INVESTIGATION OF THE STRUCTURE OF ORGANOSILICON COMPOUNDS BY ω-TECHNIQUE, I

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The main defect of Hückel's LCAO—MO method is that it leaves the interactions between electrons out of consideration. Thus it results in greater partial charges and dipole moments than the observed values. It is, however, easy to prove, that, if there is a partial charge on a carbon atom in a π-system, its coulomb integral cannot be equal to the $\alpha = \alpha_0$ value chosen as the unit, and used in the 0th approximation. (In the 0th approximation the partial charge of the atoms is 0.) For an electron density $Q < 1$, the positive charge on an atom results in the reduction of screening and in the increase of the coulomb attraction towards the nucleus. The α value (coulomb integral) of this carbon atom will be more negative. In the opposite case, when the partial charge is negative, it results in a shift of α towards more positive values. According to WHELAND and MANN [1] the coulomb integral is in linear relationship with the partial charge, as follows:

$$\alpha_r = \alpha_0 + (n_r - Q_r)\,\omega\beta$$

where α_0 is the coulomb integral used in the 0th approximation, n_r the number of electrons given by the atom r into the π-system, Q_r the electron density around the atom r, and ω is an empirical coefficient. Since the value of α_r depends on the partial charge, the problem can only be solved by successive approximation.

Modified coulomb integrals provide new charge distributions. Calculations have to be continued until the charge distribution does not change, i.e. the system becomes self-consistent.

It has been shown by STREITWIESER [2] that the method of ω-technique is similar to Pariser—Parr—Pople's semiempirical SCF method with the simplification that electron interactions are not expressed explicitly but by means of an average empirical constant. If in the case of the P—P—P method the electron repulsion integrals, γ_{rs} are neglected for $r = s$, then

$$F_{rr} = \alpha_r + \frac{1}{2} Q_r \gamma_{rr}$$

$$F_{rs} = \beta_{rs}$$

The similarity of these expressions to those used in the case of ω-technique is obvious.

The drawback of the ω-technique is that on changing the value of ω the eigenvalues, linear coefficients and partial charges of the system converge on different values. The aim of the present work has been to investigate the applicability of the ω-technique to a certain group of compounds, namely, silicon organic compounds, and to establish regularities in connection with the effect of the changes in ω and to find the optimum value of ω. Trimethyl-vinyl-silane (I), trimethyl-phenyl-silane (II), p-bis-trimethyl-silyl-benzene(III) and trimethyl-benzyl-silane (IV) have been chosen as model compounds.

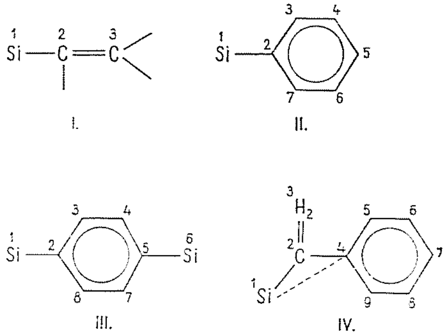


Fig. 1. Numbering of the π-system of the compounds studied

There have been accumulated a number of experimental data during the investigation of silicon organic compounds to prove that the vacant d orbitals of silicon bound to vinyl or phenyl groups overlap the π electron system on vinyl and phenyl groups to give rise to a partial $d\pi - p\pi$ bond beside a simple σ bond [3—8]. The methylene group situated between the silicon atom and phenyl group in the case of the benzyl compound has a hyperconjugative effect towards both the phenyl group and silicon atom. There exists a further interaction between the d orbital on the silicon atom and the $p\pi$ orbital on the β carbon: a $d - \pi$ effect or long bond [9]. Accordingly, compound I has a three-central, compound II a seven-central, compound III an eight-central and compound IV a nine-central π electron system. The numbering of the atoms of molecules is presented in Fig. 1. The coulomb and exchange integrals have been calculated with the knowledge of bond lengths, ionization energies and effective nuclear charges on the basis of integral equations expanded for the $2p\,\pi - 2p\,\pi$ and $2p\,\pi - 3d\,\pi$ bonds, by means of integral tables [9]. The determinants of the energy matrix of the molecules used in the 0th approximation are as follows (α is the coulomb integral of the carbon atom in benzene, β is the exchange integral of the carbon-carbon bond in benzene):

