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ON A COMPUTATIONAL METHOD OF PAIRS OF EIGENVECTORS ASSOCIATED WITH A DOUBLE DEGENERATE EIGENVALUE OF DIAGONIZABLE SQUARE MATRIX. APPLICATION TO HUCKEL'S MATRIX OF ALTERNANT HYDROCARBONS.

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I.DEFINITIONS.

We consider a square matrix $M = (m_{ik})$.Its eigenvalues are $y_\alpha, y_\beta, \ldots y_\mu, \ldots$The eigenvectors associated to these eigenvalues are $X_\alpha, X_\beta, \ldots X_\mu, \ldots$The components of the eigenvector X_μ are $x_{1\mu}, x_{2\mu}, \ldots x_{i\mu} \ldots$

M', transpose of M have the same eigenvalues.Its eigenvectors are $Z_\alpha, Z_\beta, \ldots Z_\mu, \ldots$The components of Z_μ are $z_{1\mu}, z_{2\mu}, \ldots z_{i\mu} \ldots$

II.REMINDER.[1)(2)]

F, function of variable y and matrix elements m_{ik} is the characteristic polynomial of M and M'.

y_μ being an non degenerate eigenvalue, we have

$$(1)\quad x_{k\mu} z_{i\mu} = -\left[\frac{\frac{\partial F}{\partial m_{ik}}}{\frac{\partial F}{\partial y}}\right]_{y=y_\mu}$$

If y_μ is a double degenerate eigenvalue, the eigenvectors associated to y are resp. $X_{\mu'}, X_{\mu''}$, and $Z_{\mu'}, Z_{\mu''}$ and we have the relation

$$(2)\quad P_\mu = \left[\Psi_{ki}\right]_{y=y_\mu} = \left[x_{k\mu'} z_{i\mu'} + x_{k\mu''} z_{i\mu''}\right]_{y=y_\mu} = -2\left[\frac{\frac{\partial^2 F}{\partial y \partial m_{ik}}}{\frac{\partial^2 F}{\partial y^2}}\right]_{y=y_\mu}$$

The double degenerate y_μ being root of $\frac{\partial F}{\partial y}$ and $\frac{\partial F}{\partial m_{ik}}$ we consider $\frac{\partial F}{\partial y} = [y - y_\mu]\,\Phi$ and we have

$$(3)\quad \frac{\partial^2 F}{\partial y^2} = \Phi + (y - y_\mu)\frac{d\Phi}{dy}$$

$$(4)\quad \left[\frac{\partial^2 F}{\partial y^2}\right]_{y=y_\mu} = \Phi$$

$$(5)\quad (y - y_\mu)\left[\frac{\partial^2 F}{\partial y^2}\right]_{y=y_\mu} \simeq \left[\frac{\partial F}{\partial y}\right]_{y=y_\mu}$$

In the same way we show

$$(6)\quad \frac{\partial^2 F}{\partial y\,\partial m_{ik}} = (y - y_\mu)\left[\frac{\partial F}{\partial m_{ik}}\right]_{y=y_\mu}$$

Considering (5) and (6), relation (2) becomes

$$(7)\quad P_\mu = [r_{ki}]_{y=y_\mu} = [x_{k\mu'} z_{i\mu'} + x_{k\mu''} z_{i\mu''}]_{y=y_\mu} = -\left[\frac{\frac{\partial F}{\partial m_{ik}}}{\frac{\partial F}{\partial y}}\right]_{y=y_\mu}$$

III. DETERMINATION OF PAIRS OF EIGENVECTORS ASSOCIATED WITH THE DEGENERATE EIGENVALUES.

a) Principle. We explain a computational method of determination of eigenvectors $X_{\mu'}$ and $Z_{\mu'}$; we obtain the matrix

$$(8)\quad P_{\mu'} = [x_{k\mu'} z_{i\mu'}]_{y=y_\mu} = X_{\mu'} Z_{\mu'}$$

The matrix $P_{\mu''} = P_\mu - P_{\mu'}$ determines the eigenvectors $X_{\mu''}$ and $Z_{\mu''}$.

b) Determination of eigenvectors $X_{\mu'}$ and $Z_{\mu'}$.

