

CONFIGURATION INTERACTION IN THE GENERALIZED FREE ELECTRON MOLECULAR ORBITAL METHOD. I. THEORY

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The Generalized Free Electron Molecular Orbital (G-FEMO) method has been applied to date in calculations of the ground state properties of some conjugated hydrocarbons and heterocycles containing nitrogen and oxygen atoms.

In this paper the molecular orbitals of the G-FEMO method were used as the basic functions for the construction of Slater determinants. Making use of the properties of the molecular orbitals mentioned above, a semiempirical procedure is proposed for the evaluation of molecular electronic interaction integrals. This made it possible to include the configuration interaction procedure in the G-FEMO method.

Means of calculating such molecular properties as transition energies, oscillator strengths, dipole moments and electronic charge distribution are given within the framework of the method proposed in this paper. It should be mentioned that in this method there are less empirical parameters than, for example, in the Pariser and Parr method.

1. Introduction

There have been up to now, some substantial difficulties in obtaining the exact solutions of quantum mechanical equations for molecules containing large number of electrons. Therefore, efforts towards the further developing of approximated and simple methods of calculating the electronic properties of molecules seem to be justified.

The starting points for all these methods are the Born and Oppenheimer (1927) approximation and for π -electron systems the π -electron approximation (Lykos and Parr 1956). Within the framework of these approximations the immobile nuclei and the σ electrons which maintain the geometrical arrangement, form a skeleton of the molecule. This skeleton has a positive charge which creates a potential under whose influence π electrons move. Furthermore, the electronic interaction between the π electrons is usually neglected in a first approximation.

Such assumptions lead to a few molecular orbital approaches. One of them is the Free Electron Molecular Orbital (FEMO) method (*e.g.* Ruedenberg and Scherr 1953).

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The following are the main assumptions of the FEMO method. The π electrons move under the influence of the effective core potential which is infinitely high everywhere except on the bond lines of the skeleton of the molecule, where it is finite and equals zero. Therefore, the molecular orbitals in this method depend on one coordinate x measured along the bond path of a molecule. It should be noted that if such a model is accepted, the quantum mechanical problem can be solved exactly.

However, this method could only be applied to calculations of the ground state properties of hydrocarbons. The inclusion of electronic interaction terms in the Hamiltonian and the use of Slater determinantal functions by Ham and Ruedenberg (1956) made it possible to calculate some excited state properties of the molecules. It should be noted that they proposed the semiempirical procedure in the evaluation of molecular electronic interaction integrals and molecular core integrals.

However, the range of applications of the method in this form included only aromatic hydrocarbons. Therefore, it was necessary to extend the method in such a way that it could be applicable to conjugated molecules containing heteroatoms. This was done by Woźnicki (unpublished results). He assumes that the one-electron potential energy is equal to zero on the bond lines of the skeleton of a molecule except at the nuclei, where negative delta functions with some constant strengths for each type of atoms are placed¹. This Generalized Free Electron Molecular Orbital (G-FEMO) method proved quite successful in the interpretation of the ground state properties of hydrocarbons (Woźnicki and Żurawski 1967b) as well as heterocycles containing nitrogen (Woźnicki and Żurawski 1967a) and oxygen (Żurawski 1967).

In the investigations presented in this paper, the semiempirical procedure for the evaluation of molecular electronic interaction integrals has been proposed. This made it possible to include the configuration interaction procedure in the G-FEMO method.

Accordingly, the present paper gives the description of the method of calculations within the framework of the G-FEMO method with the configuration interaction procedure. The applications of the proposed method to some aromatic molecules containing nitrogen atoms will be given in the next paper (Żurawski 1971).

2. Description of the basic assumptions in the G-FEMO model

Within the framework of π -electron approximation the total Hamiltonian for π -electrons of a molecule may be written as follows

$$K = \sum_{\nu=1}^N H_{\nu} + \sum_{\mu, \nu=1}^N g_{\nu\mu} \quad (1)$$

where N is the number of π -electrons in a molecule. Furthermore H_{ν} is the one-electron operator

$$H_{\nu} = T_{\nu} + V_{\nu} \quad (2)$$

¹) Earlier, negative delta functions in the one-electron potential energy terms were used by Frost and Leland (1956). However, their method in contradiction to the method of Woźnicki did not make it possible to take into consideration the variation of individual bond lengths in the molecule.

where T_ν is the kinetic energy operator and V_ν is the interaction operator of the ν -th π electron with the core. Moreover $g_{\mu\nu}$ is the electronic interaction operator

$$g_{\mu\nu} = \frac{e^2}{|\mathbf{r}_\nu - \mathbf{r}_\mu|}. \quad (3)$$

As a first step we look for a solution of the Schrödinger equation containing the Hamiltonian without electronic interaction terms. If this solution is to be in the form of an anti-symmetric product of one-electron functions then the problem will be reduced to a solution of a one-electron equation

$$\mathbf{H}\varphi_n = E_n\varphi_n. \quad (4)$$

In general, the different molecular orbitals, which are the solutions of the above mentioned equation, are primarily distinguished by their longitudinal profiles, along the bond path, while their transverse profiles, perpendicular to the bond path, remain essentially unchanged. This fact suggests an approximation which allows us to treat the problem one-dimensionally. Accordingly, it is assumed that the potential V in equation (2) has the form of a thin tube

