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Matrix formalism is routinely used for the solution of problems in modern chemistry. Here we consider, in particular, the problem of molecular vibration of the form [1]

$$|\underline{\underline{GF}} - \lambda \underline{\underline{E}}| = 0 , \qquad \text{/1/}$$

where $\underline{\underline{G}}$ is the inverse of the matrix of kinetic energy depending on the interatomic distances and mass of the molecule, $\underline{\underline{F}}$ is the matrix of potential energy determined by the force constants.

The problem, mentioned above, can be treated as an eigenvalue problem since the eigenvalues of the $\underline{\underline{GF}}$ matrix are proportional to the individual frequencies of the molecular vibrations, or as an "inverse eigenvalue problem" if the force constants are to be determined from the elements of the $\underline{\underline{G}}$ matrix and from the eigenvalues.

The solution of either problem becomes difficult in the case of polyatomic molecules, since the order of the matrices increases with the number of atoms involved. Efforts have been made therefore to split the given problem into a set of smaller problems. A known method in chemistry for this is the construction of symmetry coordinates using some group theoretical considerations, in terms of which the matrix of vibrational problems is reduced to the maximum extent made possible by the molecular symmetry [1].

For molecules, having a "good" symmetry, the $\underline{\underline{GF}}$ matrix has in some cases a structure such that it can be reduced in terms of pure matrix theory.

In this paper a method based on EGERVARY's theorem [2] will be

described for the complete reduction of the $\underline{\underline{GF}}$ matrix which consists of blocks commutable in pairs.

Application of the method will be shown in the case of methyl halide molecules.

1.§ DESCRIPTION OF THE METHOD

The following notation is used:

$\underline{\underline{A}} = [a_{ij}]$ . . . . is the matrix composed of the scalars a_{ij}

$[\underline{\underline{A}}_{ij}]$ . . . . is the hypermatrix composed of the blocks $\underline{\underline{A}}_{ij}$

$\langle a_1, a_2, \ldots, a_n \rangle$ . . . . is the diagonal matrix composed of the scalars a_i

$\langle \underline{\underline{A}}^{(\ell)} \rangle_1^n = \langle \underline{\underline{A}}^{(1)}, \underline{\underline{A}}^{(2)}, \ldots, \underline{\underline{A}}^{(n)} \rangle$ . . . . is the hyperdiagonal matrix of order n composed of the square matrices $\underline{\underline{A}}^{(k)}$

$\underline{\underline{A}}$ . . . . is the transpose of matrix $\underline{\underline{A}}$

$\underline{\underline{E}}_n$ . . . . is the unit matrix of order n

$\underline{u}$, $\underline{v}$ . . . . are column vectors

$\underline{u}^*$, $\underline{v}^*$ . . . . are row vectors

$\underline{\underline{A}} \cdot \times \underline{\underline{B}} = [\underline{\underline{A}} \cdot b_{ij}]$ . . . . is the direct product of the matrices $\underline{\underline{A}}$ and $\underline{\underline{B}}$

$\underline{u} \cdot \times \underline{v} = \begin{bmatrix} \underline{uv}_1 \\ \underline{uv}_2 \\ \cdot \\ \cdot \\ \cdot \\ \underline{uv}_n \end{bmatrix}$ . . . . is the direct product of vectors $\underline{u}$ and $\underline{v}$.

$\underline{\underline{T}} = [\underline{\underline{t}}_{k\ell}] = [\underline{t}_{11}, \underline{t}_{12}, \ldots, \underline{t}_{1n}; \underline{t}_{21} \underline{t}_{22}, \ldots, \underline{t}_{2n}; \ldots]$ is a matrix partitioned in the column vectors $\underline{t}_{k\ell}$

Let $[\underline{\underline{A}}_{ij}]$ $(i,j = 1,2,\ldots,n)$ be a hypermatrix of order n×m with blocks $\underline{\underline{A}}_{ij} = p_{ij}(\underline{\underline{A}})$, where $\underline{\underline{A}}$ is a symmetrical matrix of order m and $p_{ij}(x)$ are polynomials of the real variable x , subject only to the restriction $p_{ij}(x) = p_{ji}(x)$. If the spectral decomposition of matrix $\underline{\underline{A}}$ is given by

$$\underline{\underline{A}} = \underline{\underline{W}} \langle \lambda_1, \lambda_2, \ldots, \lambda_m \rangle \underline{\underline{W}}^*$$

then the blocks $\underline{\underline{A}}_{ij}$ decompose to

$$\underline{\underline{A}}_{ij} = p_{ij}(\underline{\underline{A}}) = \underline{\underline{W}} < p_{ij}(\lambda_1)\ p_{ij}(\lambda_2), \ \ldots\ ,\ p_{ij}(\lambda_m) > \underline{\underline{W}}^*.$$