Substituting in M the diagonal element m_{rr} by $m_{rr} + q_r$, we obtain matrix N. F being the characteristic polynomial of M, this polynomial for N is $F + q_r \frac{\partial F}{\partial m_{rr}}$

y_μ being a doubly degenerate eigenvalue of M, we have

$$(9)\quad (F)_{y=y_\mu} = \left(\frac{\partial F}{\partial m_{rr}}\right)_{y=y_\mu} = \left(\frac{\partial F}{\partial y}\right)_{y=y_\mu} = 0$$

y_μ is an eigenvalue of N.

The relation between eigenvectors U_μ of N and V_μ of N', transpose of N, associated to y_μ is

$$(10)\quad u_{k\mu} v_{i\mu} = -\left[\frac{\frac{\partial F}{\partial m_{ik}} + q_r \frac{\partial^2 F}{\partial m_{ik}\,\partial m_{rr}}}{\frac{\partial F}{\partial y} + q_r \frac{\partial^2 F}{\partial y\,\partial m_{rr}}}\right]_{y=y_\mu}$$

y_μ being a doubly degenerate eigenvalue of M, $\frac{\partial F}{\partial m_{ik}}$ being equal to zero

$$(11)\quad u_{k\mu} v_{i\mu} = -\left[\frac{\frac{\partial^2 F}{\partial m_{ik}}\,\partial m_{rr}}{\frac{\partial^2 F}{\partial y\,\partial m_{rr}}}\right]_{y=y_\mu}$$

U_μ and V_μ being independant of q_r, are eigenvectors of M resp. M', associated with eigenvalue y_μ.

$$(12)\quad U_\mu = X_{\mu'};\ V_\mu = Z_{\mu'}$$

Comparing relation (11) to relation (1), we see that

$$M = \begin{bmatrix} 3 & 2 & 2 & -4 \\ 2 & 3 & 2 & -1 \\ 1 & 1 & 2 & -1 \\ 2 & 2 & 2 & -1 \end{bmatrix} \qquad X_\beta = \begin{vmatrix} -2 \\ 4 \\ 1 \\ 2 \end{vmatrix} \qquad X_\gamma = \begin{vmatrix} 0 \\ 3 \\ 1 \\ 2 \end{vmatrix}$$

$y_\alpha = 1$ = double degenerate eigenvalue

$$Z_\beta = \begin{vmatrix} -1 \\ -1 \\ -1 \\ 2 \end{vmatrix} \qquad Z_\gamma = \begin{vmatrix} 1 \\ 1 \\ 1 \\ -3/2 \end{vmatrix}$$

$y_\beta = 2$

$y_\gamma = 3$

Table 1

the characteristic polynomial of N is the matrix obtained by annulation of all elements in line and column index r. We can chose N as

IV. NUMERICAL EXAMPLE. We consider the matrix M table 1.

a) We have $\left[\frac{\partial^2 F}{\partial y \partial m_{1,1}}\right]_{y=1} = \left[-3y^2 + 8y - 3\right]_{y=1} = 2$

(13) $\left[\frac{\partial^2 F}{\partial y \partial m_{2,2}}\right]_{y=1} = \left[-3y^2 + 8y - 9\right]_{y=1} = -4 \qquad \left[\frac{\partial^2 F}{\partial y \partial m_{3,3}}\right]_{y=1} = \left[-3y^2 + 10y - 9\right]_{y=1} = -2$

$\left[\frac{\partial^2 F}{\partial y \partial m_{4,4}}\right]_{y=1} = \left[-3y^2 + 16y - 13\right]_{y=1} = 0$

Our method can be applied to indices 1,2 and 3, but not to index 4, relation (11) not being applicable if $\frac{\partial^2 F}{\partial y \partial m_{k,k}} = 0$

b) Operation index 3

(14) $P_{\alpha'} = \frac{\partial^2 F}{\partial m_{i,k} \partial m_{3,3}} =$

$$\begin{vmatrix} -1 & -2 & 0 & 3 \\ 1 & 2 & 0 & 3 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix}$$

columns are $kX_{\alpha'}$, lines are $k\,Z_{\alpha'}$.