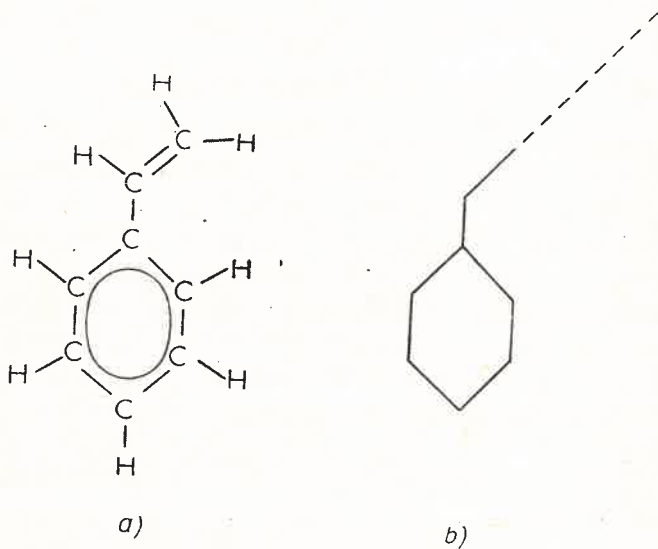


Fig. 1. Styrene molecule: (a) the structure formula, (b) the π electron skeleton of the molecule

following the π -electron bond path. Its value is infinitely high everywhere except within this tube where it is finite. Therefore, the values of molecular orbitals φ_n are equal to zero outside the tube.

In general, molecules with, so called, free ends, for example in the styrene molecule (Fig. 1) may be also investigated. However, in these cases in addition to the sectors between the atoms, the skeleton should be extended at the free ends to infinity. On this extension the molecular orbital diminishes exponentially to zero at infinity.

Let us divide the skeleton of the molecule into branches connected with the bonds and with the above mentioned extensions. Let φ_{nB} be the part of molecular orbital φ_n on the B -th branch, or precisely

$$\left. \begin{aligned} \varphi_{nB} &= \varphi_n \text{ on the } B\text{-th branch,} \\ \varphi_{nB} &\equiv 0 \text{ on all the other branches.} \end{aligned} \right\} \quad (5)$$

Therefore, one can write

$$\varphi_n = \sum_B \varphi_{nB}, \quad (6)$$

where the summation runs over all branches in the skeleton of the molecule.

On each branch, a local orthogonal coordinate system may be chosen in a such a way that x_B is tangential to the bond line and z_B is perpendicular to the plane of the molecule. Then, in the G-FEMO method, it is assumed that on the B -th branch the tube potential has the following form

$$V_B(x_B, y_B, z_B) = V_B(x_B) + V'_B(y_B, z_B). \quad (7)$$

Hence φ_{nB} on the B -th branch may be written as follows

$$\varphi_{nB}(x_B, y_B, z_B) = f_n(y_B, z_B) \Phi_{nB}(x_B). \quad (8)$$

Since we are discussing π electrons, the factors $f_n(y_B, z_B)$ are antisymmetric with respect to the molecular plane. Furthermore, it is assumed that the potential $V'_B(y_B, z_B)$ must be such that $f_n^2(y_B, z_B)$ is symmetric to the x_B, z_B plane on each branch. Moreover, the assumption is made that $V'_B(y_B, z_B)$ is the same on all branches. This approximation should be reasonable, especially if the π electrons are supplied to the conjugated system by carbon, nitrogen and oxygen atoms. Therefore, $f(y_B, z_B)$ has the same form on each branch of the skeleton of the molecule. Finally, the "tube width" is restricted by the condition that the lowest transverse excitation energies (for y_B, z_B motion) are larger than all the longitudinal excitation energies considered. Therefore $f(y_B, z_B)$ is the same for all the molecular orbitals.

Making the use of the above mentioned assumptions, the n -th molecular orbital may be written in the following form

$$\varphi_n = \sum_B f(y_B, z_B) \Phi_{nB}(x_B). \quad (9)$$

Hence the parts of the molecular orbitals which depend on the coordinates x_B measured along the bonds play the main role in this model. Accordingly, the eigenvalue problem in the G-FEMO method can be, in practice, formulated one-dimensionally.

It should be noted that if one makes use of equations (5), (6) and (7), the equation (4) decomposes into equations for each branch separately. Moreover, on each branch the equation separates into two parts, for the motion of π -electrons along the bond and the motion across the bond.

