

CONTRIBUTION OF THE ELECTRONIC REPULSION TO THE ENERGY OF THE MOLECULAR STATES FOR FURAN, PYRROLE AND THIOPHENE

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INTRODUCTION

For a molecule containing π electrons moving in the field of a core, the Hamiltonian is expressed in the form

$$H = H_{\text{core}} + \frac{1}{2} \sum_{\nu\mu} \frac{e^2}{r_{\nu\mu}} \quad \dots \quad (1)$$

and

$$H_{\text{core}} = \sum_{\nu} H_{\text{core}}(\nu)$$

where

$$\frac{1}{2} \sum_{\nu\mu} \frac{e^2}{r_{\nu\mu}}$$

is the electronic repulsion between the electrons ν and μ , $H_{\text{core}}(\nu)$ is the kinetic energy operator for the electron (ν) + its potential energy in the field of the core, the latter takes into account all other electrons also besides the π ones. The contribution of the electronic repulsion to the energy of the molecular states can be treated by the well-known perturbation method. Besides, the singlet triplet separations can also be estimated.

With respect to the determination of the energy levels of the molecules Furan, Pyrrole and Thiophene, five orbitals one on each atom of the ring and six electrons including the unshared pair on the hetero atom are considered. Let $P_1 \dots P_5$ be the five $P\pi$ wave functions on the atoms of the ring (Fig. 1). The one electron wave functions ϕ_j of the molecules are written as linear combinations of the above P_k 's

$$\phi_j = \sum_k C_{jk} P_k \quad \dots \quad (2)$$

The best values of the C_{jk} 's are obtained by solving the five equations

$$\sum_{k=1}^5 C_{jk} (H_{mk} - \Delta_{mk} E_j) = 0, \quad m = 1 \text{ to } 5$$

where †

$$\left. \begin{aligned} H_{mk} &= \int p_m^* H p_k d\tau \quad (* \text{ indicates complex conjugate}) \\ \Delta_{mk} &= \int p_m^* p_k d\tau \end{aligned} \right\} \dots \quad (3)$$

† For the calculation of the two centre integrals *vide* Roothaan's (1951) formulae.

and E_j is the energy of the electron occupying the MO ϕ_j . The secular determinant $|H_{mk} - \Delta_{mk}E_j|$ is further factorised by the application of the group theoretical methods and the MO 's are accordingly classified into different species. From the energy values, the normally existing occupied and unoccupied orbitals of the molecules are established. By resubstitution of these energy values into the equation (3) the constants are determined for each MO using the normalisation properties of the MO 's. Usually in solving problems of this type the following approximations are adopted.

$$\left. \begin{aligned} \Delta_{mk} &= 0, \text{ when } m \neq k \\ \Delta_{mk} &= 1, \text{ when } m = k \end{aligned} \right\} \dots \dots \dots (4)$$

(an assumption that all P 's are orthogonal). Such types of overlaps can, however, without resorting to this approximation, be strictly evaluated with the help of the Master Tables given by Mulliken and others (1949) using Slater AO 's.

For the molecules considered, if ϕ_1, ϕ_2, ϕ_3 be the three occupied and ϕ_4, ϕ_5 be the two unoccupied MO 's having their energies $E_1 < E_2 < E_3 < E_4 < E_5$, the ground state is that when all the six electrons occupy the three lowest MO 's ϕ_1, ϕ_2, ϕ_3 , two in each with their spins opposing, thus giving rise to a singlet state. In the three occupied MO 's, the one which is having the highest energy level is called the 'high filled orbital'. The excitation of an electron from this 'high filled orbital' to the lowest lying unoccupied orbital will correspond to longest wavelength transition ($\phi_3 \rightarrow \phi_4$).