We chose $X_{\alpha'}$ on $Z_{\alpha'}$ in manner that $X_{\alpha'}\,Z_{\alpha'} = Z_{\alpha'}\,X_{\alpha'} = 1$

We have

$$(15) \qquad X_{\alpha'} = \begin{vmatrix} 1 \\ -1 \\ 0 \\ 0 \end{vmatrix} \qquad Z_{\alpha'} = \begin{vmatrix} -1 \\ -2 \\ 0 \\ 3 \end{vmatrix}$$

Applying relation (2) to $y_\alpha = 1$, we obtain

$$(16) \qquad P_\alpha = \begin{vmatrix} -1 & -2 & -2 & 2 \\ 1 & 2 & 1 & -7/2 \\ 0 & 0 & 1 & -1/2 \\ 0 & 0 & 0 & 0 \end{vmatrix}$$

$$(17) \quad P_{\alpha''} = P_\alpha - P_{\alpha'} = X_{\alpha''} Z'_{\alpha''} = \begin{vmatrix} 0 & 0 & -2 & 1 \\ 0 & 0 & 1 & -1/2 \\ 0 & 0 & 1 & -1/2 \\ 0 & 0 & 0 & 0 \end{vmatrix}$$

Choosing $X_{\alpha''} = \begin{vmatrix} 2 \\ -1 \\ -1 \\ 0 \end{vmatrix}$, we have $Z_{\alpha''} = \begin{vmatrix} 0 \\ 0 \\ -1 \\ 1/2 \end{vmatrix}$

Sets of eigenvectors of M are given in table 2.

$X_{\alpha'} = \begin{vmatrix} 1 \\ -1 \\ 0 \\ 0 \end{vmatrix}$	$X_{\alpha''} = \begin{vmatrix} 2 \\ -1 \\ -1 \\ 0 \end{vmatrix}$	$X_\beta = \begin{vmatrix} -2 \\ 4 \\ 1 \\ 2 \end{vmatrix}$	$X_\gamma = \begin{vmatrix} 0 \\ 3 \\ 1 \\ 2 \end{vmatrix}$
$Z_{\alpha'} = \begin{vmatrix} -1 \\ -2 \\ 0 \\ 3 \end{vmatrix}$	$Z_{\alpha''} = \begin{vmatrix} 0 \\ 0 \\ -1 \\ 1/2 \end{vmatrix}$	$Z_\beta = \begin{vmatrix} -1 \\ -1 \\ -1 \\ 2 \end{vmatrix}$	$Z_\gamma = \begin{vmatrix} 1 \\ 1 \\ 1 \\ -3/2 \end{vmatrix}$

Table 2

These sets verify the relation $X'_\mu Z_\nu = Z'_\mu X_\nu = \delta_{\mu\nu}$

$\delta_{\mu\nu}$ being Kroneckers symbol.

