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COORDINATES USING CIRCULANT MATRICES

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COORDINATES USING CIRCULANT MATRICES

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ABSTRACT

A special matrix theoretical method for obtaining molecular symmetry coordinates is described. The method is based on the diagonalization of the circulant blocks of G kinetic and F potential energy matrix representing the interaction of the sets of equivalent internal coordinates. The symmetry coefficients can be obtained by using a special polynomial relation between the circulant blocks and the basic circulant matrix. A general formula for the symmetry transformation matrix depending only on the order of the matrix is derived for matrices G and F being hypermatrices with circulant blocks and being circulant blockwise with circulant blocks. The application of the method has been demonstrated for the molecules CH_3X , $\text{Y}(\text{CH}_3)_2$ and CH_2Cl_2 and the obtained symmetry coordinates are classified according to symmetry. An attempt was made to include into the method the removal of coordinate redundancy.

АННОТАЦИЯ

Дается описание матричного способа вычисления координат симметрии молекул. Способ используется в случае, когда матрицы кинематических коэффициентов G и силовых постоянных F являются клеточными матрицами с циркулянтными блоками. Коэффициенты симметрии можно вычислить из элементов собственных векторов, циркулянтно зависящих только от порядка блоков. Способ обобщается на случай, когда матрицы G и F являются клеточными циркулянтными с циркулянтными блоками. Показано использование способа в случае молекул CH_3X , $\text{Y}(\text{CH}_3)_2$ и CH_2Cl_2 . Исключения зависимых координат было предусмотрено.

KIVONAT

Egy mátrixelméleti módszert ismertetünk molekulák szimmetriakoordinátáinak meghatározására. A módszer abban az esetben alkalmazható, ha a molekula G kinetikus és F potenciális energia mátrixa ciklikus blokkokból álló hiper-mátrix. A szimmetriakoordinátákban szereplő együtthatók a ciklikus blokkok sajátvektoraiból alkotott mátrixnak, a Fourier mátrixnak elemeiből számíthatók, amelyek csupán a mátrix rendjétől függenek. A módszer általánosítható arra az esetre is, ha a G és F mátrix "többszintű" ciklikus hiper-mátrix, amelyben az egyes blokkok maguk is ciklikus blokkokból álló hiper-mátrixok. A módszer alkalmazását a CH_3X , $\text{Y}(\text{CH}_3)_2$ és a CH_2Cl_2 molekulák esetében mutatjuk be, s ez utóbbinál a redundáns koordináta kiküszöbölésére is példát adunk.

I. INTRODUCTION

Symmetry coordinates that are appropriate linear combinations of the internal coordinates (i.e. changes of bond lengths and bond angles) are usually employed to factor the secular equation for the normal vibration of symmetrical molecules.

Besides the well known Wigner group theoretical methods [1,2] several useful procedures for obtaining symmetry coordinates have previously been reported [3-13]. Most of these methods imply a knowledge of the transformation matrices under the symmetry operation of the point groups of the molecules.

In this paper a matrix theoretical method is described constructing symmetry coordinates of molecules whose Hamiltonian has a structure of a special circulant block. The method is related to those developed by Kilpatrick [3] and Morozov and Morozova as well [6] and is based on the diagonalization of the circulant matrices representing the interactions of the equivalent internal coordinates in the vibration space. The symmetry coefficients were derived using the spectral decomposition of the basic circulant. A general formula for the symmetry transformation matrix was constructed for cases when the matrices G and F have a circulant structure of higher level because of the molecular symmetry.

The method is applied to the molecules CH_3X (C_{3v}), $\text{Y}(\text{CH}_3)_2$ ($\text{Y}=\text{Zn}, \text{Cd}, \text{Hg}$) (D_{3d}) for eclipsed rigid configuration and CH_2Cl_2 (C_{2v}). In the case of the last molecule an attempt was made to include the removal of coordinate redundancy into the method.

List of mathematical symbols

$A_n = [a_{ij}]$	-----	matrix of order n with scalars a_{ij}
\tilde{A}_n	-----	transpose of A_n
u_n	-----	column vector of order n
\tilde{v}_n	-----	row vector of order n
\bar{w}	-----	conjugate of the complex number w
$[A_{ij}]_{m,n}$	-----	composite matrix of type (m,n) and order mxn
A^*	-----	conjugate transpose of A

$\Sigma_n = \text{diag}(\sigma_1, \dots, \sigma_n)$ ----- diagonal matrix with elements σ_i

I_n ----- identity matrix of order n

$A \cdot xB = [a_{ij}B]$ ----- direct product of matrices A and B

$A \oplus B = \text{diag}(A, B) =$

$$= \begin{pmatrix} A & 0 \\ 0 & B \end{pmatrix} \text{ ----- direct sum of matrices } A \text{ and } B$$

$$\tilde{u} \cdot x \tilde{v} = [uv_1, uv_2, \dots, uv_n] = [u_1v_1, u_2v_1, \dots, u_nv_1]$$

