Theoret. chim. Acta (Berl.) 7, 85—88 (1967)

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

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Received November 4, 1966

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.

On propose une méthode pratique pour obtenir la matrice de transformation d'une base donnée en une base de symétrie, en employant soit la matrice hamiltonienne, soit une matrice relative à un autre opérateur, pourvu qu'il ait les mêmes propriétés de symétrie que l'hamiltonien.

La méthode s'applique très aisément aux calculs d'orbitales moléculaires et de constantes de force.

Es wird eine Methode entwickelt, die die Transformationsmatrix von einer gegebenen Basis zu einer der Hamiltonmatrix symmetrieadaptierten Basis bestimmt. Statt der Hamiltonmatrix können beliebige Matrizen vorliegen, insofern sie Operatoren entsprechen, die gleiches Symmetrieverhalten wie der Hamiltonoperator aufweisen. Die Methode läßt sich ohne Schwierigkeit bei MO-Rechnungen und der Berechnung von Kraftkonstanten anwenden.

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 desiderable 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 WILSON $\boldsymbol{G}^{-1} + \boldsymbol{F}$ matrix in force constant calculations.

Theory

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_α vectors which tranform according to the irreducible representation Γ^α of dimension n_α. Each of the n_α possible vectors will have n_α partners.

In addition the following theorem can be proved: "The *structure* of the matrix obtained from a set of equivalent vectors with any operator $\mathscr{P}$ which commutes with all and only the symmetry operations R of a group used to generate, from a given vector φ, 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

$$P_{1,j} = \langle E\varphi \mid \mathscr{P} \mid R_j\, \varphi\rangle\,. \tag{1}$$

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 $\mathscr{P}$ is the operator defined in the above theorem.

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

$$\langle R_k\,\varphi \mid \mathscr{P} \mid R_j\,\varphi\rangle = \langle \varphi \mid R_k^{-1}\mathscr{P} \mid R_j\,\varphi\rangle = \langle \varphi \mid \mathscr{P} \mid R_k^{-1}\,R_j\,\varphi\rangle = \langle \varphi \mid \mathscr{P} \mid R_l\,\varphi\rangle \tag{2}$$

where $R_l\,\varphi = R_k^{-1}\,R_j\,\varphi$ is one of the equivalent vectors.

Therefore all rows of the matrix $\boldsymbol{P}$ will contain the same elements of the first one, variously ordinated 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 $\mathscr{P}$. 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 $\boldsymbol{P}$ constructed with a particular basis comprising of several equivalent sets, and with an operator $\mathscr{P}$ 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 $\boldsymbol{P}^{s_1}$, $\boldsymbol{P}^{s_2}$, ... $\boldsymbol{P}^{s_i}$ obtained by extracting from the matrix $\boldsymbol{P}$ all elements due to the equivalent sets s_1, s_2 ..... s_i ... and construct new matrices $\boldsymbol{B}^{s_1}$, $\boldsymbol{B}^{s_2}$ .... $\boldsymbol{B}^{s_i}$ ..... which have structures identical to $\boldsymbol{P}^{s_1}$, $\boldsymbol{P}^{s_2}$ ... $\boldsymbol{P}^{s_i}$ ... but with arbitrary elements (it must be excluded the case where $\boldsymbol{B}^{s_i}$ is proportional to $\boldsymbol{P}^{s_i}$).

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

If the set s_i yields no more than one vector for each of the irreducible representations then $\boldsymbol{U}^{s_i}$ will diagonalize $\boldsymbol{P}^{s_i}$ too and all matrices with the same structure.

On the other hand if the set s_i yields m_α vectors which belong to the same irreducible representation Γ^α of dimension n_α ($m_\alpha > 1$; $m_\alpha \leqq n_\alpha$) the above is no longer true because the off diagonal elements between parallel partners of the m_α different vectors are in general different from zero. Therefore the complete diagonalization will be dependent upon the structure and the numerical values of the elements of the matrix $\boldsymbol{B}^{s_i}$. Thus to distinguish between these two situations it is sufficient to see if the matrix $\boldsymbol{F}^{s_i} = \boldsymbol{U}^{s_i\dagger} \boldsymbol{P}^{s_i} \boldsymbol{U}$ is diagonal.