On joining all the equations for the motion of the π -electrons along the bonds the eigenvalue problem in the G-FEMO method may be written as:

$$\mathbf{H}(x)\Phi_n(x) = \epsilon_n\Phi_n(x), \quad (10)$$

where x is the coordinate measured along the bonds, or more precisely

$$x_B = x \quad \text{on the } B\text{-th branch}, \quad (11)$$

and

$$\mathbf{H}(x) = \mathbf{T}(x) + \mathbf{V}(x). \quad (12)$$

$\mathbf{T}(x)$ is the kinetic energy operator for the motion along the bonds or the extensions of the skeleton to infinity and $\mathbf{V}(x)$ is the one-dimensional effective potential operator which is equal to $V_B(x_B)$ on each branch.

Therefore, the eigenvalue problem is formulated in a one-dimensional but multi connected space. This space reflects the topology of the molecule and its bonding situation (*cf.* Hummel and Ruedenberg 1965).

Ruedenberg and Scherr (1953) in their method, assume that $V(x)$ is constant and equal to zero. In the G-FEMO method it has been assumed that

$$V(x) = - \sum_p^M V_p \delta(x-x_p), \quad (13)$$

where x_p is the coordinate of the p -th atom and M is the number of atoms contributing the π electrons to the conjugated system. The quantity V_p in Eq. (13) is a measure of the "strength" of the delta-type singularity connected with the p -th atom and is treated as an empirical parameter. The number of such parameters is equal to the number of different types of atoms in the conjugated system.

Molecular orbitals in the Eq. (10) may be written in the form of a topological sum (*cf.* Eqs (5) and (6))

$$\Phi_n(x) = \sum_B \Phi_{nB}(x_B), \quad (14)$$

where the functions $\Phi_{nB}(x_B)$ are the exact solutions of the one-dimensional G-FEMO eigenvalue problem on each branch. They are expressed as the linear combination of exponential functions.

The molecular orbitals $\varphi_n(x, y, z)$ may be normalized to unity. Taking into consideration (5) and (6), the normalization condition for $\varphi_n(x, y, z)$ may be written

$$\begin{aligned} \int \varphi_n^2(x, y, z) dV &= \sum_B \int \varphi_{nB}^2(x_B, y_B, z_B) dV_B \\ &= \sum_B \int f^2(y_B, z_B) dQ_B \int \Phi_{nB}^2(x_B) dx_B = 1, \end{aligned} \quad (15)$$

where $dQ_B = dy_B dz_B$. It should be noted, however, that if we require the function $f(y_B, z_B)$ to be separately normalized to unity

$$\int f^2(y_B, z_B) dQ_B = 1 \quad (16)$$

for all the branches, then taking into consideration (14), the normalization condition for $\varphi_n(x, y, z)$ changes into the normalization condition for $\Phi_n(x)$, that is

$$\int \Phi_n^2(x) dx = \sum_B \int \Phi_{nB}^2(x_B) dx_B = 1. \quad (17)$$

More details about the G-FEMO method, in particular the basic equations of the method and the means for their solutions, have been given in this journal previously (Woźnicki and Żurawski 1967 *a, b*). Therefore, their description will be omitted here.

3. Configuration interaction

If one wants to investigate the spectroscopic properties of molecules then the Hamiltonian (1) and the configuration interaction procedure should be used.

In the present treatment a given electronic state function, Ψ_t , is approximated by a linear combination of singly excited configuration functions, $\theta_{(ik)}$, and the ground state function θ_0 . However, there are not any difficulties, except numerical ones, to include the multi excited configurations.

Therefore, in the present investigations, for a given state t we look for a many electron function in the following form

$$\Psi_t = \sum_{(ik)} A_{(ik),t} \theta_{(ik)}, \quad (18)$$

where $A_{(ik),t}$ are the variational coefficients and the summation runs over the singly excited configurations and the ground state. The index (ik) means the excitation $\varphi_i \rightarrow \varphi_k$. The configuration functions are, in general, linear combinations of Slater determinants for the construction of which, molecular orbitals, being the solutions of equation (4), have been used.

The variation procedure leads to the familiar equations

$$|K_{ik,jl} - S_{ik,jl} E| = 0 \quad (19)$$

and

$$\sum_{(ik)} A_{(ik)} (K_{ik,jl} - S_{ik,jl} E) = 0, \quad (20)$$

where

$$K_{ik,jl} = \int \theta_{(ik)} \mathbf{K} \theta_{(jl)} d\tau \quad (21)$$

and

$$S_{ik,jl} = \int \theta_{(ik)} \theta_{(jl)} d\tau. \quad (22)$$

Taking into account Eq. (1), one may write:

$$K_{ik,jl} = I_{ik,jl} + G_{ik,jl}, \quad (23)$$

where

$$I_{ik,jl} = \int \theta_{(ik)} \sum_{\nu=1}^N \mathbf{H}_{\nu} \theta_{(jl)} d\tau \quad (24)$$

and

$$G_{ik,jl} = \int \theta_{(ik)} \sum_{\mu>\nu=1}^N \mathbf{g}_{\nu\mu} \theta_{(jl)} d\tau. \quad (25)$$