$\begin{bmatrix} | & & | \\ u_1v_2 & u_2v_2 & \dots & u_nv_2 \\ | & & | \end{bmatrix}, \dots, \begin{bmatrix} | & & | \\ u_1v_n & u_2v_n & \dots & u_nv_n \\ | & & | \end{bmatrix}$ ----- direct product of vectors \tilde{u} and \tilde{v}

$A \in B_{m,n}$ ----- matrix A belongs to the class of matrices $B_{m,n}$

II. THE METHOD

If the internal coordinates of a molecule can be divided into sets of equivalent coordinates that are transformed among themselves under the symmetry operations of the molecule then the reduction to irreducible representations of the matrix GF of the vibration operator is equivalent to diagonalization of its submatrices representing the interactions of the equivalent coordinates of a different kind. Because of the molecular symmetry these submatrices (for three equivalent coordinates) have the circulant form

$$\text{circ}(a, b, b) = \begin{pmatrix} a & b & b \\ b & a & b \\ b & b & a \end{pmatrix} . \quad (1)$$

Matrices of this type are characterized by the first row; their spectral decomposition (proved in the Appendix) can be written for odd order $n = 2m+1$ as:

$$\begin{aligned} A_{2m+1} &= \text{circ}(a, b_1, b_2, \dots, b_m, b_m, \dots, b_1) = \\ &= \tilde{\mathcal{F}}_{2m+1} \Lambda_{2m+1} \mathcal{F}_{2m+1} \end{aligned} \quad (2)$$

where

$$\Lambda_{2m+1} = aI_n + \sum_{v=1}^m b_v (\Omega_n^v + \Omega_n^{-v}) \quad (3)$$

and $\Omega_n = \text{diag}(1, w, w^2, \dots, w^{n-1})$ with the elements $w = \exp\left(\frac{2\pi i}{n}\right) = \cos \frac{2\pi}{n} + i \cdot \sin \frac{2\pi}{n}$. The single eigenvalue $\lambda_0 = a + 2 \sum_{v=1}^m b_v$ is proportional to the

frequency of the symmetrical vibration; the multiple eigenvalues

$\lambda_k = a + 2 \sum_{v=1}^m b_v \cos \frac{2\pi v k}{2m+1}$ ($k = 1, 2, \dots, m$) give the frequencies of double degenerate vibrations.

For even order $n = 2m$

$$A_{2m} = \text{circ}(a, b_1, b_2, \dots, b_m, \dots, b_2, b_1) = \widetilde{F}_{2m} \Lambda_{2m} \widetilde{F}_{2m} \quad (4)$$

where

$$\Lambda_{2m} = a I_n + \sum_{v=1}^{m-1} b_v (\Omega_n^v + \Omega_n^{-v}) + b_m \Omega_n^m \quad (5)$$

The single eigenvalues $\lambda_0 = a + 2 \sum_{v=1}^{m-1} b_v + b_m$ and $\lambda_n = a + 2 \sum_{v=1}^{m-1} (-1)^v b_v + (-1)^m b_m$ are proportional to the symmetrical and antisymmetrical vibrational frequencies respectively; the double degenerate vibrational frequencies can be obtained from the eigenvalues $\lambda_k = a + 2 \sum_{v=1}^{m-1} b_v \cos \frac{k\pi v}{m} + (-1)^k b_m$ ($k = 1, 2, \dots, m-1$). The eigenvector matrix (for proof, see Appendix) is:

$$\widetilde{F}_{2m} = \sqrt{\frac{2}{n}} \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & \cos \varphi & & -\sin \varphi \dots \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & \cos \left(\frac{2\pi k}{n} - \varphi \right) & & \sin \left(\frac{2\pi k}{n} - \varphi \right) \dots \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & \cos \left(\frac{2\pi k}{n} 2 - \varphi \right) & & \sin \left(\frac{2\pi k}{n} 2 - \varphi \right) \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{1}{\sqrt{2}} & (-1)^v \frac{1}{\sqrt{2}} & \cos \left(\frac{2\pi k}{n} v - \varphi \right) & & \sin \left(\frac{2\pi k}{n} v - \varphi \right) \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & \cos \left(\frac{2\pi k}{n} (n-1) - \varphi \right) & & \sin \left(\frac{2\pi k}{n} (n-1) - \varphi \right) \dots \end{bmatrix} \quad (6)$$

The first column belongs to the symmetric the second to the antisymmetric species; the cosine and sine column pairs correspond to the double degenerate species E_i ($i = 1, 2, \dots, (n-1)$) (the second column for odd order is missing). By changing the value of parameter φ we can achieve the simultaneous transformation of the degenerate coordinates ([14], p.287). For odd n (n is the order of the rotation axis) $\varphi = 0$ and for even n , $\varphi = \pi/n$. However the numbering of the internal coordinates should follow the rule: e.g. for odd order molecules CH_3X ($n = 3$), $\alpha_1 = r_1^4 r_3$, $\alpha_2 = r_1^4 r_3$, $\alpha_3 = r_1^4 r_2$; $\beta_1 = r_1^4 \text{C-X}$ ($i = 1, 2, 3$); for even order, e.g. the molecule XY_4 ($n = 4$), $\alpha_i = r_i^4 r_{i+1}$ ($i = 1, 2, 3, 4$).