The matrix $\boldsymbol{U}$ formed with all the $\boldsymbol{U}^{s_i}$, retaining the ordering of the rows of $\boldsymbol{B}$ is used now to evaluate the matrix $\boldsymbol{F} = \boldsymbol{U}^\dagger \boldsymbol{P} \boldsymbol{U}$ which represents the operator $\mathscr{P}$ in the new symmetry adapted basis.

In case of degeneracy it still remains to orient correctly the partners of different vectors (2), arising from different sets s_i belonging to the same irreducible representation Γ^α, n_α times degenerate (The partners of different vectors arising from a same set are already parallel to each other).

This can be achieved by chosing as reference the orientation of the vectors arising from an arbitrary set and rotating appropriately the partners of the vectors arising from the other sets. After this operation is performed the $\boldsymbol{F}$ matrix in the new basis will be completely factorized, and the only off-diagonal elements will arise between parallel partners of different vectors belonging to the same irreducible representation.

That such rotations are indeed possible in an easy way is shown as follows: let $g_{j\lambda}^{s_i\alpha}$ be the λ partner of the j new basis vector belonging to the Γ^α irreducible representation. This vector being obtained by the transformation $\boldsymbol{U}$ from the equivalent vectors of the set s_i.

This vector can be imagined as one obtained from the symmetry adapted vectors $\varphi_{k\mu}^{s_i\alpha}$ which were constructed by applying the projection operators [*1*, *2*, *4*].

These symmetry vectors are defined as

$$\varphi_{k\mu}^{s_i\alpha} = N_k^{s_i} \sum_R \frac{n_\alpha}{g} \Gamma^\alpha(R)_{\mu k}^* \, R\varphi^{s_i} \tag{3}$$

where $N_k^{s_i}$ is a normalisation constant independent from μ and φ^{s_i} indicates the vector generating the set s_i.

The $g_{j\lambda}^{s_i\alpha}$ is related to the $\varphi_{k\mu}^{s_i\alpha}$ trough

i) a rotation $\boldsymbol{R}^{s_i\alpha}$ of dimension n_α which will mix the partners μ of each of the m_α vectors $\varphi_{k\cdot}^{s_i\alpha}$ to give the new vectors $f_{l\nu}^{s_i\alpha}$
and

ii) a unitary transformation $\boldsymbol{O}^{s_i\alpha}$ of dimension m_α among the parallel partners ν of the functions $f_{\cdot\nu}^{s_i\alpha}$.

The transformation $\boldsymbol{R}^{s_i\alpha}$ will be independent of l, and the transformation $\boldsymbol{O}^{s_i\alpha}$ will be independent of ν.

Thus

$$g_{j\lambda}^{s_i\alpha} = \sum_k \sum_\mu \boldsymbol{O}_{jk}^{s_i\alpha} \boldsymbol{R}_{\mu\lambda}^{s_i\alpha} \varphi_{k\mu}^{s_i\alpha} \, . \tag{4}$$

Let us consider the elements of $\boldsymbol{F}$ between the partners of the vector $g_{j\cdot}^{s_i\alpha}$ arising from the set s_i and the partners of the vectors $g_{p\cdot}^{s_t\alpha}$ arising from the set s_t and belonging to the same irreducible representation Γ^α.

The partners of a same vector are easily recognizable because their diagonal elements will be identical.

The general element is given by

$$\langle g_{j\lambda}^{s_t\alpha} \mid \mathscr{P} \mid g_{p\varrho}^{s_t\alpha}\rangle = \sum_k \sum_\mu \sum_l \sum_\sigma \boldsymbol{O}_{jk}^{s_t\alpha *} \boldsymbol{R}_{\mu\lambda}^{s_t\alpha *} \boldsymbol{O}_{pl}^{s_t\alpha} \boldsymbol{R}_{\sigma\varrho}^{s_t\alpha} \langle \varphi_{k\mu}^{s_t\alpha} \mid \mathscr{P} \mid \varphi_{l\sigma}^{s_t\alpha}\rangle . \tag{5}$$