Making use of the orthonormalization conditions for the molecular orbitals and the spin functions, one can obtain

$$S_{ik,jl} = \delta_{(ik),(jl)}, \quad (26)$$

whereas $I_{ik,jl}$ can be expressed in general as the sum of appropriate core molecular integrals

$$I_{ik} = \int \varphi_i(\nu) \mathbf{H}_\nu \varphi_k(\nu) dV(\nu) \quad (27)$$

and similarly $G_{ik,jl}$ as the appropriate sum of electronic integrals

$$(ij|kl) = \iint \varphi_i(\nu) \varphi_j(\nu) \mathbf{g}_{\nu\mu} \varphi_k(\mu) \varphi_l(\mu) dV(\nu) dV(\mu). \quad (28)$$

4. Core molecular integrals

The core molecular integrals I_{ik} (Eq. (27)) may be expressed by means of the orbital energies ε_k of the G-FEMO method and a quantity E^{tr} which appears from the integration over the coordinates perpendicular to each bond line in the skeleton of a molecule.

Namely, taking into account equations (5) and (6) the integral I_{ik} may be written as the sum of integrals on all branches

$$I_{ik} = \sum_B \int \varphi_{iB}(x_B, y_B, z_B) \mathbf{H}_B(x_B, y_B, z_B) \varphi_{kB}(x_B, y_B, z_B) dV_B. \quad (29)$$

Subsequently, let us notice that after taking into consideration Eq. (7) the Hamiltonian has the following form on the B -th branch in the local coordinate system

$$\mathbf{H}_B(x_B, y_B, z_B) = \mathbf{H}_B(x_B) + \mathbf{H}'_B(y_B, z_B). \quad (30)$$

Hence, making the use from the above and additionally from Eq. (9)

$$I_{ik} = \sum_B \left[\int f^2(y_B, z_B) dQ_B \int \Phi_{iB}(x_B) \mathbf{H}_B(x_B) \Phi_{kB}(x_B) dx_B + \right. \\ \left. + \int f(y_B, z_B) \mathbf{H}'_B(y_B, z_B) f(y_B, z_B) dQ_B \int \Phi_{iB}(x_B) \Phi_{kB}(x_B) dx_B \right]. \quad (31)$$

Finally, taking into consideration the model assumption related to $V'_B(y_B, z_B)$ and the normalization conditions (16) and (17) and the orthogonality of the molecular orbitals $\Phi(x)$ of the G-FEMO method, the core molecular integral may be written

$$I_{ik} = (\varepsilon_k + E^{tr}) \delta_{ik}, \quad (32)$$

where the quantity E^{tr} for all integrals is the same. It is not necessary to know the value of E^{tr} if only the transition energies are investigated. However, if we want to calculate for example the ionization potentials or electron affinities, the value of E^{tr} must be established. It is reasonable in these cases to treat the quantity E^{tr} as an empirical parameter.

5. *Electronic interaction molecular integrals*

An exact evaluation of the electronic interaction molecular integrals $(ij|kl)$ is quite complicated. Therefore, it is justified to look for an approximate method of evaluation for these integrals which is comparable in simplicity with the G-FEMO model.

There are some methods of evaluation of these integrals in the framework of the FEMO theory. One of them is the *ab initio* type method proposed by Olszewski (1955–1966). However, this method has been only applied to the systems containing the linear chain of conjugated bonds. There is also the semiempirical method of Ham and Ruedenberg (1956) which, was the most frequently applied. However, this method requires the assumption that all the interatomic distances are equal in the molecule, not necessary in the G-FEMO method. Moreover, the method of Ham and Ruedenberg was not applied to the π electron systems containing heteroatoms, whereas these systems can be investigated by means of the G-FEMO method.

Therefore, the following semiempirical procedure is proposed to make the most of all the advantages of the G-FEMO method. Let us notice that the integral

$$(ij|kl) = \iint \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \varphi_k(\mathbf{r}') \varphi_l(\mathbf{r}') dV dV' \quad (33)$$

after taking into consideration the equations (5) and (6) may be written in the form of

$$(ij|kl) = \sum_B \sum_C \iint \varphi_{iB}(\mathbf{r}_B) \varphi_{jB}(\mathbf{r}_B) \frac{e^2}{|\mathbf{r}_B-\mathbf{r}_C|} \varphi_{kC}(\mathbf{r}_C) \varphi_{lC}(\mathbf{r}_C) dV_B dV_C, \quad (34)$$

where \mathbf{r}_B and \mathbf{r}_C are vectors which determine the positions of electrons in the regions of the B -th and C -th branches, respectively. Moreover, if we take into account Eq. (9) then the above integral may be expressed as follows

$$(ij|kl) = \sum_B \sum_C \iint \Phi_{iB}(x_B) \Phi_{jB}(x_B) G(x_B, x_C) \Phi_{kC}(x_C) \Phi_{lC}(x_C) dx_B dx_C, \quad (35)$$

where

$$G(x_B, x_C) = G(R) = \iint f^2(y_B, z_B) \frac{e^2}{|\mathbf{r}_B-\mathbf{r}_C|} f^2(y_C, z_C) dQ_B dQ_C. \quad (36)$$