According to the number and type of the symmetry elements the matrices G and F can be:

(a) Symmetrical hypermatrix with circulant blocks

Designation of the class of these matrices: $\mathcal{FB}_{m,n}$

An n-fold rotation axis and m vertical planes (C_{nv}) cause matrices G and F to be $A_{m,n} = [A_{ij}]_{m,n}$ which consists of m blocks each being a circulant matrix of order n. Thus $A_{m,n} \in \mathcal{FB}_{m,n}$.

The spectral decomposition of the blocks A_{ij} ($i, j = 1, 2, \dots, m$) is of the form

$$A_{ij} = \tilde{F}_n \Lambda_{ij} F_n \quad (7)$$

where, if the order of the block is odd, Λ_{ij} ($i, j = 1, 2, \dots, m$) are diagonal matrices of type (3) and, if n is even of type (5) respectively with the appropriate coefficients, a_{ij}, b_{ij} ($i, j = 1, 2, \dots, m$).

The decomposition of matrix $A_{m,n} = [A_{ij}]_{m,n} \in \mathcal{FB}_{m,n}$ is as follows:

$$A_{m,n} = (I_m \cdot x \tilde{F}_n) [A_{ij}] (I_m \cdot x F_n) \quad (8)$$

If σ designates the mapping

$$\sigma: \begin{pmatrix} 1 & 2 & \dots & n & n+1 & \dots & 2n & 2n+1 & \dots & mxn \\ 1 & n+1 & \dots & 2n+1 & 2 & \dots & 2n+2 & n & \dots & mxn \end{pmatrix} \begin{matrix} i \\ \sigma(i) \end{matrix} \quad (9)$$

then $P = [a_{ij}]$, where $a_{i\sigma(i)} = 1$; $a_{ij} = 0$ otherwise, is a permutation matrix that changes the order of the rows (or columns) of a matrix according to σ . Pre- and postmultiplying the matrix (8) by the matrices \tilde{P}_σ and P_σ respectively ($\tilde{P}_\sigma = P_\sigma^{-1} = P_\sigma$) one obtains for even n

$$\tilde{P}_\sigma A_{m,n} P_\sigma = \tilde{T} \text{diag} (A_m, E_m^{(1)}, E_m^{(2)}, \dots, E_m^{(n/2-1)}, B_m) T \quad (10)$$

where $T = (I_m \cdot x F_n) P_\sigma$ and the diagonal matrix is of the maximum reduced form according to molecular symmetry. For odd n the species B_m is missing and the superscript of the species E runs instead of n/2-1 up to (n-1)/2.

(b) Symmetrical hypermatrix which are block circulant with circulant blocks

Designation of the class of these matrices: $\mathcal{BFFB}_{m,n}$

The presence of a C_n rotation axis and symmetry planes perpendicular to it (for example D_{nd}) cause matrices G and F to be $A_{m,n} = \text{circ} (A_1 A_2 \dots A_m)$ where each block is a circulant of order n. Matrices of this kind are block circulant with circulant blocks.

It can easily be seen by using the appropriate power of the basic circulant $C_m = \text{circ} (0, 1, \dots, 0)$ (see Appendix) that

$$A_{m,n} = \text{circ} (A_0 A_1 \dots A_{m-1}) = \sum_{k=0}^{m-1} C_m^k \cdot x \Lambda_k \quad (11)$$

Substituting the decomposition $C_m = \tilde{F}_m \Omega_m F_m$ (for proof see Appendix) and the decomposition of type (7) into equn. (11) we obtain the spectral decomposition of a block circulant with circulant blocks as

$$A_{m,n} = \text{circ} (A_0 A_1 \dots A_m) = (\tilde{F}_m \cdot x \tilde{F}_n) \left(\sum_{k=0}^{m-1} \Omega_m^k \cdot x \Lambda_k \right) (F_m \cdot x F_n) \quad (12)$$

where Λ_k is a diagonal matrix of type (3) if n is odd and of type (5) if n is even. It is convenient to determine the symmetry type of each individual row of the matrix $T = (F_m \cdot x F_n)$ at the application of the method for a given molecule.