Trimethyl-vinyl-silane

$$\begin{bmatrix} \alpha - 1.8152\,\beta - E & 0.3374\,\beta & 0 \\ 0.3374\,\beta & \alpha - E & 1.0324\,\beta \\ 0 & 1.0324\,\beta & \alpha - E \end{bmatrix} = 0$$

Trimethyl-phenyl-silane

$$\begin{bmatrix} \alpha-1.81524\beta-E & 0.337396\beta & 0 & 0 & 0 & 0 & 0 \\ 0.337396\beta & \alpha+0.373168\beta-E & \beta & 0 & 0 & 0 & \beta \\ 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta \\ 0 & \beta & 0 & 0 & 0 & \beta & \alpha-E \end{bmatrix} = 0$$

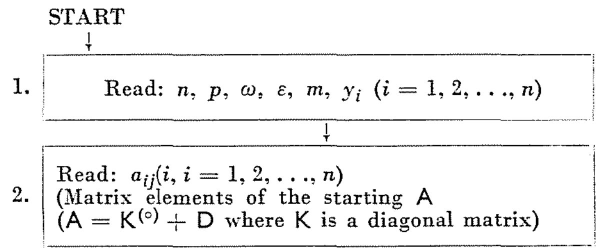
p-bis-trimethyl-silyl-benzene

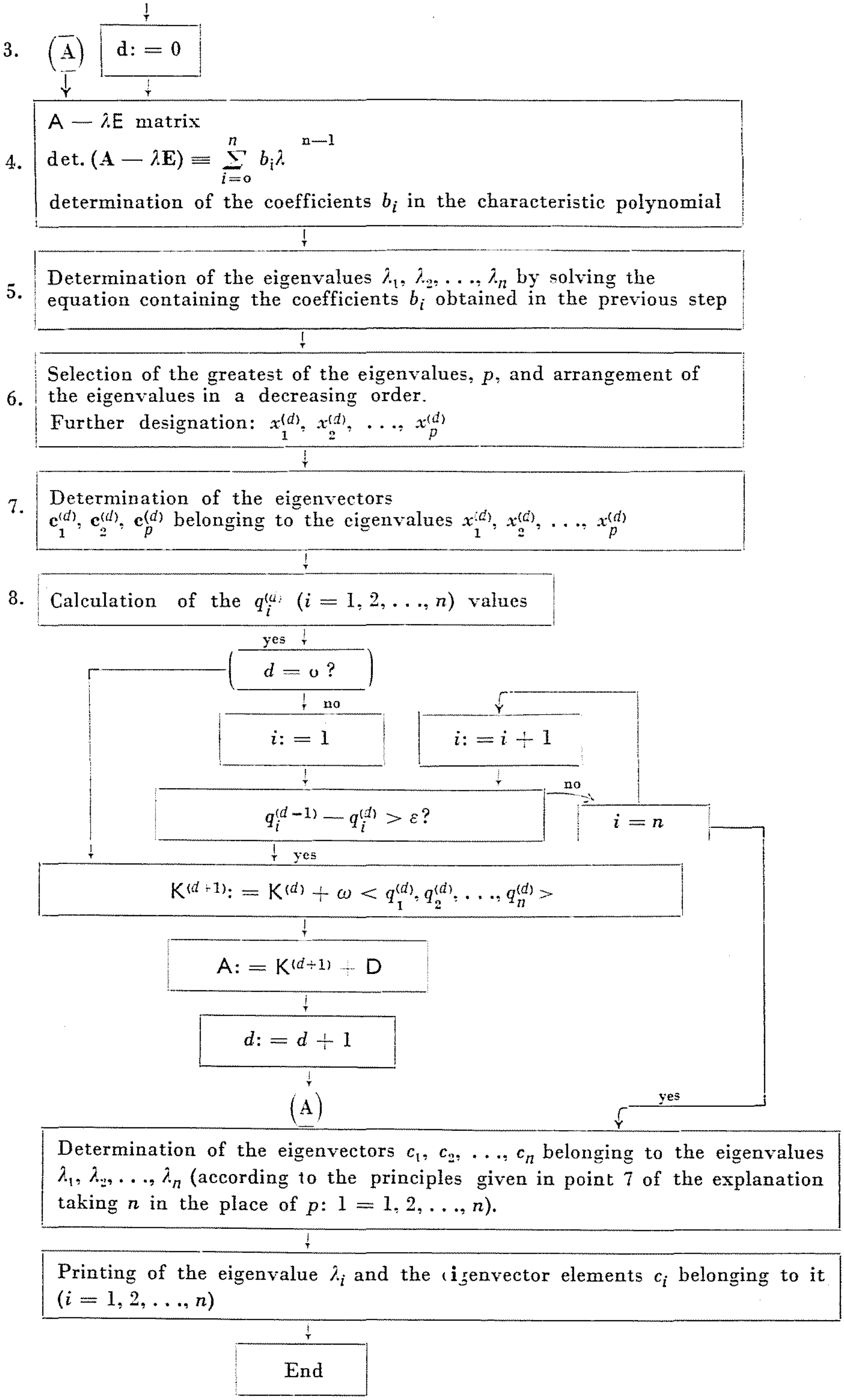
$$\begin{bmatrix} \alpha-1.815240\beta-E & 0.337396\beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0.337396\beta & \alpha+0.373168\beta-E & \beta & 0 & 0 & 0 & 0 & \beta \\ 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta & \alpha+0.373168\beta-E & 0.337396\beta & \beta & 0 \\ 0 & 0 & 0 & 0 & 0.337396\beta & \alpha-1.815240\beta-E & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta & 0 & \alpha-E & \beta \\ 0 & \beta & 0 & 0 & 0 & 0 & \beta & \alpha-E \end{bmatrix} = 0$$