The latter represents the mutual electrostatic interaction energy of two area charge distribution of the form $f^2(y, z)$ connected with the B -th and C -th branches (Fig. 2). The surfaces on which the charges are distributed are perpendicular to the bond lines. Their diameters are very small in connection with the model assumption. The quantity R in Eq. (36) should be understood as the distance between the centres of gravity of these areas charges. Since the function $f^2(y, z)$ is symmetric with regard to the bond axis, R may be treated as the distance between two points on the line of skeleton. Therefore in this sense R , and in connection with this $G(R)$, are functions of the coordinates x_B and x_C along the B -th and C -th bonds respectively.

The G-FEMO molecular orbital on the B -th branch, as it was mentioned above, are expressed as the linear combination of exponential functions. Hence between the atoms p

and q it may be expressed as the sum of two functions, one connected with the point p and the other with q (Fig. 3a)

$$\Phi_{iB}(x_B) = \Phi_i(p)\chi_p^i(x_B) + \Phi_i(q)\chi_q^i(x_B). \quad (37)$$

where $\Phi_i(p)$ and $\Phi_i(q)$ are the values of the i -th molecular orbital $\Phi_i(x)$ on atoms p and q respectively. The function $\chi_p^i(x_B)$ connected with atom p has the following form

$$\chi_p^i(x_B) = \begin{cases} -\frac{\sin h [k_i(x_B - \xi_{pq})]}{\sin h (k_i \xi_{pq})} & \text{on branch } B, \\ 0 & \text{on the other branch,} \end{cases} \quad (38)$$

where ξ_{pq} is the bond distance between the atoms p and q . In the above equation the origin of the local coordinate system is placed on atom p . As it may be seen from Eq. (38) $\chi_p^i(x_B)$ has the following properties (cf. Fig. 3a)

$$\chi_p^i(x_B) = \begin{cases} 1 & \text{if } x_B = 0, \\ 0 & \text{if } x_B = \xi_{pq}. \end{cases} \quad (39)$$

Analogously, the function $\chi_q^i(x_B)$ is defined, for which the origin of the local coordinate system is located on the atom q .

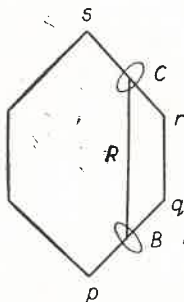


Fig. 2. The skeleton of six-membered molecule

In the case of free ends where the molecular orbitals are extended to infinity (Fig. 2) the function on an extension may be expressed as

$$\Phi_i(x_S) = \Phi_i(p)\chi_p^i(x_S), \quad (40)$$

where

$$\chi_p^i(x_S) = e^{-k_i x_S}. \quad (41)$$

In the above equations, as in the preceding ones, the origin of the coordinate system is located on atom p so that x_S varies from 0 on the p -th atom to infinity.

Taking into consideration the equations (37) and (40) the G-FEMO molecular orbital $\Phi_i(x)$ may be represented by means of the sum over the functions connected with the atoms in the skeleton of the molecule

$$\Phi_i(x) = \sum_{p=1}^M \Phi_i(p) D_p^i(x), \quad (42)$$

where M is the number of all atoms, which supply the π electrons to the conjugated system and $D_p^i(x)$ are the Frost and Leland (1956) Delta Atomic Orbitals (DAO). The DAO $D_p^i(x)$ is the sum of all functions, (39) and/or (41), connected with the p -th atom. Namely

$$D_p^i(x) = \sum_{B=1}^{m_p} \chi_B^i(x_B), \quad (43)$$

where the summation runs over the branches joined in the p -th point and m_p is the number of such branches (cf. Avdiejew *et al.*, 1965). In the case when three branches come together

