irreducible representations of the group of symmetry operations which commute with the hamiltonian operator, and usually the transformation matrices are derived manually by the use of the character tables.

In fully automatized computer programs used for these problems it is desirable to reduce such manual computations and, at the same time, to minimize the input data.

In order to decrease the probability of human errors in such calculations and for the more estetical reason of supplying the machine only the truly necessary quantities which define the problem a new method is proposed.

In this method, the properties of the hamiltonian matrix, or any other matrix which commute with all and only the symmetry operations which leave the hamiltonian invariant, are exploited, and a unitary matrix which transforms the given basis into a symmetry adapted basis is obtained. Suitable matrices which can be treated by the present method are for instance: the nuclear attraction matrix in molecular orbital calculations and the \( \text{WILSON } G^{-1} + F \) matrix in force constant calculations.
A given basis is supposed to contain equivalent and complete sets of vectors. Such complete sets satisfy the following theorems [2, 5]:

a) The numbers of equivalent vectors in a given set cannot exceed the order \( g \) of the group.

b) A set of equivalent vectors can give no more than \( n_s \) vectors which transform according to the irreducible representation \( \Gamma_s \) of dimension \( n_s \). Each of the \( n_s \) possible vectors will have \( n_s \) partners.

In addition the following theorem can be proved: “The structure of the matrix obtained from a set of equivalent vectors with any operator \( \mathcal{P} \) which commutes with all and only the symmetry operations \( R \) of a group used to generate, from a given vector \( \varphi \), the complete set, is independent of the particular operator.”

The proof of this last theorem, which will elucidate what is intended as the structure of a matrix, follows.

Let us consider a matrix whose first row elements \( P_{1,j} \) are given by

\[
P_{1,j} = \langle E \varphi \mid \mathcal{P} \mid R_j \varphi \rangle.
\]

(1)

Here, \( E \) is the identity operation, \( R_j \) one of the symmetry operation, \( R_j \varphi = \varphi_j \) is one of the equivalent vectors and \( \mathcal{P} \) is the operator defined in the above theorem.

The \( k \) row of the \( P \) matrix has the elements \( \langle R_k \varphi \mid \mathcal{P} \mid R_j \varphi \rangle \), which, because \( \mathcal{P} \) commutes with all \( R \), can be expressed as follows:

\[
\langle R_k \varphi \mid \mathcal{P} \mid R_j \varphi \rangle = \langle \varphi \mid R_k^{-1} \mathcal{P} \mid R_j \varphi \rangle = \langle \varphi \mid \mathcal{P} \mid R_k^{-1} R_j \varphi \rangle = \langle \varphi \mid \mathcal{P} \mid R_j \varphi \rangle
\]

(2)

where \( R_j \varphi = R_k^{-1} R_j \varphi \) is one of the equivalent vectors.

Therefore all rows of the matrix \( P \) will contain the same elements of the first one, variously ordained and such as to give an hermitian matrix. The ordering of the elements in each row and the other possible equations of the type (2) which can be written among the elements of a row are independent of the particular operator \( \mathcal{P} \). This is what is called the structure of a matrix. Probably a word which would have more clearly indicated the inherent topological properties of the matrix would be preferable, but for our purposes which are essentially practical, the word structure gives a more easy grasp of what is meant.

Thus the structure of a matrix is established only by the Eq. (2) and this means that two or more matrices can have identical structures with different numerical values of their elements. A simple consequence of Eq. (2) is that all diagonal elements are identical.

Given a matrix \( P \) constructed with a particular basis comprising of several equivalent sets, and with an operator \( \mathcal{P} \) satisfying the previous mentioned requirements we begin by recognizing the vectors belonging to the same equivalent set. These are easily identified because they have identical diagonal elements. Let us consider now the particular matrices \( P^{s_1}, P^{s_2}, \ldots, P^{s_t} \) obtained by extracting from the matrix \( P \) all elements due to the equivalent sets \( s_1, s_2, \ldots, s_t \) and construct new matrices \( B^{s_1}, B^{s_2}, \ldots, B^{s_t} \) which have structures identical to \( P^{s_1}, P^{s_2}, \ldots, P^{s_t} \) but with arbitrary elements (it must be excluded the case where \( B^{s_i} \) is proportional to \( P^{s_i} \)).

Since the \( B^{s_i} \) matrices are hermitian they can be diagonalized into \( \Lambda^{s_i} \) by unitary matrices \( U^{s_i} \) whose numerical determination is a routine computer operation.