Since

$$\langle \varphi_{k\mu}^{s_t\alpha} \mid \mathscr{P} \mid \varphi_{l\sigma}^{s_t\beta}\rangle = \delta_{\alpha\beta} \cdot \delta_{\mu\sigma} N_k^{s_t} \langle \varphi^{s_t} \mid \mathscr{P} \mid \varphi_{lk}^{s_t\beta}\rangle , \tag{6}$$

Eq. (5) becomes

$$\begin{aligned}\langle g_{j\lambda}^{s_t\alpha} \mid \mathscr{P} \mid g_{p\varrho}^{s_t\alpha}\rangle &= \sum_k \sum_l \sum_\sigma \boldsymbol{O}_{jk}^{s_t\alpha *} \boldsymbol{R}_{\sigma\lambda}^{s_t\alpha *} \boldsymbol{O}_{pl}^{s_t\alpha} \boldsymbol{R}_{\sigma\varrho}^{s_t\alpha} N_k^{s_t} \langle \varphi^{s_t} \mid \mathscr{P} \mid \varphi_{lk}^{s_t\alpha}\rangle \\ &= (\boldsymbol{R}^{s_t\alpha\dagger} \boldsymbol{R}^{s_t\alpha})_{\lambda\varrho} [\sum_k \sum_l N_k^{s_t\alpha} \boldsymbol{O}_{jk}^{s_t\alpha *} \boldsymbol{O}_{pl}^{s_t\alpha} \langle \varphi^{s_t} \mid \mathscr{P} \mid \varphi_{lk}^{s_t\alpha}\rangle] . \end{aligned} \tag{7}$$

Eq. (7) indicates that the square matrices of order n_α, $(\boldsymbol{F}_{jp}^{s_ts_t})^\alpha$ formed with these elements are given by a unitary matrix $(\boldsymbol{R}^{s_t\alpha\dagger} \cdot \boldsymbol{R}^{s_t\alpha})$ which is independent of the particular couple of vectors j and p, multiplied by a scalar quantity which depends upon the couple j, p.

The unitary matrix $\boldsymbol{R}^{s_i\alpha\dagger} \boldsymbol{R}^{s_t\alpha}$ (which is one of the $(\boldsymbol{F}_{jp}^{s_is_t})^\alpha$ matrices except for an easily evaluable normalization constant) is the sought transformation for the vectors arising from the equivalent set s_i if the orientation of the vectors arising from the set s_t is chosen as reference. In fact by performing these transformation upon all the $g_{j\lambda}^{s_t\alpha}$ vectors arising from all the equivalent sets s_i the general matrix $(\boldsymbol{F}_{kl}^{s_vs_q})^\alpha$ becomes

$$(\boldsymbol{R}^{s_v\alpha\dagger} \boldsymbol{R}^{s_t\alpha})^\dagger \, (\boldsymbol{F}_{kl}^{s_vs_q})^\alpha \, (\boldsymbol{R}^{s_q\alpha\dagger} \boldsymbol{R}^{s_t\alpha}) = \boldsymbol{I}^{n_\alpha} \cdot A_{kl} \tag{8}$$

where the second term of the product at the right of Eq. (7) has been indicated by A_{kl}. The diagonal elements of $\boldsymbol{F}$ will not change.

Therefore the product of the matrix $\boldsymbol{U}$ times the unitary matrix formed with all the $\boldsymbol{R}^{s_i\alpha\dagger} \boldsymbol{R}^{s_t\alpha}$ matrices will be the unitary matrix which tranforms the given basis in a new symmetry adapted basis. With this new basis the maximum factorization by symmetry is achieved.

Acknowledgments. The author is grateful to Prof. M. Maestro for many valuable discussions. The financial help of the Consiglio Nazionale delle Ricerche is gratefully acknowledged.

References

[1] Koster, G. F.: Notes on Group Theory. Technical Report No. 8 of the Solid State and Molecular Theory Group. M.I.T. 1956.
[2] McWeeny, R. C.: Symmetry. Oxford-London-New York-Paris: Pergamon Press 1963.
[3] Roothaan, C. C. J.: Rev. mod. Physics **23**, 69 (1951).
[4] Wigner, E. P.: Group Theory. New York and London: Academic Press 1959.
[5] Wilson, E. B., J. C. Decius, and P. C. Cross: Molecular Vibrations. New York: McGraw Hill 1955.

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