Thus, $\left[\underline{\underline{A}}_{ij}\right]$ can be factorised as

$$\left[\underline{\underline{A}}_{ij}\right] = \left(\underline{\underline{W}} \cdot \times \underline{\underline{E}}_n\right) \cdot \underline{\underline{P}} \cdot < \underline{\underline{\Lambda}}^{(1)}, \underline{\underline{\Lambda}}^{(2)}, \ldots, \underline{\underline{\Lambda}}^{(m)} > \cdot \underline{\underline{P}}^* \cdot \left(\underline{\underline{W}}^* \cdot \times \underline{\underline{E}}_n\right), \qquad /2/$$

where $\underline{\underline{\Lambda}}^{(k)} = \left[p_{ij}(\lambda_k)\right]$ and $\underline{\underline{P}}$ is the permutation matrix which transforms the sequence of ordered pairs

$$(11)(12) \ldots (1m)(21)(22) \ldots (2m) \ldots (n1)(n2) \ldots (nm)$$

into the sequence

$$(11)(21) \ldots (n1)(12)(22) \ldots (n2) \ldots (1m)(2m) \ldots (nm)\ [2].$$

On multiplying the left and right hand side of /2/ by $\underline{\underline{P}}^* \cdot \left(\underline{\underline{W}}^* \cdot \times \underline{\underline{E}}_n\right)$ and $\left(\underline{\underline{W}} \cdot \times \underline{\underline{E}}_n\right) \cdot \underline{\underline{P}}$, respectively, we obtain

$$\underline{\underline{P}}^* \cdot \left(\underline{\underline{W}}^* \cdot \times \underline{\underline{E}}_n\right) \cdot \left[\underline{\underline{A}}_{ij}\right] \cdot \left(\underline{\underline{W}} \cdot \times \underline{\underline{E}}_n\right) \cdot \underline{\underline{P}} = <\underline{\underline{\Lambda}}^{(k)}>_1^m. \qquad /3/$$

The transformation matrix $\left(\underline{\underline{W}} \cdot \times \underline{\underline{E}}_n\right) \cdot \underline{\underline{P}}$ can be written in the form

$$\underline{\underline{T}} = \left[\underline{\underline{t}}_{k\ell}\right] = \left[\underline{w}_k \cdot \times \underline{e}_\ell\right]\ \left(k=1,2,\ldots,m;\ \ell=1,2,\ldots,n\right), \qquad /4/$$

where $\underline{w}_k$ is the column k of matrix $\underline{\underline{W}}$, that is the eigenvector corresponding to the eigenvalue λ_k of the matrix $\underline{\underline{A}}$, while $\underline{e}_\ell$ is the unit vector ℓ of order n. If ℓ runs over the values $1,2,\ldots,n$, the direct products in /4/, for fixed k, form the "block-column" k of the matrix $\underline{\underline{T}}$.

If the matrix $\left[\underline{\underline{A}}_{ij}\right]$ is bordered by a row and a column vector in the following manner

$$\begin{bmatrix} c & \underline{w}_p^* \cdot \times \underline{v}^* \\ \hline \underline{w}_p \cdot \times \underline{u} & \left[\underline{\underline{A}}_{ij}\right] \end{bmatrix}$$

/5/

where c is constant, $\underline{w}_p$ is the characteristic vector p of $\underline{A}$, $\underline{v}^*$ and $\underline{u}$ are vectors of order n, then the transformation matrix $\underline{T}$ - which is bordered by unit vectors - transforms the form /5/ into

$$
\begin{bmatrix} 1 & 0 \\ \hline 0 & \left[\underline{w}_k^* \cdot {}^\times \underline{e}_\ell^*\right] \end{bmatrix} \cdot \begin{bmatrix} c & \underline{w}_p^* \cdot {}^\times \underline{v}^* \\ \hline \underline{w}_p \cdot {}^\times \underline{u} & \left[\Lambda_{ij}\right] \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 \\ \hline 0 & \left[\underline{w}_k \cdot {}^\times \underline{e}_\ell\right] \end{bmatrix} =
$$