III. APPLICATION

The potential energy matrix of the methyl halides CH_3X (C_{3v}) written in the internal valence coordinates $\Delta R, \Delta r_i, \Delta \alpha_i, \Delta \beta_i$ ($i = 1, 2, 3$) is

$$F = \begin{bmatrix} f_{11} & \tilde{f}_1 \cdot x \tilde{u} \\ f_1 \cdot x u & [F_{ij}] \end{bmatrix}, \quad (13)$$

where the blocks F_{ij} ($i, j = 1, 2, 3$) are symmetric circulant matrices of order 3, f_1 is the first eigenvector of the blocks F_{ij} while the vector $\tilde{u} = (\sqrt{3} b, \sqrt{3} c, \sqrt{3} d)$. The matrix $[F_{ij}]_{3,3}$ is a composite symmetric matrix of type (3,3) so $[F_{ij}]_{3,3} \in \mathcal{P} \mathcal{B}_{3,3}$. Therefore by using the transformation matrix $T = \text{diag} (1, (I_3 \cdot x F_3) P_\sigma)$ where

$$F_3 = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{-1}{\sqrt{6}} & \frac{-1}{\sqrt{6}} & \frac{2}{\sqrt{6}} \\ \frac{-1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \end{bmatrix} \quad (14)$$

and P_σ is the permutation matrix corresponding to the following mapping

$$\sigma: \begin{bmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 1 & 4 & 7 & 2 & 5 & 8 & 3 & 6 & 9 \end{bmatrix} \quad (15)$$

we obtain the reduced form of matrix F as

$$\tilde{TFT} = \text{diag} (F_4^{(a)}, F_3^{(e)}, F_3^{(e)}) \quad (16)$$

where

$$F_4^{(a)} = \left[\begin{array}{c|c} f_{11} & \tilde{u} \\ \hline u & F_3^{(a)} \end{array} \right] \quad (17)$$

and $F_3^{(a)}$ is a 3x3 block with the elements $f_{ij}^{(a)} = a_{ij} + 2 b_{ij}$ ($i, j = 1, 2, 3$) while the two identical blocks $F_3^{(e)}$ of order three are the double degenerate representations with the elements $F_{ij}^{(e)} = a_{ij} - b_{ij}$.

Since the order of the rotation axis or what is the same the order of matrix (14) $n = 3$ is odd we know in advance that there is not an antisymmetric species but there is $(n-1)/2 = 1$ a double degenerate species. So it is easy to establish that the first row of matrix (14) belongs to the symmetric, the second and third rows to the double degenerate species. The multiplication of matrix (14) and the valence bond length vector $\Delta r = (\Delta r_1, \Delta r_2, \Delta r_3)$ together with ΔR give the symmetry valence bond stretching coordinates (Table I).

Table I
Set of symmetry bond stretching coordinates for CH_3X (C_{3v})

$S(a) = (1/\sqrt{3})(\Delta r_1 + \Delta r_2 + \Delta r_3)$
$S_1(e) = (1/\sqrt{6})(2\Delta r_1 - \Delta r_2 - \Delta r_3)$
$S_2(e) = (1/\sqrt{6})(\Delta r_2 - \Delta r_3)$
$S(a) = \Delta R$

We can get similar expressions for the valence angle bending $\Delta\alpha_i, \Delta\beta_i$ ($i = 1, 2, 3$). So the reduced form (16) is the maximum one according to the molecular symmetry.

In the case of the molecules for eclipsed rigid configuration $\text{Y}(\text{CH}_3)_2$ (D_{3d}) ($\text{Y} = \text{Zn, Cd, Hg}$) (Fig. 1) the sets of the equivalent internal coordinates are a consequence of a threefold rotation axis C_3 and a plane σ_n perpendicular to it. The potential energy matrix in terms of the internal coordinates $\Delta R_1, \Delta R_2, \Delta r_i, \Delta\alpha_i, \Delta\beta_i$ ($i = 1, 2, \dots, 6$), $\Delta\epsilon, \Delta\epsilon'$ is:

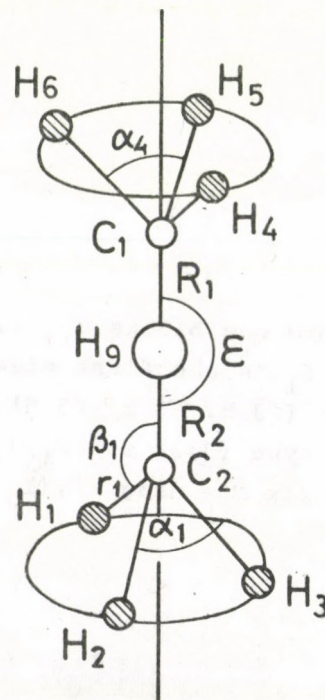


Fig. 1. Symmetry of the molecule $\text{Y}(\text{CH}_3)_2$ and its internal coordinates

$$F = \begin{array}{c|ccc|cc} \Delta R_1 & \Delta R_2 & \Delta r_1 - \Delta \beta_6 & \Delta \epsilon \Delta \epsilon' & & \\ \hline & F_{RR} & \begin{array}{c} \tilde{u} \\ \tilde{v} \end{array} & \begin{array}{c} d \\ d \end{array} & \begin{array}{c} d \\ d \end{array} & \\ \hline & & [F_{ij}] & \begin{array}{c} w \\ z \end{array} & & \\ \hline & \text{Symm.} & & F_{\epsilon\epsilon'} & & \end{array} \quad (18)$$

where the blocks $F_{RR} = \text{circ}(a, b)$, $[F_{ij}]_{3,6}$ and $F_{\epsilon\epsilon'} = \text{diag}(c, c)$ belong to the interactions of the equivalent internal coordinate groups $(\Delta R_1, \Delta R_2)$, $(\Delta r_1, \dots, \Delta \beta_6)$ and $(\Delta \epsilon, \Delta \epsilon')$ respectively. The block $[F_{ij}]_{3,6} \in \mathcal{P} \mathcal{B}_{3,6}$ while each $F_{ij} \in \mathcal{P} \mathcal{B}_{2,3}$.