In the present calculations, the contribution of the electronic repulsion to the ground state and two of the excited states, $\phi_3 \rightarrow \phi_4$ and $\phi_3 \rightarrow \phi_5$, are evaluated first in terms of molecular integrals which are then reduced to the atomic integrals. The method is similar to that described by Goeppert Mayer and Sklar (1938) in which the wave functions of the ground and the excited states were antisymmetrised by the proper determinantal method taking into consideration the spin eigenfunction.

METHOD OF CALCULATION

Let the molecular wave function ψ_g of the ground state be written as the product of all occupied MO 's.

$$\psi_g = \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_3(6) \dots \dots \dots (5)$$

The number in brackets refer to the electrons occupying the ϕ_j ($j = 1, 2$ and 3). Each MO has two electrons with opposite spins and hence the spin function is

$$\chi_g^{(s)} = \alpha_1\beta_2\alpha_3\beta_4\alpha_5\beta_6 \dots \dots \dots (6)$$

Then the antisymmetrised molecular wave functions for the ground state taking spin factor also into consideration is obtained by performing all 6! permutations P of electrons on the product of spin and co-ordinate functions, multiplying the result by $+1$ to the order (odd or even) of the permutation and adding, i.e.

$$\psi_g = \frac{1}{\sqrt{6!}} \sum_P (-1)^p P \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_3(6)\alpha_1\beta_2\alpha_3\beta_4\alpha_5\beta_6 \dots \dots (7)$$

the energy of the molecule in the ground state due to the electron interaction is

$$\int \Psi_g^* H' \Psi_g d\tau \dots \dots \dots (8)$$

where H' is the electronic interaction operator given by

$$H' = \frac{1}{2} \sum_{\nu\mu} \frac{e^2}{r_{\nu\mu}} \dots \dots \dots (9)$$

($r_{\nu\mu}$ is the distance between the two electrons ν and μ and the summation is carried over all the electrons). The energy will then contain chiefly two types of integrals, namely (1) Coulomb integrals of the type

$$\gamma_{ll'} = \iint \frac{e^2}{r_{\nu\mu}} |\phi_l(\nu)|^2 |\phi_{l'}(\mu)|^2 d\tau_\nu d\tau_\mu \quad \dots \quad (10)$$

where l and l' refer to MO 's, ν and μ refer to electrons and (2) exchange integral of type

$$\delta_{ll'} = \iint \frac{e^2}{r_{\nu\mu}} \phi_l(\nu) \phi_{l'}(\mu) [\phi_l(\mu) \phi_{l'}(\nu)]^* d\tau_\nu d\tau_\mu \quad \dots \quad (11)$$

The energy of the molecule in the ground state consists of two factors (a) sum of the energies of occupied MO 's counting once for each electron and (b) energy due to electronic interaction, i.e. Coulomb and exchange energies cited above.

The following permutations are considered:—

(1) Considering the identity permutation and summing over all $\frac{e^2}{r_{\nu\mu}}$, the Coulomb energy of the molecule in the ground state is

$$\gamma_{11} + \gamma_{22} + \gamma_{33} + 4\gamma_{12} + 4\gamma_{13} + 4\gamma_{23} \quad \dots \quad (12)$$

(2) The permutations involving one interchange of electrons ($P = 1$) having opposite spins need not be considered as they do not contribute to the energy term. The permutations involving one interchange of the electrons designated in the brackets need be considered.

$$P(13), P(15), P(35), P(24), P(26) \text{ and } P(46).$$

These types of permutations will result in the exchange energy

$$-2\delta_{12} - 2\delta_{13} - 2\delta_{23} \quad \dots \quad (13)$$

While considering the permutations involving a particular interchange of electrons, the integration should be carried over only for those particular electrons under consideration, as all the other terms will contribute nothing to the energy.