Trimethyl-benzyl-silane

$$\begin{bmatrix} \alpha-1.8152\beta-E & 0.3374\beta & 0 & 0.1284\beta & 0 & 0 & 0 & 0 & 0 \\ 0.3374\beta & \alpha-E & 0.06\beta & 0.8\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 3.06\beta & \alpha-0.5\beta-E & 0 & 0 & 0 & 0 & 0 & 0 \\ 0.1283\beta & 0.8\beta & 0 & \alpha-E & \beta & 0 & 0 & 0 & \beta \\ 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E \end{bmatrix} = 0$$

A computer program has been elaborated for the LCAO—MO method improved by the ω-technique to calculate molecular structures. The block diagram of the program is as follows:





3. (A) $d := 0$

4. $A - \lambda E$ matrix

$\det.(A - \lambda E) \equiv \sum_{i=o}^{n} b_i \lambda^{n-1}$

determination of the coefficients b_i in the characteristic polynomial

5. Determination of the eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_n$ by solving the equation containing the coefficients b_i obtained in the previous step

6. Selection of the greatest of the eigenvalues, p, and arrangement of the eigenvalues in a decreasing order.
Further designation: $x_1^{(d)}, x_2^{(d)}, \ldots, x_p^{(d)}$

7. Determination of the eigenvectors $\mathbf{c}_1^{(d)}, \mathbf{c}_2^{(d)}, \mathbf{c}_p^{(d)}$ belonging to the eigenvalues $x_1^{(d)}, x_2^{(d)}, \ldots, x_p^{(d)}$

8. Calculation of the $q_i^{(d)}$ $(i = 1, 2, \ldots, n)$ values

Determination of the eigenvectors $c_1, c_2, \ldots, c_n$ belonging to the eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_n$ (according to the principles given in point 7 of the explanation taking n in the place of p: $1 = 1, 2, \ldots, n$).