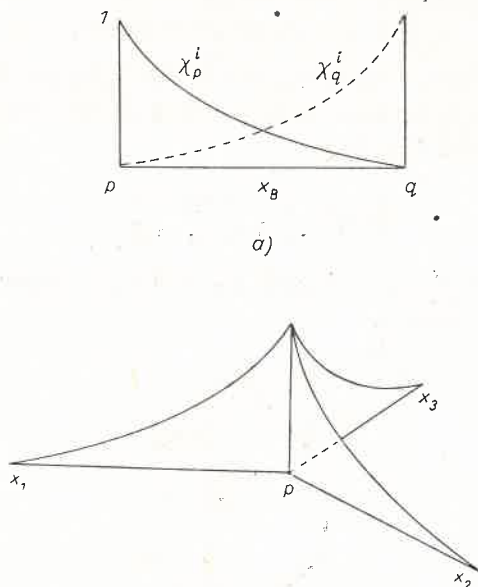


Fig. 3. (a) The one-dimensional functions $\chi_p^i(x_B)$ and $\chi_q^i(x_B)$ connected with the atoms p and q respectively. (b) The DAO function (see text)

on atom p the DAO is represented grafically on Fig. 3b. It should be noted that, contrary to the atomic orbitals which have been used in the simple LCAO MO methods, the DAOs for the given atom p are different for different molecular orbitals.

It is convenient to formulate the expansion of the molecular integrals $(ij|kl)$ into atomic integrals. Let us put in equation (35) the formulae (37) or (40). After the selection of components connected with the individual atoms in the skeleton of the molecule, the molecular integral $(ij|kl)$ may be written as follows

$$(ij|kl) = \sum_{p, q, r, s=1}^M \Phi_i(p) \Phi_j(q) \Phi_k(r) \Phi_l(s) \begin{pmatrix} ij & | & kl \\ pq & | & rs \end{pmatrix}, \quad (44)$$

where $\Phi_i(p)$, $\Phi_j(q)$, $\Phi_k(r)$, $\Phi_l(s)$ are the values of molecular orbitals on atoms q , p , r and s respectively and $\begin{pmatrix} ij & | & kl \\ pq & | & rs \end{pmatrix}$ may be considered as the atomic integrals

$$\begin{pmatrix} ij & | & kl \\ pq & | & rs \end{pmatrix} = \iint D_p^i(x) D_q^j(x) G(x; x') D_r^k(x') D_s^l(x') dx, dx'. \quad (45)$$

Taking into consideration the properties of DAOs (Eqs (43), (38) and (39)) it is obvious that the values of some integrals $\left(\begin{smallmatrix} ij \\ pq|rs \end{smallmatrix} \middle| kl \right)$ are equal to zero. The only atomic integrals different from zero are of the following type

- 1° $\left(\begin{smallmatrix} ij \\ pp|rr \end{smallmatrix} \middle| kl \right)$,
- 2° $\left(\begin{smallmatrix} ij \\ pp|rs \end{smallmatrix} \middle| kl \right)$ if r and s are the neighbouring atoms,
- 3° $\left(\begin{smallmatrix} ij \\ pq|rs \end{smallmatrix} \middle| kl \right)$ if the neighbours are the p -th and q -th as well as the r -th and s -th atoms.

Let us notice that all written formulae for the integrals $(ij|kl)$ up to this point are exact. However, some approximations will be introduced in the following. Namely, the three and four centres atomic integrals will be approximated by means of a sum of two centres integrals $\left(\begin{smallmatrix} ij \\ pp|rr \end{smallmatrix} \middle| kl \right)$. For these purposes the product of two DAO functions D_p^i and D_q^j , connected with the neighbouring atoms p and q in the skeleton of the molecule, is approximated by the following formula

$$D_p^i D_q^j = S_{pq}^{ij} (D_p^i D_p^j + D_q^i D_q^j), \quad (46)$$

where S_{pq}^{ij} is a constant. Its value is chosen in such a way that the result of integration of (46) on the left is equal to the result on the right. The expression (46) is similar to the well known Mulliken (1949) approximation in the methods of LCAO type.

The application of Eq. (46) reduces the problem of calculation molecular integrals $(ij|kl)$ to the determination of values of two centres atomic integrals $\left(\begin{smallmatrix} ij \\ pp|rr \end{smallmatrix} \middle| kl \right)$ only, for which the following approximation is adopted

$$\left(\begin{smallmatrix} ij \\ pp|rr \end{smallmatrix} \middle| kl \right) = G(p, r) \int D_p^i(x) D_p^j(x) dx \int D_r^k(x') D_r^l(x') dx', \quad (47)$$

Let

$$F_p^{ij} = \int D_p^i(x) D_p^j(x) dx, \quad (48)$$

then

$$\left(\begin{smallmatrix} ij \\ pp|rr \end{smallmatrix} \middle| kl \right) = G(p, r) F_p^{ij} F_r^{kl}. \quad (49)$$

The quantity $G(p, r)$ in the above written equations is the value of $G(x_B, x_C)$ function for $x_B = x_p$ and $x_C = x_r$, that is for R which is equal to the distance between the p -th and r -th atoms in the molecule. It is difficult to determine the precise form of $G(R)$ (*cf.* Ham and Ruedenberg (1956)). However, the approximated form of $G(R)$ may be determined in a semiempirical way. Namely, for some given interatomic distances R_{pq} the respective values of

$G(R)$ may be treated as empirical parameters and their values may be evaluated by fitting the results of theory to the experimental data.