(3) All permutations involving more than one interchange of electrons for any $\frac{e^2}{r_{\nu\mu}}$ will not contribute anything to the energy term. Hence the energy of the molecule in the ground state (singlet) is given by

$$2E_1 + 2E_2 + 2E_3 + \gamma_{11} + \gamma_{22} + \gamma_{33} + 4\gamma_{12} + 4\gamma_{13} + 4\gamma_{23} - 2\delta_{12} - 2\delta_{13} - 2\delta_{23} \quad \dots \quad (14)$$

The expression is same for the three molecules Furan, Pyrrole and Thiophene, but while evaluating the actual energy value of that level the proper MO 's and the energies $E_1 \dots E_3$ should be introduced.

Excited State

The molecular eigen function when an electron from the occupied $MO \phi_3$ jumps into the unoccupied $MO \phi_4$ resulting in longest wavelength transition, is given by

$$\psi_s = \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_4(6) \quad \dots \quad (15)$$

Here, two cases must be distinguished; the spins of electrons 5 and 6, the only ones which are unpaired, may be parallel or anti-parallel. In case of anti-parallel

spins, the spin functions must be made antisymmetric giving rise to a singlet state, i.e.

$$\chi_e^{(s)} = \frac{1}{\sqrt{2}} \alpha_1 \beta_2 \alpha_3 \beta_4 (\alpha_5 \beta_6 - \beta_5 \alpha_6). \quad \dots \quad (16)$$

The second case where they are parallel spins for the electrons 5 and 6 can be represented in three ways giving rise to triplets in each case.

$$\left. \begin{aligned} \chi_e^{(t)} &= \alpha_1 \beta_2 \alpha_3 \beta_4 \alpha_5 \alpha_6, \\ &\quad \alpha_1 \beta_2 \alpha_3 \beta_4 \beta_5 \beta_6, \\ &\quad \frac{1}{\sqrt{2}} \alpha_1 \beta_2 \alpha_3 \beta_4 (\alpha_5 \beta_6 + \beta_5 \alpha_6) \end{aligned} \right\} \dots \quad (17)$$

Since the perturbing potential H' is independent of spin, the spin states singlet and triplet will not interact. The energy for the latter three states is the same. In the present calculations the spin function for the singlet is taken as

$$\frac{1}{\sqrt{2}} \alpha_1 \beta_2 \alpha_3 \beta_4 (\alpha_5 \beta_6 - \beta_5 \alpha_6) \quad \dots \quad (18)$$

and for the triplet state

$$\chi_e^{(t)} = \alpha_1 \beta_2 \alpha_3 \beta_4 \alpha_5 \alpha_6 \quad \dots \quad (19)$$

The antisymmetrised molecular wave function for the excited state (triplet) is given by (when the electronic transition is from $\phi_3 \rightarrow \phi_4$)

$$\psi_e^{(t)} = \frac{1}{\sqrt{6!}} \sum_P (-1)^p p \phi_1(1) \phi_1(2) \phi_2(3) \phi_2(4) \phi_3(5) \phi_4(6) \alpha_1 \beta_2 \alpha_3 \beta_4 \alpha_5 \alpha_6 \quad \dots \quad (20)$$

and for the singlet state

$$\psi_e^{(s)} = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{6!}} \sum_P (-1)^p p \phi_1(1) \phi_1(2) \phi_2(3) \phi_2(4) \phi_3(5) \phi_4(6) \alpha_1 \beta_2 \alpha_3 \beta_4 (\alpha_5 \beta_6 - \beta_5 \alpha_6) \quad (21)$$

The energy due to the electronic interaction term for the excited triplet state is given by

$$\int \Psi_e^{(t)*} H' \Psi_e^{(t)} d\tau \quad \dots \quad (22)$$

and that for the singlet state is given by

$$\int \Psi_e^{(s)*} H' \Psi_e^{(s)} d\tau \quad \dots \quad (23)$$

The following permutations need be considered for the triplet state.