Printing of the eigenvalue λ_i and the eigenvector elements c_i belonging to it $(i = 1, 2, \ldots, n)$

End

The following comments can be made on the block diagram:

1. Of input data

n is the order of the initial matrix A (i.e. the matrix A is of the type nxn);

p is the number of eigenvalues selected of the ones determined by calculation, in fact the selection of p molecular orbitals where electrons occur;

m is the number of electrons on the p^{th} molecular orbital, i.e. 2 or 1;

$y_1, y_2, \ldots, y_n$ are the number of electrons given by atoms designated by $1, 2, \ldots, n$ into the π electron system. Their possible value: 0, 1 or 2;

ω is the parameter used in the ω-technique;

ε is a limiting number to the studies on the q_i values, which actually gives the required accuracy of the procedure (e.g. $\varepsilon = 10^{-4}$).

2. a_{ij} is the symbol of the initial matrix A ($i, j = 1, 2, \ldots, n$). Matrix A can be considered as the sum of the diagonal matrix $\mathsf{K}^{(0)}$ and matrix D:

$$\mathsf{A} = \mathsf{K}^{(0)} + \mathsf{D}$$

D is a matrix in the diagonal of which all elements equal 0. Matrix D remains unchanged during calculation.

3. d is the serial number of approximation cycles $(0, 1, 2, \ldots)$. It is given as the upper index in round brackets in the symbols.

4. Daniilevskii's method has been applied to the determination of the b_i coefficients in the characteristic polynomial $\det(\mathsf{A} - \lambda\, \mathsf{E}) \equiv \sum_{i=0}^{n} b_i\, \lambda^{n-i}$ of the matrix $\mathsf{A} - \lambda\, \mathsf{E}$. The essence of the method is that the matrix A has to be brought in the Frobenius form using similarity transformations (10).

5. For the solution of the n^{th} order algebraic equation $\sum_{i=0}^{n} b_i\, \lambda^{n-i} = 0$ a program designed for this purpose by the authors was used (11).

6. By selecting p highest eigenvalues (λ_i) actually the eigenenergies (E_i) of the p lowest energy molecular orbitals are selected, since $E_i = \alpha - \lambda_i\, \beta$, and β is negative.

7. The basic equation for a given eigenvalue $x_l^{(d)}$ is

$$\mathbf{A}^{(d)}\, \mathbf{c}_l^{(d)} = x_l^{(d)}\, \mathbf{c}_l^{(d)} \quad (l = 1, =, \ldots p)\,.$$

Since this basic equation is actually

$$(\mathsf{A}^{(d)} - x_l^{(d)}\, \mathsf{E})\, \mathbf{c}_l^{(d)} = 0$$

which is a homogeneous linear system of equations. It has $c_l^{(d)} \neq 0$ not trivial solution only if the condition

$$\det(\mathsf{A}^{(d)} - x_l^{(d)}\, \mathsf{E}) = 0$$

is fulfilled in any case. This is true when $x_l^{(d)}$ is an eigenvalue.

In our case (dyadic matrix) all eigenvalues are real and single. The $c_l^{(d)}$ eigenvector belonging to the eigenvalue $x_l^{(d)}$ can be obtained by normalization as follows:

$$(c_l^{(d)})^T \cdot c_l^{(d)} = 1 .$$

In the course of the calculation of the eigenvectors $\mathbf{c}_l^{(d)}$ belonging to the eigenvalues $x_l^{(d)}$ $(l = 1, 2, \dots, p)$ a n — 1-st order inhomogeneous system of equations was constructed of the elements of the $(n - 1)$. n type $(\mathsf{F}, \mathbf{t})$ matrix obtained by omitting the n-th row of the matrix $\mathsf{K}^{(d)} + \dot{\mathsf{D}}$ (where the matrix F is of the type $(n - 1) \times (n - 1)$, t is column vector). The extended coefficient matrix of the system of equations is $(\mathsf{F} - x_l\, \mathsf{E} - \mathbf{t})$. The elimination method of Gauss was used for solving the system of equations in the course of the program. The elements of the resultant vector in the place of $-\mathbf{t}$ are $t_1, t_2 \dots t_{n-1}$. Owing to the normalization condition

