ON SYMMETRY REDUCTION OF ENERGY OPERATORS IN THE THEORY OF MOLECULAR VIBRATIONS

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Abstract

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ON SYMMETRY REDUCTION OF ENERGY OPERATORS IN THE THEORY OF MOLECULAR VIBRATIONS

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In the present article a matrix technique is proposed for finding transformations from natural coordinates to symmetry coordinates, constructed on the basis of group-theoretical representations.

The first step in solving this problem, as follows from our preceding communication ([1]), is the determination of the eigenvalues and eigenvectors of the material symmetric submatrices A_j (the diagonalization operation). A distinctive feature of the submatrices A_j is the presence of identical elements on the main diagonal; moreover, each row of the block A_j differs from any other row only by a permutation of elements; thus the block A_j possesses a definite symmetry in the arrangement of its elements, arising from the presence of spatial symmetry in the molecule.

The operation of diagonalizing the submatrices A_j can be carried out in two ways. The first method consists in solving the characteristic equation

$$|A_j - \lambda E| = 0. \tag{1}$$

The presence of the indicated symmetry in the arrangement of elements in the blocks A_j makes it possible to find the roots of equation (1) without expanding the determinant.

Since the sum of the elements of each row of determinant (1) is the same, the value of λ that makes this sum vanish is a root of the characteristic equation (1); in other words, one of the eigenvalues is equal to the sum of all the elements of an arbitrary row of the block A_j.

In a number of cases it is possible to determine an eigenvalue by "equalizing" the rows of determinant (1); here λ is determined so that two (or more) rows of the determinant become identical. And finally, in most cases the following procedure proves useful: a linear combination of the rows of determinant (1) is

constructed with coefficients $+1$ and -1, forming a row whose elements either are identical or differ in sign. Since λ enters these elements to the first power, by determining it from the condition that such an element be equal to zero, we find the desired eigenvalue. In this way one can readily determine the eigenvalues of submatrices A_j of the second, third, and fourth orders; the corresponding eigenvectors are then found in the usual way.

The second method consists in solving the characteristic equation

$$|S_j - \mu E| = 0, \tag{2}$$

where S_j is a submatrix of the symmetry operator, permutable with A_j (see (7) from ([1])). From the set of symmetry operators forming the representation G_j of the point symmetry group in the subspace of equivalent coordinates Q_j, such an S_j is chosen for which equation (2) does not yield multiple eigenvalues. For example, in the case of a subspace of 5 equivalent coordinates such an operator may be C_5, the rotation operator of order 5. The characteristic equation for C_5 is $\mu^5 = 1$.

In other words, the eigenvalues of the operator C_5 are the roots of the 5th power of unity. The corresponding eigenvectors, defined in the usual way, will also be eigenvectors of the submatrix A_j of order 5, which commutes with C_5. Since the eigenvectors of the matrix operator C_5 will have pairwise complex-conjugate coordinates, each 2 such vectors must correspond to one and the same real eigenvalue λ of the cell A_j, i.e., they must form a proper subspace of dimension 2 of the matrix A_j with eigenvalue λ.

Taking, instead of each pair of eigenvectors with complex-conjugate coordinates, the sum of these vectors and their difference multiplied by i, we obtain a system of eigenvectors of A_j with real coordinates.

Analogously, the diagonalization of A_j of any other order, for example the 7th, can be carried out.

Formulas (3a) and (4a) indicate the structure of the matrices A_j of the 2nd and 4th orders, which, upon application of the corresponding transformations (5a) and (6a), obtained on the basis of the considerations set forth above, are brought to diagonal form (7a) and (8a).

The collection of formulas (3a)–(8a) can be used further when describing the operation of diagonalization of large cells corresponding to subspaces Q_j of high orders. In these cases the submatrices A_j must first be correlated, i.e., brought to the form (3b) or (4b):

$$\begin{Vmatrix} p & q \\ p & q \end{Vmatrix}, \qquad \begin{Vmatrix} P & Q \\ Q & P \end{Vmatrix}, \tag{3}$$

(a) (b)

$$\left\| \begin{matrix} p_1 & p_2 & q_1 & q_2 \\ p_2 & p_1 & q_2 & q_1 \\ q_1 & q_2 & p_1 & p_2 \\ q_2 & q_1 & p_2 & p_1 \end{matrix} \right\|, \qquad \left\| \begin{matrix} P_1 & P_2 & Q_1 & Q_2 \\ P_2 & P_1 & Q_2 & Q_1 \\ Q_1 & Q_2 & P_1 & P_2 \\ Q_2 & Q_1 & P_2 & P_1 \end{matrix} \right\|. \tag{4}$$

(a) (b)

In (3b) and (4b), P and Q are square cells of order respectively 2 and 4 times smaller than the order of A_j. The similarity of the structures (a) and (b) makes it possible to construct similar transformations

$$\left\| \begin{matrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{matrix} \right\|, \qquad \left\| \begin{matrix} \frac{1}{\sqrt{2}}E & \frac{1}{\sqrt{2}}E \\ \frac{1}{\sqrt{2}}E & -\frac{1}{\sqrt{2}}E \end{matrix} \right\|, \tag{5}$$

(a) (b)

$$\left\| \begin{matrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \end{matrix} \right\|, \qquad \left\| \begin{matrix} \frac{1}{2}E & \frac{1}{2}E & \frac{1}{2}E & \frac{1}{2}E \\ \frac{1}{2}E & \frac{1}{2}E & -\frac{1}{2}E & -\frac{1}{2}E \\ \frac{1}{2}E & -\frac{1}{2}E & \frac{1}{2}E & -\frac{1}{2}E \\ \frac{1}{2}E & -\frac{1}{2}E & -\frac{1}{2}E & \frac{1}{2}E \end{matrix} \right\|, \tag{6}$$