- (1) The identity permutation $P = 0$, the expression for the Coulomb integrals is given by

$$\gamma_{11} + \gamma_{22} + 4\gamma_{12} + 2\gamma_{23} + 2\gamma_{13} + 2\gamma_{14} + 2\gamma_{24} + \gamma_{34}. \quad \dots \quad (24)$$

- (2) Permutations involving interchange of electrons having same spin such as $P(13)$, $P(15)$, $P(16)$, $P(35)$, $P(36)$, $P(56)$ and $P(24)$. The expression for the exchange integrals is then given by

$$-2\delta_{12} - \delta_{13} - \delta_{14} - \delta_{23} - \delta_{24} - \delta_{34}. \quad \dots \quad (25)$$

The total energy of the triplet excited state is

$$W_e(\text{triplet}) = 2E_1 + 2E_2 + E_3 + E_4 + \gamma_{11} + \gamma_{22} + 4\gamma_{12} + 2\gamma_{13} + 2\gamma_{23} \\ + 2\gamma_{14} + 2\gamma_{24} + \gamma_{34} - 2\delta_{12} - \delta_{13} - \delta_{14} - \delta_{23} - \delta_{24} - \delta_{34}. \quad \dots (26)$$

Consider singlet state.—

The integral in equation (23) is split into the following four integrals:—

$$+\frac{1}{2} \int \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_4(6)\alpha_1\beta_2\alpha_3\beta_4\alpha_5\beta_6^* \\ \sum \frac{e^2}{r_{\nu\mu}} \\ \sum (-1)^p p \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_4(6)\alpha_1\beta_2\alpha_3\beta_4\alpha_5\beta_6 \, d\tau \quad \dots (27)$$

$$+\frac{1}{2} \int \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_4(6)\alpha_1\beta_2\alpha_3\beta_4\beta_5\alpha_6^* \\ \sum \frac{e^2}{r_{\nu\mu}} \\ \sum_P (-1)^p p \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_4(6)\alpha_1\beta_2\alpha_3\beta_4\beta_5\alpha_6 \, d\tau \quad \dots (28)$$

$$-\frac{1}{2} \int \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_4(6)\alpha_1\beta_2\alpha_3\beta_4\alpha_5\beta_6^* \\ \frac{e^2}{r_{\nu\mu}} \\ \sum_P (-1)^p p \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_4(6)\alpha_1\beta_2\alpha_3\beta_4\beta_5\alpha_6 \, d\tau \quad \dots (29)$$

$$-\frac{1}{2} \int \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_4(6)\alpha_1\beta_2\alpha_3\beta_4\beta_5\alpha_6^* \\ \sum \frac{e^2}{r_{\nu\mu}} \\ \sum (-1)^p p \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_4(6)\alpha_1\beta_2\alpha_3\beta_4\alpha_5\beta_6 \, d\tau \quad \dots (30)$$

The following permutations are considered for the integrals (27) and (28):—
The values of the integrals in expressions (27) and (28) are just the same.

(1) The identity permutation gives rise to Coulomb integrals

$$\gamma_{11} + \gamma_{22} + 4\gamma_{12} + 2\gamma_{13} + 2\gamma_{23} + 2\gamma_{14} + 2\gamma_{24} + \gamma_{34}.$$

(2) The permutations having interchange of electrons with same spin such as $P(13)$, $P(15)$, $P(35)$, $P(24)$, $P(26)$ and $P(46)$ give rise to exchange integrals $-2\delta_{12} - \delta_{13} - \delta_{23} - \delta_{14} - \delta_{24}$. While dealing with the integrals in (29) and (30) identity permutations involving one interchange (interchanges of electrons having same spins) will not contribute anything to the energy term. In this case only permutation that results in an exchange energy term is $P(56)$ and the integral is

designated by $+\delta_{34}$. Hence the energy of the excited singlet state of the molecule is

$$W_e(\text{singlet}) = 2E_1 + 2E_2 + E_3 + E_4 + \gamma_{11} + \gamma_{22} + 4\gamma_{12} + 2\gamma_{13} + 2\gamma_{23} \\ + 2\gamma_{14} + 2\gamma_{24} + \gamma_{34} - 2\delta_{12} - \delta_{13} - \delta_{23} - \delta_{14} - \delta_{24} + \delta_{34}.$$

Similar expressions are derived for the electronic transition when the electron from the occupied $MO \phi_3$ is excited to the unoccupied $MO \phi_5$. In all these cases the difference between the singlet ground state and singlet and triplet excited states correspond to the transition energies of the molecules Furan, Pyrrole and Thiophene.