Therefore by applying a combination of the decomposition formulae (12) and (8) we obtain the symmetry transformation matrix

$$T = \text{diag} (F_2, I_3 \cdot (F_2 \cdot F_3), I_2) \quad (19)$$

which diagonalizes the blocks belonging to the interactions of the equivalent coordinate groups. In equn. (19)

$$F_2 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \quad (20)$$

and F_3 is matrix (14). On the basis of the symmetry point group of the molecule, matrix F_2 belongs to the symmetry operation i so its rows are of type A_g and A_u . Thus, by using the symmetry type of the rows of F_3 established in the previous molecule and the rule of multiplication properties of direct products of irreducible representations ([1], p.331) one obtains

$$F_2 \cdot F_3 = \left. \begin{array}{ccc|ccc} \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\ \frac{2}{\sqrt{12}} & \frac{-1}{\sqrt{12}} & \frac{-1}{\sqrt{12}} & \frac{2}{\sqrt{12}} & \frac{-1}{\sqrt{12}} & \frac{-1}{\sqrt{12}} \\ 0 & \frac{1}{2} & -\frac{1}{2} & 0 & \frac{1}{2} & \frac{-1}{2} \end{array} \right\} \begin{array}{l} A_g \\ E_g \end{array} \quad \cdot \quad (21)$$

$$\left. \begin{array}{ccc|ccc} \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{-1}{\sqrt{6}} & \frac{-1}{\sqrt{6}} & \frac{-1}{\sqrt{6}} \\ \frac{2}{\sqrt{12}} & \frac{-1}{\sqrt{12}} & \frac{-1}{\sqrt{12}} & \frac{-2}{\sqrt{12}} & \frac{1}{\sqrt{12}} & \frac{1}{\sqrt{12}} \\ 0 & \frac{1}{2} & \frac{-1}{2} & 0 & \frac{-1}{2} & \frac{1}{2} \end{array} \right\} \begin{array}{l} A_{2u} \\ E_u \end{array}$$

Multiplication of matrix (21) with the vector $\Delta r = (\Delta r_1, \dots, \Delta r_6)$ and matrix F_2 with the vector $(\Delta R_1, \Delta R_2)$ gives the symmetry stretching coordinates to

be seen in Table II. We obtain the same linear combinations for $\Delta\alpha_i, \Delta\beta_i$ ($i = 1, 2, \dots, 6$) as was obtained for Δr_i including the redundancy whose presence is necessary because of symmetry considerations. An attempt to include the removal of redundancy can be seen in the case of the following molecule. The internal deformation coordinates $\Delta\epsilon$ and $\Delta\epsilon'$ are themselves symmetry coordinates of the type E_u so the determination of the symmetry type of the rows of matrix (19) is complete.

Table II

Symmetry stretching coordinates for the molecules $Y(CH_3)_2 (D_{3d})$

$$\begin{aligned}
 s(a_{1g}) &= \frac{1}{\sqrt{6}} \left(\sum_{i=1}^3 \Delta r_i + \sum_{j=4}^6 \Delta r_j \right) \\
 s(a_{1g}) &= \frac{1}{\sqrt{2}} (\Delta R_1 + \Delta R_2) \\
 \left\{ \begin{aligned}
 s^{(a)}(e_g) &= \frac{1}{\sqrt{12}} (2\Delta r_1 - \Delta r_2 - \Delta r_3 + 2\Delta r_4 - \Delta r_5 - \Delta r_6) \\
 s^{(b)}(e_g) &= \frac{1}{2} (\Delta r_2 - \Delta r_3 + \Delta r_5 - \Delta r_6)
 \end{aligned} \right. \\
 s(a_{2u}) &= \frac{1}{\sqrt{6}} \left(\sum_{i=1}^3 \Delta r_i - \sum_{j=4}^6 \Delta r_j \right) \\
 s(a_{2u}) &= \frac{1}{\sqrt{2}} (\Delta R_1 - \Delta R_2) \\
 \left\{ \begin{aligned}
 s^{(a)}(e_u) &= \frac{1}{\sqrt{12}} (2\Delta r_1 - \Delta r_2 - \Delta r_3 - 2\Delta r_4 + \Delta r_5 + \Delta r_6) \\
 s^{(b)}(e_u) &= \frac{1}{2} (\Delta r_2 - \Delta r_3 - \Delta r_4 + \Delta r_6)
 \end{aligned} \right.
 \end{aligned}$$