c)Operation indices 1 and2.Results see table 3

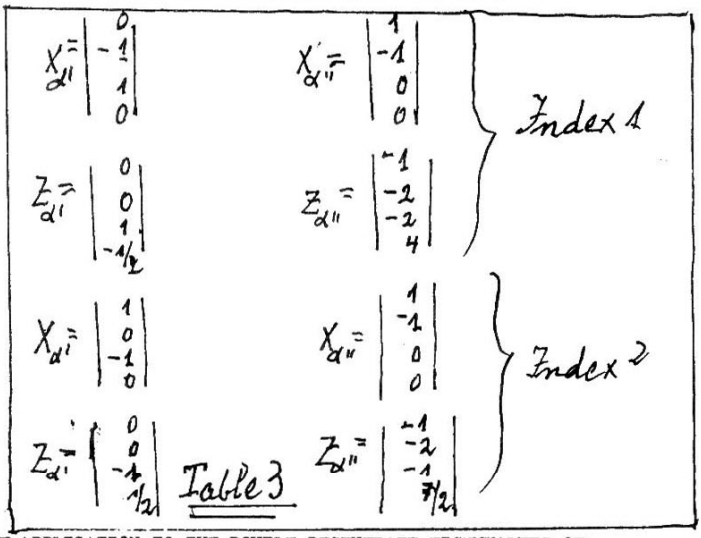


Table 3

V.APPLICATION TO THE DOUBLE DEGENERATE EIGENVALUES OF SYMMETRIC MATRICES USED IN THE HUCKEL'S METHOD [3] APPLIED TO ALTERNANT HYDROCARBONS.

We shall recall the relations for symmetric matrices. $X_\mu = Z_\mu$ an $X'_\mu X_\nu = \partial_{\mu\nu}$

In most cases the symmetry of the molecule permits the decomposition of the matrix in several matrices corresponding to the irreductible representations of the symmetric group of the molecule.If two different representations correspond to the the degenerateeigenvalue y_μ ,the eigenvectors X_μ' and X_μ'' are eigenvectors of non-degenerate eigenvalue y_μ of two different matrices.But if y_μ is a doubly degenerate eigenvalue of a matrix corresponding to a same irreductible representation, our computational method (as others [4])may be used.

Example.1/3Naphtoquinodimethane.

Application of Huckel's H.M.O.method leads to matrix represented by graph fig.1.Vertex index i represents diagonal element m_{ii}

of the matrix. Edge ij represents the element m_{ij} and m_{ji}. All diagonal elements of M are equal to zero. Non diagonal elements $m_{ij} = 1$, if ij is an edge of the graph; $m_{ij} = 0$ in the other case. Table 4 gives eigenvalues and eigenvectors of this matrix. We consider the eigenvalue $y_\mu = 0$, which is doubly degenerate. Our method gives no results, if we operate to indices 1, 3, 5, 7 or 9 $= 0$ if r = 1, 3, 5, 7 or 9.

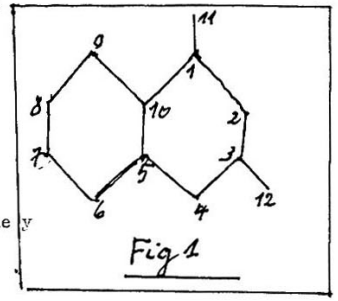


Fig 1

Table 5 gives graphs of pairs of eigenvectors, associated to the degenerate eigenvalue $y_\mu = 0$

A) Pair of eigenvectors corresponding table 4

B) Pair obtained by operation index 2

C) " " " " " INDICES 4, 6, 8, 10

D) " " " " index 11

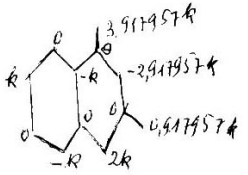
E) " " " index 12

x_i \ y_μ	1 2.37983	2 1.76769	3 1.50078	4 1.12413	5 .83343	6 .00000	7 -.00001	8 -.83343
1	.38858	-.19916	-.49915	-.02582	-.27584	-.00000	.00001	.27584
2	.27769	-.37111	-.11597	.24023	-.20634	-.51820	-.27263	-.20634
3	.29430	-.45691	.32510	.29688	.10386	.00000	.00001	-.10386
4	.29905	-.17822	.38725	-.17057	.16829	.35518	-.46551	.16829
5	.41740	.14185	.25608	-.48863	.03639	.00000	-.00001	-.03639
6	.25362	.29732	.29762	-.12221	-.44537	-.17759	.23276	-.44537
7	.18620	.38379	.19068	.33999	-.40758	-.00002	-.00001	.40758
8	.18950	.38117	-.01160	.51443	.10568	.17759	-.23276	.10568
9	.26480	.29008	-.20799	.23831	.49566	.00000	-.00001	-.49566
10	.44068	.13166	-.30055	-.24652	.30742	-.17759	.23276	.30742
11	.15403	-.11286	-.33259	-.02386	-.33097	.89579	.02987	-.33097
12	.12366	-.25845	.21662	.26408	.12462	.17302	.73814	.12462

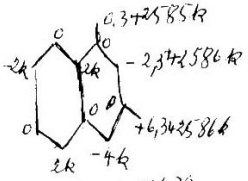
Levels 9, 10, 11 and 12 not used in our study are not introduced in this table.