$$
= \begin{bmatrix} c & \left(\underline{w}_p^* \cdot {}^\times \underline{v}^*\right)\left[\underline{w}_k \cdot {}^\times \underline{e}_\ell\right] \\ \hline \left[\underline{w}_k^* \cdot {}^\times \underline{e}_\ell^*\right]\left(\underline{w}_p \cdot {}^\times \underline{u}\right) & \left[\underline{w}_k^* \cdot {}^\times \underline{e}_\ell^*\right] \cdot \left[\Lambda_{ij}\right] \cdot \left[\underline{w}_k \cdot {}^\times \underline{e}_\ell\right] \end{bmatrix} \qquad /6/
$$

Performing the multiplication for the lowest block on the left we get

$$
\left[\underline{w}_k^* \cdot {}^\times \underline{e}_\ell^*\right]\left(\underline{w}_p \cdot {}^\times \underline{u}\right) = k\left[\left(\underline{w}_k^* \cdot \underline{w}_p\right)\left(\underline{e}_\ell^* \underline{u}\right)\right]\ell = \delta_{kp} u_\ell \qquad /7/
$$

The product of $\underline{T}^*$ and $(\underline{w}_p \cdot {}^\times \underline{u})$ is non zero only if $k = p$ and this product is precisely the product of the "block-row" p of $\underline{T}^*$ and the vector $(\underline{w}_p \cdot {}^\times \underline{u})$ ./In fact, for $p \neq k$ on the right hande side of /7/ we have the product of two eigenvectors corresponding to different eigenvalues of $\underline{A}$, which is equal to zero./ If ℓ runs over the values $1,2,\ldots,n$, we obtain the vector $\underline{u}$. Consequently, the hyperdiagonal matrix /6/ is bordered by vectors partitioned into m parts, the p-th of which is only differing from zero, therefore the bordering row and column vectors can be written as

$(\underline{e}_p^* \cdot \times \underline{v}^*)$ and $(\underline{u} \cdot \times \underline{e}_p)$ respectively. Thus /6/ becomes

$$
\begin{bmatrix}
c & \underline{e}_p^* \cdot \times \underline{v}^* \\
\hline
\underline{u} \cdot \times \underline{e}_p & <\underset{\approx}{\tilde{A}}{}^{(k)} \cdot >_1^m
\end{bmatrix}
\qquad , \qquad /8/
$$

where $<\underset{\approx}{\tilde{A}}{}^{(k)}>_1^m$ is the hyperdiagonal matrix defined by /3/.

Without loss of generality, we may put $p = 1$ choosing an appropriate numbering of the eigenvalues. In this case the hyperdiagonal matrix /8/ will have the form

$$
\begin{bmatrix}
c & \underline{v}^* & & & & \\
\underline{u} & \underset{=}{\tilde{A}}{}^{(1)} & & & O & \\
 & & \tilde{A}^{(2)} & & & \\
 & O & & \ddots & & \\
 & & & & & \underset{=}{\tilde{A}}{}^{(m)}
\end{bmatrix}
\qquad /9/
$$

In the solution of a given vibrational problem it frequently occurs that the hypermatrices have blocks $\underset{=}{A}_{ij}$ with a cyclic structure, that is, blocks, whose elements are related as

$$
c_{ij} = \begin{cases} c_{j-i} & \text{if } j \geq i \\ c_{n+j-i} & \text{if } j < i \end{cases} .
$$

These matrices are uniquely determined by their first row:

$$
\underset{=}{c} (c_o\ c_1\ c_2 \ldots c_{n-1}) .
$$

It is well known, that any cyclic matrix of order n can be written as a maximum $(n-1)$-th order polynomial of the primitive cyclic matrix $\underset{=}{\Omega} = \underset{=}{c}(0\ 1\ 0 \ldots 0)$ of order n. The eigenvalues of $\underset{=}{\Omega}$ are the n-th roots of 1 and the components of their eigenvectors are the powers of these n-th roots of 1 [3].