The energy expressions for the ground state and two excited states in each of the transitions $\phi_3 \rightarrow \phi_4$ and $\phi_3 \rightarrow \phi_5$ are given in Table I, the contribution of the electronic term being measured in terms of $\gamma_{\mu\nu}S$ and $\delta_{\mu\nu}S$, i.e. Coulomb and exchange energies.

TABLE I

Ground state	.. $\phi_1^2 \phi_2^2 \phi_3^2$	Singlet	$2E_1 + 2E_2 + 2E_3 + \gamma_{11} + \gamma_{22} + \gamma_{33} + 4\gamma_{12} + 4\gamma_{13} + 4\gamma_{23} - 2\delta_{12} - 2\delta_{13} - 2\delta_{23}$
Excited state	.. $\phi_1^2 \phi_2^2 \phi_3 \phi_4$	Singlet	$E + E_4 + \gamma_{34} + 2\gamma_{24} + 2\gamma_{14} - \delta_{14} - \delta_{24} + \delta_{34}$
$(\phi_3 \rightarrow \phi_4)$..	Triplet	$E + E_4 + \gamma_{34} + 2\gamma_{24} + 2\gamma_{14} - \delta_{14} - \delta_{24} - \delta_{34}$
$(\phi_3 \rightarrow \phi_5)$.. $\phi_1^2 \phi_2^2 \phi_3 \phi_5$	Singlet	$E + E_5 + \gamma_{35} + 2\gamma_{25} + 2\gamma_{15} - \delta_{15} - \delta_{25} + \delta_{35}$
		Triplet	$E + E_5 + \gamma_{35} + 2\gamma_{25} + 2\gamma_{15} - \delta_{15} - \delta_{25} - \delta_{35}$

Where E is the energy factor common to all excited states and is given by

$$2E_1 + 2E_2 + E_3 + \gamma_{11} + \gamma_{22} + 4\gamma_{12} + 2\gamma_{13} + 2\gamma_{23} - 2\delta_{12} - \delta_{13} - \delta_{23}$$

REDUCTION OF THE INTEGRALS TO AO FORMS

All the Coulomb integrals $\gamma_{\mu\nu}$ and the exchange integrals $\delta_{\mu\nu}$ in Table I over the molecular orbitals are now to be expressed in terms of atomic integrals over the atomic eigen functions p_k 's. The reduction of these integrals to the various types of the atomic integrals is carried out as follows.

Let ϕ_I and ϕ_V be the two MO 's the form of which is given in equation (2). The Coulomb energy of the type $\gamma_{\mu\nu}$ given in equation (10) is written as

$$*\gamma_{\mu\nu} = \iint \frac{e^2}{r_{\nu\mu}} (ap_1 + bp_2 + cp_3 + dp_4 + ep_5)^2(\nu) \\ (a'p_1 + b'p_2 + c'p_3 + d'p_4 + e'p_5)^2(\mu) d\tau_\nu d\tau_\mu \quad \dots (31)$$

where a, b, c, d, e are the coefficients of p_1, p_2, p_3, p_4 and p_5 respectively occurring in the $MO \phi_I$. Similarly the primes refer to those of ϕ_V . The exchange integral as given in expression (11) is

$$\delta_{\mu\nu} = \iint \frac{e^2}{r_{\nu\mu}} (ap_1 + bp_2 + cp_3 + dp_4 + ep_5)(\nu) \\ (a'p_1 + b'p_2 + c'p_3 + d'p_4 + e'p_5)(\mu) \\ (ap_1 + bp_2 + cp_3 + dp_4 + ep_5)(\mu) \\ (a'p_1 + b'p_2 + c'p_3 + d'p_4 + e'p_5)(\nu) d\tau_\nu d\tau_\mu \quad \dots (32)$$

where ν and μ refer to electrons. In the process of reduction of these integrals to the atomic integrals the following types are considered. These were first adopted

by Sklar (1938) in the *ASMO* treatment of the Benzene molecule and also by Ramamurty (1954) in the calculation of the energy levels of Indene. These are—