In the sum (44) the approximations mentioned above permit the selection of components connected with the individual centres. Namely, for the given centre p the quantity may be introduced

$$U_p^{ij} = F_p^{ij}[\Phi_i(p)\Phi_j(p) + \Phi_i(p) \sum_{q=1}^M \Phi_j(q)S_{pq}^{ij} + \Phi_j(p) \sum_{q=1}^M \Phi_i(q)S_{pq}^{ij}], \quad (50)$$

where M is the number of atoms in the skeleton of the molecule. Therefore the molecular electronic interaction integrals $(ij|kl)$ with the aid of the quantities of type (50) may be written in the form of

$$(ij|kl) = \sum_{p,r=1}^M G(p,r)U_p^{ij}U_r^{kl}. \quad (51)$$

6. Dipole moments and intensities

The intensities of the transitions are measured in terms of the oscillator strengths. The calculations of the oscillator strengths as well as of the dipole moments are reduced to the calculation of integrals of orbital transition moments (*cf.* Pariser 1956)

$$m_{ij} = \int \varphi_i \mathbf{r} \varphi_j dV. \quad (52)$$

Taking into consideration the equations (5), (6) and (9) the orbital transition moments may be written as follows

$$m_{ij} = \sum_B \int \Phi_i(x_B)R(x_B)\Phi_j(x_B)dx_B, \quad (53)$$

where

$$R(x_B) = \int f^2(y_B, z_B)\mathbf{r}(x_B, y_B, z_B)dQ_B \quad (54)$$

The vector $\mathbf{r}(x_B, y_B, z_B)$ in the above equation points from an arbitrary origin to the volume element $dQ_B dx_B = dx_B dy_B dz_B$. The expression (54) which depends on x_B , determines the position of the centre of gravity for charge distribution $f^2(y_B, z_B)$ in the plane y_B, z_B , perpendicular to the direction of the B -th bond. Therefore, taking into account the symmetry properties of $f(y_B, z_B)$, $\mathbf{R}(x_B)$ may be considered as the vector which determines the positions along the B -th bond.

The components of vector $\mathbf{R}(x_B)$ for the individual bonds, in Cartesian coordinate system X, Y, Z , connected with the molecule, but *not* with the particular bond, may be expressed as follows

$$\mathbf{R}_w(x_B) = \mathbf{A}_w + \mathbf{B}_w x_B, \quad w = X, Y, Z \quad (55)$$

where \mathbf{A}_w and \mathbf{B}_w are the constant vectors which depend on the positions of particular bonds in the molecule.

7. Charge distribution

To define the charges on the individual atoms in the conjugated system it is convenient to profit from the matrices density formalism (see *e. g.* McWeeny 1960). Let

$$\rho_1(tt|11') = N \int [\psi_t^*(1', 2, 3, \dots, N) \psi_t(1, 2, 3, \dots, N)] \omega'_1 \rightarrow \omega_1 d\omega_1 d\tau_2 \dots d\tau_N \quad (56)$$

be the reduced one-particle density matrix for the state t . In the above equation the integration over the spin is denoted by $d\omega$ and integration over spin and space variables by $d\tau$. The quantity N in our case is the number of π electrons in the molecule.

The diagonal elements will further play a substantial role. Henceforth, only the expressions for these elements will be written.

Let us first consider the case of ground state which is described by a one-determinantal configuration function θ_0 . It may be written as

$$\rho_1(00|11) = N \int \theta_0^2(1, 2, 3, \dots, N) d\omega_1 d\tau_2 d\tau_3 \dots, d\tau_N, \quad (57)$$

whence for the closed shell systems

$$\rho_1(00|11) = 2 \sum_{i=1}^n \varphi_i^2, \quad (58)$$

where φ_i are the molecular orbitals of the type (6) and n is the number of occupied orbitals in θ_0 . Making use of the normalization of the density matrix, one obtains

$$N = 2 \sum_{i=1}^n \int \varphi_i^2 dV. \quad (59)$$

Taking into consideration equations (5), (6) and (9), the above may be written

$$N = 2 \sum_{i=1}^n \sum_B \int \varphi_{iB}^2 dV_B = 2 \sum_{i=1}^n \sum_B \int f^2(y_B, z_B) dQ_B \int \Phi_{iB}^2(x_B) dx_B, \quad (60)$$

and taking into account the normalization condition for $f(y, z)$

$$N = 2 \sum_{i=1}^n \sum_B \int \Phi_{iB}^2(x_B) dx_B. \quad (61)$$

Subsequently, on each branch $\Phi_{iB}(x_B)$ are decomposed on parts connected with the individual atoms (Eq. 37) (in the case of free ends, Eq. (40) should be used). Then, the approximation (46) may be used. Finally, after the selection of expression connected with the particular atoms and making use of the quantity (50), the equation (61) may be written as follows:

$$N = 2 \sum_{i=1}^n \sum_{r=1}^M U_r^{ii}, \quad (62)$$

or

$$N = \sum_{r=1}^M P_r^{00}, \quad (63)$$

where

$$P_r^{00} = 2 \sum_{i=1}^n U_r^{ii} \quad (64)$$

and M is the number of atoms in the skeleton of the molecule. Since N is the total π electronic charge in the molecule, the quantity P_r^{00} may be considered as the π electron charge connected with the r -th atom.