Specifically, if the cyclic matrix of order 3 is symmetrical

$$\underline{C} (c_o \ c_1 \ c_1) \qquad , \qquad\qquad /10/$$

its spectral decomposition is

$$\underline{C} (c_o \ c_1 \ c_1) = \underline{\underline{W}} < \lambda_o, \lambda_1, \lambda_2 > \underline{\underline{W}}^* ,$$

where $\lambda_o = c_o + 2c_1$, $\lambda_1 = \lambda_2 = c_o - c_1$ and

$$\underline{\underline{W}} = \begin{bmatrix} \dfrac{1}{\sqrt{3}} & \dfrac{2}{\sqrt{6}} & 0 \\[2mm] \dfrac{1}{\sqrt{3}} & -\dfrac{1}{\sqrt{6}} & \dfrac{1}{\sqrt{2}} \\[2mm] \dfrac{1}{\sqrt{3}} & -\dfrac{1}{\sqrt{6}} & -\dfrac{1}{\sqrt{2}} \end{bmatrix} \qquad . \qquad\qquad /11/$$

2.§ APPLICATION

The vibrational problem of a given molecule can be formulated
in terms of internal coordinates, i.e. coordinates determined by the changes
in the interatomic distances and in the angles betwen chemical bonds, which
are the most physically significant set for
use in describing the potential energy of
the molecule [1].
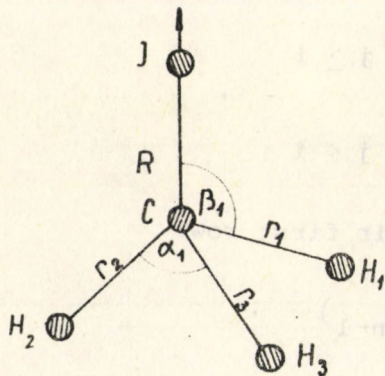
For the methyl halide molecules
the internal coordinates are the changes in
the distances R, r_i $(i = 1,2,3)$ and in the
angles $\alpha_i \ \beta_i$ $(i = 1,2,3)$. /See the methyl
iodide molecule CH_3J in Fig. 1/.

For the present purpose we write
down the $\underline{F}$ matrix only, since entirely
analogous arguments can be applied to the G
matrix and eventually to the secular equa-
tion /1/. The $\underline{F}$ matrix in terms of internal coordinates has the form [4]:

Fig. 1.

$$
\underline{\underline{F}} = \left[\underline{\underline{F}}_{ij}\right] =
\begin{bmatrix}
f_{11} & f_{12} & f_{12} & f_{12} & f_{13} & f_{13} & f_{13} & f_{14} & f_{14} & f_{14} \\
 & f'_{22} & f_{22} & f_{22} & f'_{23} & f_{23} & f_{23} & f'_{24} & f_{24} & f_{24} \\
 & f_{22} & f'_{22} & f_{22} & f_{23} & f'_{23} & f_{23} & f_{24} & f'_{24} & f_{24} \\
 & f_{22} & f_{22} & f'_{22} & f_{23} & f_{23} & f'_{23} & f_{24} & f_{24} & f'_{24} \\
 & & & & f'_{33} & f_{33} & f_{33} & f'_{34} & f_{34} & f_{34} \\
 & & & & f_{33} & f'_{33} & f_{33} & f_{34} & f'_{34} & f_{34} \\
 & & & & f_{33} & f_{33} & f'_{33} & f_{34} & f_{34} & f'_{34} \\
 & & & & & & & f'_{44} & f_{44} & f_{44} \\
 & & & & & & & f_{44} & f'_{44} & f_{44} \\
 & & & & & & & f_{44} & f_{44} & f'_{44}
\end{bmatrix}
\qquad /12/
$$

$$
i,j = 1,2,3,4. \qquad \underline{\underline{F}}_{ij} = \underline{\underline{F}}_{ji}
$$

Using the notation /10/ for the blocks $\underline{\underline{F}}_{ij}$, /12/ can be written as /5/:

$$
\begin{bmatrix}
f_{11} & \underline{w}_{o}^{*} \cdot \times \underline{u}^{*} \\
\underline{w}_{o} \cdot \times \underline{u} &
\begin{array}{c|c|c}
\underline{\underline{C}}(f'_{22}\ f_{22}\ f_{22}) & \underline{\underline{C}}(f'_{23}\ f_{23}\ f_{23}) & \underline{\underline{C}}(f'_{24}\ f_{24}\ f_{24}) \\
\hline
 & \underline{\underline{C}}(f'_{33}\ f_{33}\ f_{33}) & \underline{\underline{C}}(f'_{34}\ f_{34}\ f_{34}) \\
\hline
 & & \underline{\underline{C}}(f'_{44}\ f_{44}\ f_{44})
\end{array}
\end{bmatrix}
\qquad /13/
$$

where $\underline{w}_{o}$ is the first column vector of matrix /11/ and

$$
\underline{u} =
\begin{bmatrix}
\sqrt{3} \cdot f_{12} \\
\sqrt{3} \cdot f_{13} \\
\sqrt{3} \cdot f_{14}
\end{bmatrix}
$$