The CH_2Cl_2 molecule (Fig. 2) is of lower symmetry than the previous two, however, the method works well in this case too. Matrix F, in terms of internal coordinates, is

$$F = \begin{array}{c} \begin{array}{c} \Delta r_1 - \Delta r_4 \quad \Delta\alpha_{12} \quad \Delta\alpha_{34} \quad \Delta\alpha_{13} - \Delta\alpha_{23} \\ \left[\begin{array}{cc|cc} F_{rr} & & u & v & F_{ra} \\ & & & & \tilde{w} \\ & & F_{\alpha\alpha}^{(1)} & & \tilde{z} \\ \text{Symm.} & & & & F_{\alpha\alpha}^{(2)} \end{array} \right] \end{array} \end{array} \quad (22)$$

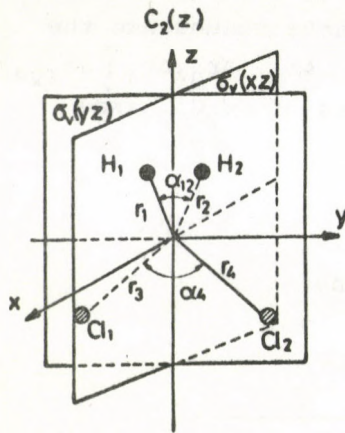


Fig. 2. Symmetry of the CH_2Cl_2 molecule and its internal coordinates

where the blocks presenting the interaction of the equivalent coordinates are F_{rr} , $F_{\alpha\alpha}^{(1)}$ and $F_{\alpha\alpha}^{(2)}$. According to their structures $F_{rr} \in \mathcal{C} \mathcal{B}_{2,2}$, $F_{\alpha\alpha}^{(1)} = \text{circ}(a,b)$ and $F_{\alpha\alpha}^{(2)} \in \mathcal{B} \mathcal{P} \mathcal{B}_{2,2}$. Therefore the matrix which diagonalizes these blocks is

$$T = (I_3 \cdot x F_3) \oplus (F_2 \cdot x F_2) \quad (23)$$

where F_2 is matrix (20), i.e. the same matrix belongs to each pair of internal coordinates $(\Delta r_1, \Delta r_2)$, $(\Delta r_3, \Delta r_4)$ and $(\Delta \alpha_{12}, \Delta \alpha_{34})$. However the symmetry type of the rows of the blocks is different. Because the order of the rotation axis $n = 2$ is less than three there are only symmetric and antisymmetric species. On the

basis of the molecular symmetry the species of the rows of the block in order are (a_1, b_1) , (a_1, b_2) and (a_1, a_1) . By applying the multiplication rule of the species of the first two blocks one obtains

$$F_2 \cdot x F_2 = \left[\begin{array}{cc|cc} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\ \hline \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \end{array} \right] \left. \begin{array}{l} \} a_1 \\ \} b_1 \\ \} b_2 \\ \} a_2 \end{array} \right\} \quad (24)$$

Choosing the permutation matrix P_σ as

$$P_\sigma = \begin{bmatrix} P_{a_1} \\ P_{b_1} \\ P_{b_2} \\ P_{a_2} \end{bmatrix} \quad (25)$$

with the blocks

$$P_{a_1} = \begin{bmatrix} \tilde{e}_1 \\ \tilde{e}_3 \\ -\frac{2}{\sqrt{6}} \tilde{e}_5 + \frac{1}{\sqrt{3}} \tilde{e}_7 \\ \tilde{e}_6 \end{bmatrix}, \quad P_{b_1} = \begin{bmatrix} \tilde{e}_2 \\ \tilde{e}_8 \end{bmatrix}, \quad P_{b_2} = \begin{bmatrix} \tilde{e}_4 \\ \tilde{e}_{10} \end{bmatrix}, \quad P_{a_2} = \tilde{e}_9 \quad (26)$$

where the e_i 's are unit vectors of order 10 and the special linear combination of the vectors \tilde{e}_5 and \tilde{e}_7 is used to remove coordinate redundancy the result of the matrix-vector product $P_{\sigma}T_s$ where $\tilde{s} = (\Delta r_1, \Delta r_2, \Delta r_3, \Delta r_4, \Delta\alpha_{12}, \Delta\alpha_{34}, \Delta\alpha_{13}, \Delta\alpha_{23}, \Delta\alpha_{14}, \Delta\alpha_{24})$ gives the symmetry coordinates of CH_2Cl_2 (see Table III).

Table III

Normalized symmetry coordinates for the CH_2Cl_2 molecule

Species	Symmetry coordinates
$a_1:$	$S_1 = \frac{1}{\sqrt{2}} (\Delta r_1 + \Delta r_2)$
	$S_2 = \frac{1}{\sqrt{2}} (\Delta r_3 + \Delta r_4)$
	$S_3 = \frac{1}{\sqrt{2}} (-2\Delta\alpha_{12} - 2\Delta\alpha_{34} + \Delta\alpha_{13} + \Delta\alpha_{24} + \Delta\alpha_{14} + \Delta\alpha_{23})$
	$S_4 = \frac{1}{\sqrt{2}} (\Delta\alpha_{12} - \Delta\alpha_{34})$
$b_1:$	$S_5 = \frac{1}{\sqrt{2}} (\Delta r_1 - \Delta r_2)$
	$S_6 = \frac{1}{2} (\Delta\alpha_{13} - \Delta\alpha_{23} + \Delta\alpha_{14} - \Delta\alpha_{24})$
$b_2:$	$S_7 = \frac{1}{\sqrt{2}} (\Delta r_3 - \Delta r_4)$
	$S_8 = \frac{1}{2} (\Delta\alpha_{13} - \Delta\alpha_{23} - \Delta\alpha_{14} + \Delta\alpha_{24})$
$a_2:$	$S_9 = \frac{1}{2} (\Delta\alpha_{13} + \Delta\alpha_{23} - \Delta\alpha_{14} - \Delta\alpha_{24})$