(1) Integrals of Coulomb type between electrons on the same and different atoms designated by

$$A = \iint \frac{e^2}{r_{\nu\mu}} p_m^2(\nu) p_n^2(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (33)$$

where m and n refer to atoms (Fig. 1, for the position of the atoms in all the three molecules).

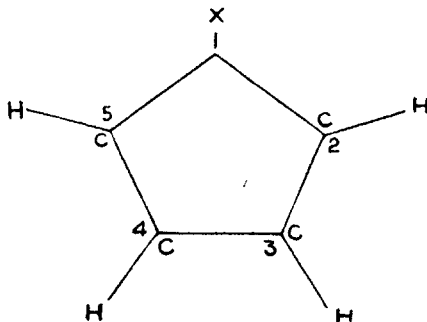


FIG. 1.

X = O, Furan
S, Thiophene
NH, Pyrrole.

$$m = 1 \text{ to } 5, \quad n = 1 \text{ to } 5.$$

* The coefficients a, \dots, e' are used instead of C_{jk} 's for convenience only.

These are further classified into six types, $A_0, A'_0, A_1, A'_1, A_2$ and A'_2 , the primes refer to the integrals in which the $p\pi$ wave function on the hetero atom, which is different from the $p\pi$ wave function on the carbon atom, is involved

$$A_0 = \iint \frac{e^2}{r_{\nu\mu}} p_m^2(\nu) p_n^2(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (34)$$

where $m = n \neq 1, \quad m = 2 \text{ to } 5.$

$$A'_0 = \iint \frac{e^2}{r_{\nu\mu}} p_1^2(\nu) p_1^2(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (35)$$

$$A_1 = \iint \frac{e^2}{r_{\nu\mu}} p_m^2(\nu) p_n^2(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (36)$$

where $m \neq n \neq 1.$ m takes the values from 2 to 5. n is then the immediate neighbour to $m.$ For example when $m = 2, n = 3;$ when $m = 3, n$ takes two values 2 or 4 and so on.

$$A'_1 = \iint \frac{e^2}{r_{\nu\mu}} p_1^2(\nu) p_n^2(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (37)$$

where n takes either 2 or 5 only.

$$A_2 = \iint \frac{e^2}{r_{\nu\mu}} p_m^2(\nu) p_n^2(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (38)$$

Here also $m \neq n \neq 1$, but n refers to an atom always a second neighbour to m , i.e. if $m = 2$, n is either 4 or 5 and so on.

$$A'_2 = \iint \frac{e^2}{r_{\nu\mu}} p_1^2(\nu) p_n^2(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (39)$$

where n is the second neighbour to atom 1, i.e. $n = 3$ or 4 only.

(2) Mixed exchange and Coulomb integral, the interaction between an electron on one atom with one that is shared between the same and the neighbouring atom designated by B where

$$B = \iint \frac{e^2}{r_{\nu\mu}} p_m^2(\nu) p_n(\mu) p_n(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (40)$$

In this case the interaction between electrons which are partially on atoms which are not nearest neighbours is neglected. This is further classified into three types, namely B , B' and B'' , as follows:—

$$B = \iint \frac{e^2}{r_{\nu\mu}} p_m^2(\nu) p_n(\mu) p_n(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (41)$$

$m \neq n \neq 1$, n being immediate neighbour to m . For example when $m = 2$, $n = 3$ only and when $m = 3$, n is either 2 or 4 and so on.

$$B' = \iint \frac{e^2}{r_{\nu\mu}} p_1^2(\nu) p_1(\mu) p_n(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (42)$$

where n is immediate neighbour to atom 1, i.e. either 2 or 5 only.

$$B'' = \iint \frac{e^2}{r_{\nu\mu}} p_m^2(\nu) p_m(\mu) p_1(\mu) d\tau_\nu d\tau_\mu \quad \dots \quad (43)$$

where $m = 2$ or 5.