Let us now consider a more general case where the wave function for the given state t (Eq. (18)) was obtained from the configuration interaction procedure. In this case

$$\varrho_1(tt|11) = \sum_{(ik)} \sum_{(jl)} A_{(ik),t} A_{(jl),t} \varrho_1((ik)(jl)|11), \quad (65)$$

where $\varrho_1((ik)(jl)|11)$ is the one-particle transition density matrix for $(ik) \rightarrow (jl)$.

The following formulae may be written for different combinations of indices (ik) , (jl) taking into consideration that the configuration functions are linear combinations of Slater determinants, constructed from the molecular orbitals

$$\varrho_1(00|11) = 2 \sum_n \varphi_n^2(1), \quad (66)$$

$$\varrho_1((ik)(ik)|11) = 2 \sum_{n \neq i} \varphi_n^2(1) + \varphi_i^2(1) + \varphi_k^2(1), \quad (67)$$

$$\varrho_1(0(ik)|11) = \sqrt{2} \varphi_i(1) \varphi_k(1), \quad (68)$$

$$\varrho_1((ik)(il)|11) = \varphi_k(1) \varphi_l(1). \quad (69)$$

$$\varrho_1((ik)(jk)|11) = -\varphi_i(1) \varphi_j(1), \quad (70)$$

$$\varrho_1((ik)(jl)|11) = 0. \quad (71)$$

In the above equations the indices i and j refer to the orbitals occupied in θ_0 , whereas k and l to unoccupied ones. Moreover, the summation in equations (66) and (67) are over the occupied orbitals in θ_0 .

Further proceeding is identical as in the previous case. Finally, one obtains

$$N = \sum_{(ik)} \sum_{(jl)} A_{(ik),t} A_{(jl),t} \sum_{r=1}^M P_r^{(ik)(jl)}, \quad (72)$$

where

$$P_r^{00} = 2 \sum_n U_r^{nn}, \quad (73)$$

$$P_r^{(ik)(ik)} = 2 \sum_{n \neq i} U_r^{nn} + U_r^{ii} + U_r^{kk}, \quad (74)$$

$$P_r^{0(ik)} = \sqrt{2} U_r^{ik}. \quad (75)$$

$$P_r^{(ik)(il)} = U_r^{kl}, \quad (76)$$

$$P_r^{(ik)(jk)} = -U_r^{ij}, \quad (77)$$

$$P_r^{(ik)(jl)} = 0. \quad (78)$$

Equation (72) may be also written as follows

$$N = \sum_{r=1}^M q_r, \quad (79)$$

where

$$q = \sum_{(ik)} \sum_{(jl)} A_{(ik),r} A_{(jl),r} P_r^{(ik)(jl)}. \quad (80)$$

Therefore, it may be seen from the above equation that the quantity q_r may be defined as the π electron charge on the r -th atom.

8. Conclusions

In this paper the G-FEMO method was extended to include explicitly, electron interaction terms in the hamiltonian and to include the configuration interaction procedure. The G-FEMO molecular orbitals were used as the basic functions for the construction of Slater determinants and the semiempirical method of evaluation the molecular electronic interaction and core integrals was proposed.

Therefore the method of calculating of the electronic properties of conjugated molecules, proposed in the present paper, has a semiempirical character. However, the present method differs from the others (*e. g.* Ham and Ruedenberg (1956), Pariser and Parr (1953)) in the initial choice of molecular orbitals and in the evaluation of molecular integrals. Moreover, there are less empirical parameters than, for example, in the method of Pariser and Parr (1953). Namely, in the present method the delta strengths V_p appear, the number of which is equal to the number of different types of atoms in the conjugated system. Also, the quantity E^{rr} appears, only one for all types of conjugated molecules. Finally there is one curve $G(R = G(p, r))$ the shape of which should be independent of the kind of atoms in the conjugated bonds path. In fact, the calculations for one ring systems, the results of which will be given in the second paper of this series (Żurawski 1971), indicate that this is true.

Additionally, it should be noted that in contradiction to Ham and Ruedenberg (1956), the present method provides the possibility of taking into account the variation of individual bond lengths in the molecule. Moreover, the molecules containing heteroatoms may be investigated.

Finally, the proposed method is very simple and may be applied even to large molecules using small computers.

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