It should be noted that the method in its present form is suitable for determining molecular symmetry coordinates only when the reduced form of the representation of the molecule's point group does not contain triple degenerate representations. This means that for triple degenerate species, matrix (6) should contain three angle parameters instead of one (ϕ) in order to ensure the simultaneous transformation of the triple degenerate species.

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APPENDIX

The definition of the basic circulant of order n is

$$C_n = \text{circ} (0, 1, \dots, 0) \quad (27)$$

the elements of which are defined as

$$C_{jk} = \begin{cases} 1 & \text{if } j = k-1 \\ 0 & \text{if } j \neq k-1 \end{cases} \pmod{n}. \quad (28)$$

Its spectral decomposition is

$$C_n = F_n^* \Omega F_n \quad (29)$$

where

$$\Omega = \text{diag} (1, w, w^2, \dots, w^{(n-1)}) \quad (30)$$

and F_n is the so-called Fourier matrix of order n

$$F_n^* = \frac{1}{\sqrt{n}} [w^{(i-1)(j-1)}] \quad i, j = 1, 2, \dots, (n-1) \quad (31)$$

with the elements $w = \exp \left(\frac{2\pi i}{n} \right) = \cos \frac{2\pi}{n} + i \sin \frac{2\pi}{n}$ $i = \sqrt{-1}$.

By multiplying matrix (31) by matrix (30) the j -th row of the matrix product

$$\frac{1}{\sqrt{n}} (w^{(j-1)\ell} w^\ell) = \frac{1}{\sqrt{n}} w^{j\ell} \quad \ell = 0, 1, \dots, (n-1) \quad (32)$$

then multiplying equn. (32) with the k -th column $(1/\sqrt{n})(\bar{w}^{(k-1)r})$ ($r = 0, 1, \dots, (n-1)$) of matrix (31) and taking into account the relation $\bar{w}^{-k} = w^{-k} = w^{n-k}$ we obtain the (j,k) -th element of matrix (29) to be

$$\frac{1}{n} \sum_{r=0}^{n-1} w^{jr} w^{(k-1)r} = \frac{1}{n} \sum_{r=0}^{n-1} w^{r(j-k+1)} = \begin{cases} 1 & \text{if } j=k-1 \\ 0 & \text{if } j \neq k-1 \end{cases} \pmod{n}. \quad (33)$$

this is equivalent to definition (28) ([15] p.72).

By using the relation $C_n^{-k} = C_n^{n-k}$ we can easily see that any circulant matrix of order n can be written as a maximum $(n-1)$ -th order polynomial of the basic circulant matrix of order n . That is, for odd $n = 2m+1$

$$\begin{aligned} A_{2m+1} &= \text{circ} (a, b_1, b_2, \dots, b_m, b_m, \dots, b_1) = \\ &= aI_n + \sum_{v=1}^m b_v (C_n^v + C_n^{-v}) \end{aligned} \quad (34)$$

and for even order $n = 2m$

$$\begin{aligned} A_{2m} &= \text{circ} (a_1, b_1, b_2, \dots, b_m, \dots, b_2, b_1) = \\ &= aI_n + \sum_{v=1}^{m-1} b_v (C_n^v + C_n^{-v}) + b_m C_n^m. \end{aligned} \quad (35)$$

Substituting equn. (29) into equns. (34) and (35) one obtains

$$A_{2m+1} = \mathcal{F}_{2m+1}^* \left\{ aI_n + \sum_{v=1}^m b_v (\Omega_n^v + \Omega_n^{-v}) \right\} \mathcal{F}_{2m+1} \quad (36)$$

and

$$A_{2m} = \mathcal{F}_{2m}^* \left\{ aI_n + \sum_{v=1}^{m-1} b_v (\Omega_n^v + \Omega_n^{-v}) + b_m \Omega_n^m \right\} \mathcal{F}_{2m}. \quad (37)$$

By substituting equn. (30) into equns. (35) and (36) we obtain for the eigenvalues of A_{2m+1} [16]

$$\lambda_0 = a + 2 \sum_{v=1}^m b_v \quad (38)$$

and

$$\lambda_k = a + 2 \sum_{v=1}^m b_v \cos \frac{2\pi v k}{2m+1} \quad k = 1, 2, \dots, m \quad (39)$$

while for the eigenvalues of A_{2m}

$$\lambda_0 = a + 2 \sum_{v=1}^{m-1} b_v + b_m \quad (40)$$

$$\lambda_n = a + 2 \sum_{v=1}^{m-1} (-1)^v b_v + (-1)^m b_m \quad (41)$$

and

$$\lambda_k = a + 2 \sum_{v=1}^{m-1} b_v \cos \frac{k\pi v}{m} + (-1)^k b_m. \quad (42)$$

Equations (38)-(42) show that any symmetric circulant matrix of odd order ($n = 2m+1$) has one single and m double eigenvalues whereas any symmetric circulant matrix of even order ($n = 2m$) has two single and $(m-1)$ double eigenvalues.