(a) (b)

reducing the matrices A_j under consideration to diagonal (a) and block-diagonal (b) form:

$$\left\| \begin{matrix} p+q & 0 \\ 0 & p-q \end{matrix} \right\|, \qquad \left\| \begin{matrix} P+Q & 0 \\ 0 & P-Q \end{matrix} \right\|, \tag{7}$$

(a) (b)

$$\left\| \begin{matrix} p_1+p_2+q_1+q_2 & 0 & 0 & 0 \\ 0 & p_1+p_2-q_1-q_2 & 0 & 0 \\ 0 & 0 & p_1-p_2+q_1-q_2 & 0 \\ 0 & 0 & 0 & p_1-p_2-q_1+q_2 \end{matrix} \right\|,$$

$$\left\| \begin{matrix} P_1+P_2+Q_1+Q_2 & 0 & 0 & 0 \\ 0 & P_1+P_2-Q_1-Q_2 & 0 & 0 \\ 0 & 0 & P_1-P_2+Q_1-Q_2 & 0 \\ 0 & 0 & 0 & P_1-P_2-Q_1+Q_2 \end{matrix} \right\|. \tag{8}$$

In (5b) and (6b), E is the identity matrix of the same order as the blocks in (3b) and (4b), respectively.

The correlation operation is performed by means of a second-order operator forming a group of order 2, with respect to which the complete set of $2n$ equivalent natural coordinates decomposes into two sets of n coordinates each, in such a way that under the action of this operator the coordinates of one set pass into the coordinates of the other; then, arranging the coordinates that pass into one another so that they stand in the corresponding positions in these sets, we achieve that the matrix of the indicated second-order operator will have the form

$$S_j = \left\| \begin{matrix} 0 & E \\ E & 0 \end{matrix} \right\|. \tag{9}$$

Now the submatrix A_j, invariant with respect to such an operator S_j, will have the structure (3b).

In the case where the point symmetry group to which the molecule belongs has one more second-order symmetry operator that commutes with the first, the correlation operation may be repeated with respect to each of the obtained sets of coordinates. As a result, the submatrix A_j, written in correlated equivalent coordinates, will have the structure (4b).

In the preceding communication we indicated that, when constructing the matrix C from C_j (see (12) of [1]), one should carry out an orientation operation, i.e. an operation of matching the eigenvectors of the submatrices A_k and A_l belonging to different subspaces of equivalent coordinates Q_k and Q_l, in the case where the eigensubspaces corresponding to these vectors are transformed under the action of the symmetry operators according to equivalent irreducible representations.

We propose a direct method for carrying out the orientation operation, based on the requirement of identity of the equivalent irreducible representations induced in Q_k and Q_l $(k \neq l)$.

In practice this is easily accomplished in the following way. For definiteness, let us consider a threefold expression. Let $\bar{f}_1^{(k)}$, $\bar{f}_2^{(k)}$, $\bar{f}_3^{(k)}$ be eigenvectors corresponding to the triply degenerate eigenvalue $\lambda^{(k)}$ of the submatrix A_k, and $\bar{f}_1^{(l)}$, $\bar{f}_2^{(l)}$, $\bar{f}_3^{(l)}$ be eigenvectors corresponding to the triply degenerate eigenvalue $\lambda^{(l)}$ of the submatrix A_l, and moreover both these three-dimen-

the proper subspaces transform under the action of the group of symmetry operators according to equivalent irreducible representations.

In the coordinate expressions of 3 vectors $\vec{f}_i^{(k)}$ $(i = 1, 2, 3)$ there will be 9 arbitrary parameters (3 in each), on which we impose 6 orthonormality conditions. We do the same with the vectors $\vec{f}_i^{(l)}$ from the second proper subspace.

The vectors $\vec{f}_i^{(k)}$ and $\vec{f}_i^{(l)}$ are used to construct the matrices C_k and C_l, fundamental for A_k and A_l.

Let us now choose in the symmetry group G generating elements, one of which is, for example, $\overline{S^m}$; construct the matrices of this operator S_k^m and S_l^m in the subspaces Q_k and Q_l. Then perform the transformation

$$C_k^{-1} S_k^m C_k = S_k^{m'}, \qquad C_l^{-1} S_l^m C_l = S_l^{m'}. \tag{10}$$

We now impose the requirement of identity on the matrices belonging to equivalent irreducible representations contained in $S_k^{m'}$ and $S_l^{m'}$; in this way new equations will be obtained for the still undetermined arbitrary parameters. In the same sense, the remaining generating elements of the group may be used.

Thus we arrive at a system of algebraic equations for the arbitrary parameters, based on the requirements of normalization, orthogonality, and identity. Since identical representations are contained in the class of equivalent representations, in order to satisfy the identity requirement it is sufficient to change the basis of only one subspace among those being matched; then in the expressions of the basis vectors of the other subspace there will remain 3 arbitrary constants, which may be chosen at the very beginning of solving the aforementioned system of equations. The system of equations considered in carrying out the orientation operation is always compatible.

Of special interest is the case when at least two equivalent irreducible representations of degenerate symmetry types are induced in one subspace of equivalent coordinates. In this case the requirement of diagonalizing A_j in order to obtain a completely reduced representation (see (1)) is sufficient, but not necessary, since, in accordance with Schur' s lemma, on the diagonal of the reduced matrix A_j there must appear a block of dimension equal to the multiplicity of the degeneracy.

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REFERENCES

1. N. K. Morozova, V. P. Morozov, DAN, 161, 817 (1965).

Note: Figure translations are in progress. See original paper for figures.