$$c = \frac{1}{\sqrt{t_1^2 + t_2^2 + \dots + t_{n-1}^2 + 1}}$$

and using this, the elements of the eigenvector $\mathbf{c}_l^{(d)}$ are

$$\begin{aligned} c_{1,l}^{(d)} &= c t_1 \\ c_{2,l}^{(d)} &= c \cdot t_2 \\ &\vdots \\ c_{n-1,l}^{(d)} &= c \cdot t_{n-1} \\ c_{n,l} &= c . \end{aligned}$$

8. The values of $q_i^{(d)}$ $(i = 1, 2, \dots, n)$ were calculated by means of the following relationships:

$$Q_i^{(d)} = 2\,(c_{i,1}^{(d)})^2 + 2\,(c_{i,2}^{(d)})^2 + \dots + 2\,(c_{i,p-1}^{(d)})^2 + 2\,(c_{i,p}^{(d)})^2$$

where Q_i is the electron density around the i-th atom,

$$q_i^{(d)} = y_i - Q_i^{(d)}$$

where q_i is the partial charge of the i-th atom.

Computation was made by a National Elliott 803 B electronic computer, which ran a cycle within 60—70 seconds in the case of a 7×7 matrix. The program suits to compute maximum 30-th order matrixes (i.e. thirty-central π-systems).

The iteration calculations were performed using different values of ω for different compounds (varying ω from 0 to 1.4). By increasing ω the systems converge more slowly, the number of cycles to obtain the self-consistent data

Table 1

Number of iteration cycles used in the case of different ω values

Compound	Number of centres	Number of iteration cycles								
		$\omega = 0.1$	0.3	0.5	0.7	0.8	0.9	1.0	1.2	1.4
Vinyl silane	3		6	9	15			65	diverges	diverges
Phenyl silane	7			9	13		23	35	110	diverges
Bis-silyl benzene	8	4		6		8		10	12	converges
Benzyl silane	9		6	9				22	34	60

at the required accuracy also increases. In the case of compounds containing odd numbered centres, at a certain value of ω the system becomes self-consistent only after an infinite number of iteration cycles, and increasing the value of ω the system will not converge but diverge (at ω of about 1.2—1.4). In the case of an even-numbered π-system (e.g. bis-phenyl compound), no divergence was observed, and the system was found to converge more rapidly than in the case of compounds containing a similar, but odd number of atoms. The rate of convergence also depends on the number of centres. Increasing the number of centres of systems containing an odd number of centres, the number of necessary cycles decreases. The values of ω and the number of iteration cycles used in the case of the compounds studied are summarized in Table 1.

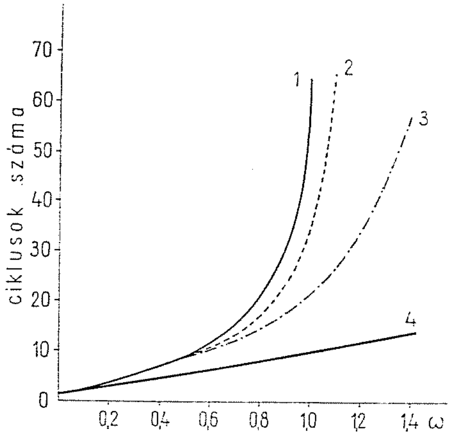


Fig. 2. Number of iteration cycles vs ω plot. 1. vinyl-silane; 2. phenyl-silane; 3. benzyl-silane; 3. bis-silyl-benzene

The rate of convergence is clearly reflected by Fig. 2 where the number of cycles is plotted against ω for various compounds.

Summary

The effect of the variation of ω on the data calculated for π systems was studied in the case of LCAO—MO calculations made by the ω-techniques. Trimethyl vinyl silane, trimethyl phenyl silane, p-bis-trimethyl silyl benzene and trimethyl benzyl silane were used as model compounds. A computer program has been worked out. The results of computations show that the rate of convergence changes remarkably with ω.

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