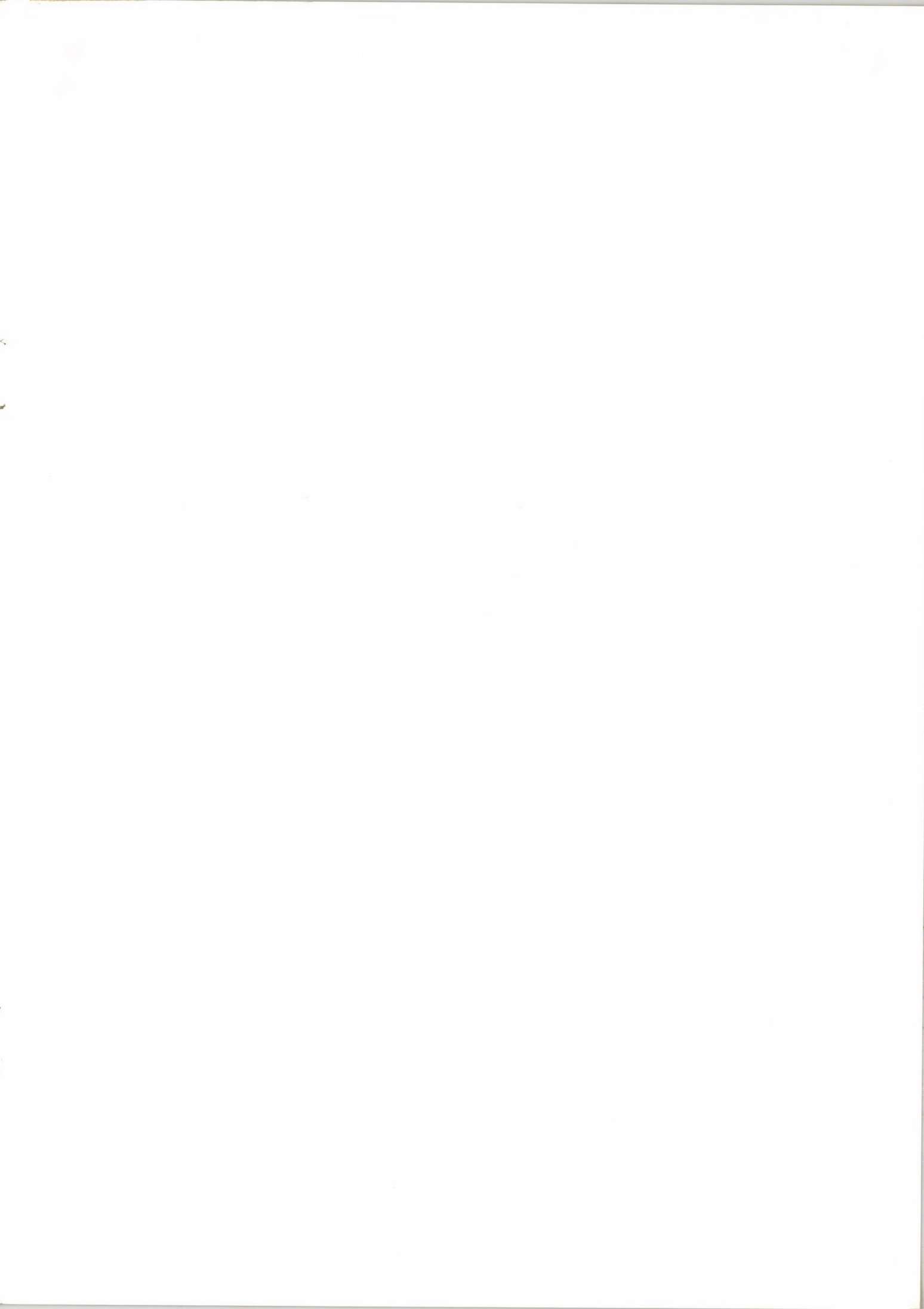
By using the following linear combinations of the column vectors of matrix (31) [16]

$$\frac{1}{\sqrt{2}} (f_k + f_{2m+1-k}) \quad \text{and} \quad \frac{1}{i\sqrt{2}} (f_k - f_{2m+1-k}) \quad k = 1, 2, \dots, m \quad (43)$$

the imaginary parts of the eigenvectors can be eliminated and we obtain matrix (6) for even order. For odd order the second column is missing.

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