Applying the method, described in § 1., matrix /13/ can be transformed by making use of the matrix

$$
\underline{\underline{T}} =
\begin{bmatrix}
1 & O \\
O & \underline{\underline{W}} \times \underline{\underline{E}}_3
\end{bmatrix}
\cdot
\begin{bmatrix}
1 & O \\
O & \underline{\underline{P}}
\end{bmatrix}
=
\begin{bmatrix}
1 & O \\
O & [\underline{w}_k \cdot \times \underline{e}_\ell]
\end{bmatrix}
\qquad /14/
$$

$$
\underline{\underline{T}}\underline{\underline{T}}^{*} = \underline{\underline{E}} \ , \ (k,\ell = 1,\ 2,\ 3),
$$

to the hyperdiagonal form:

$$
\begin{bmatrix}
\underline{f}_{11} & \underline{u}^* & & \\
\underline{u} & \underline{\tilde{F}}^{(0)} & & O \\
& & \underline{\tilde{F}}^{(1)} & \\
O & & & \underline{\tilde{F}}^{(2)}
\end{bmatrix}
$$

where

$$
\underline{\tilde{F}}^{(k)} = \left[p_{ij}(\omega_k) \right] = \left[f'_{ij} + 2f_{ij} \cos \frac{2k\pi}{3} \right]
$$

$k = 0, 1, 2; \; i,j = 2,3,4$ and ω_k are the cube roots of 1.

Thus the given vibrational problem of order 10 has been reduced to a problem of order 4 and two identical problems of order 3.

Let us see now, whether the matrix /15/ is the completely reduced form.

The methyl halide molecules CH_3X belong to the symmetriy point group C_{3v}, composed of the following operations: two rotations by $\frac{2\pi}{3}$ and $\frac{4\pi}{3}$ about the axis coinciding with the $C - X$ bond, three reflections through the vertical planes σ_i ($i = 1,2,3$) each passing through one of the $C - H_i$ bonds and the identity operation E. This operations are called the symmetry operations which carry the molecule into a configuration equivalent to its initial configuration [1].

The internal coordinates, introduced above, separate into sets which do not mix with one another, thus, the members of each set transforms only among themselves, consequently the matrices, representing the symmetry operations are in diagonal block form, that is, the matrix representation of the symmetry point group C_{3v} is reducible [1].

It is known from representation theoretical consideration [4] that the C_{3v} symmetry point group has four 1-dimensional and three 2-dimensional irreducible representations, consequently the completely reduced form of matrix $\underline{R}$, representing any symmetry operation of the molecule, contains four 1-dimensional blocks and three 2-dimensional blocks. That is

$$
\underline{R} = \begin{bmatrix}
R^{(1)} & & & & & & \\
& R^{(1)} & & & & & \\
& & R^{(3)} & & & O & \\
& & & R^{(1)} & & & \\
& & & & R^{(3)} & & \\
& O & & & & R^{(1)} & \\
& & & & & & R^{(3)}
\end{bmatrix}
$$

The matrix of potential energy commutes with all group representation matrices and if it is partitioned to correspond with the diagonal blocks of $\underline{R}$, the commutable rule will be valid for the individual blocks too, thus by Schur's lemma we find, by merely permuting rows and columns, that in the final form the $\underline{F}$ matrix contains one 4-dimensional block and two 3-dimensional blocks [4]. Consequently the form /15/ is <u>completely reduced form.</u>

Alternatively, it can be shown, that applying the transformation with the matrix $\underline{T}$ for the 10-th order vector of the internal coordinates, we obtain the well known symmetry coordinates of methyl halide molecules [5], including the redundant coordinate the removal of which requires some chemical considerations.

<u>Note.</u> The methyl halide molecules have a "good" symmetry, therefore the matrix of the vibrational problem consists of blocks of a special cyclic structure, however, the method, described above, can be applied also to molecules having a "less good" symmetry. Attempts at the extension of the method to such molecules as well as the development of the method for the removal of redundant coordinates are in progress.

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