Table 4

A

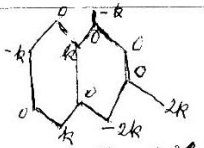


$k = 0,177559$

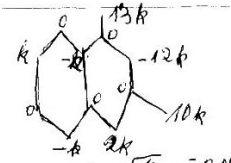


$k = 0,116638$

B

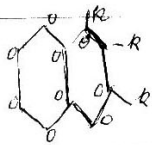


$k = \sqrt{9/12} = 0,8660254...$

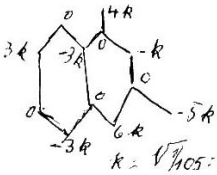


$k = \sqrt{1/420} = 0,0487944$

C

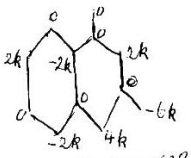


$k = \sqrt{1/3} = 0,5773502$

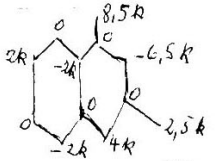


$k = \sqrt{1/105} = 0,0975899$

D

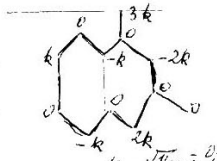


$k = 0,1242078$

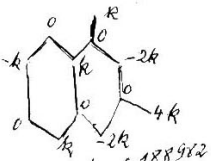


$k = 0,0814924$

E



$k = \sqrt{1/20} = 0,2236067$



$k = 0,1889822$

Table 5

The eigenvector of each pair (table 5)is orthogonal to its associate and also to the others eigenvectors of the matrix.

π ELECTRON DENSITY (H.M.O.METHOD)

We consider an alternant hydrocarbon,containing 2n carbon atoms. We recall that $x^2_{i\mu'}$ and $x^2_{i\mu''}$,diagonal elements of $P_{\mu'}$ resp.$P_{\mu''}$ are depending of the choice of pair of eigenvectors (see chap.III and IV),$x^2_{i\mu'} + x^2_{i\mu''}$,diagonal element of P_μ is independant of this choice Four ground state and closed shell molecules ,each of the lower levels contains 2 electrons;the π electron density H.M.O.Method of atom i is given by (18)

$$(18) \qquad q_i = 2 \sum_{\mu=1}^{n} x^2_{i\mu} = 1$$

If the level y_μ with $\mu < n$ is doubly degenerate,the sum $x^2_{i\mu'} + x^2_{i\mu''}$ is independant of the choice of pair of eigenvectors; But if the highest occupied level y_μ is doubly degenerate (see our example $y = 9$) , the relation (18) is valid only, if each of the two levels contains 1 electron.

Numerical example:Atom 2 (see table 4)

The sum of the electron densities of levels 1 to 5 is

$2(0,27769^2 + 0,37111^2 + 0,11597^2 + 0,24023^2 + 0,20634^2) = 0,6571396$

$2\, x^2_{2\mu'} = 2.0,5182^2 = 0,5370624$

$2\, x^2_{2\mu''} = 2.0,2763^2 = 0,1486542$

$x^2_{2\mu'} + x^2_{2\mu''} = 0,3428583$

$0,6571396 + 0,3428583 = 1$

(1) I.Samuel,Match ,Number 15,1984,p.107

(2) P.O.Löwdin,J.Chem.Phys.18,365 (1950)

(3) E.Hückel,Z.Physik,70,204 (1931)

(4) E.Heilbronner,Das H.M.O.Modell und seine Anwendungen Verlag chemie Weinheim 1968,P.127/8