(3) The exchange integral between electrons on neighbouring atoms and is designated by C where

$$C = \iint \frac{e^2}{r_{\nu\mu}} p_m(\nu) p_n(\mu) p_m(\mu) p_n(\nu) d\tau_\nu d\tau_\mu \quad \dots \quad (44)$$

In this case also the interaction between electrons which are partially on atoms which are not nearest neighbours is neglected. The exchange integral C is further classified into two types C and C' . The first type

$$C = \iint \frac{e^2}{r_{\nu\mu}} p_m(\nu) p_n(\mu) p_m(\mu) p_n(\nu) d\tau_\nu d\tau_\mu \quad \dots \quad (45)$$

where $m \neq n \neq 1$ but n is immediate neighbour to m , i.e. when $m = 2$, $n = 3$ and when $m = 3$, $n = 2$ or 4. In the second case

$$C' = \iint \frac{e^2}{r_{\nu\mu}} p_1(\nu) p_n(\mu) p_1(\mu) p_n(\nu) d\tau_\nu d\tau_\mu \quad \dots \quad (46)$$

where n is 2 or 5 only. This classification is done by fixing a value to m . The same holds good if the value for n is first fixed. Such types of integrals are also considered.

With the help of the above integrals, γ_{μ} is written as a linear combination, of A 's, B 's and C 's, the coefficients of each type of atomic integral is given below in Tables 2 and 3.

TABLE 2

<i>Atomic integrals.</i>	<i>Coefficients.</i>
A_0'	$a^2a'^2$
A_0	$b^2b'^2 + c^2c'^2 + d^2d'^2 + e^2e'^2$
A_1	$b^2c'^2 + c^2b'^2 + c^2d'^2 + d^2c'^2 + d^2e'^2 + e^2d'^2$
A_1'	$a^2b'^2 + b^2a'^2 + a^2e'^2 + e^2a'^2$
A_2	$b^2d'^2 + d^2b'^2 + b^2e'^2 + e^2b'^2 + c^2e'^2 + e^2c'^2$
A_2'	$a^2c'^2 + c^2a'^2 + a^2d'^2 + d^2a'^2$
B	$2(b'c'b^2 + b'c'c^2 + c^2c'd' + d^2c'd' + d^2d'e'e^2d'e' +$ $+ bcb'^2 + bcc'^2 + cdc'^2 + cdd'^2 + ded'^2 + dee'^2)$
B'	$2(a^2a'b' + a^2a'e' + aba'^2 + aea'^2)$
B''	$2(b^2a'b' + abb'^2 + e^2a'e' + aee'^2)$
C	$4(bcb'c' + cdc'd' + ded'e')$
C'	$4(aba'b' + aea'e')$

Similar procedure is adopted for the reduction of δ_{μ} 's also. The coefficients are the various atomic integrals occurring in this case are given below.

TABLE 3

<i>Atomic integrals.</i>	<i>Coefficients.</i>
A_0	$b^2b'^2 + c^2c'^2 + d^2d'^2 + e^2e'^2$
A_0'	$a^2a'^2$
A_1	$2(bb'cc' + cc'dd' + dd'ee')$
A_1'	$2(aa'bb' + aa'ee')$
A_2	$2(bb'dd' + bb'ee' + cc'ee')$
A_2'	$2(aa'cc' + aa'dd')$
B	$2\{(bc' + cb')(cc' + bb') + (cd' + c'd)(cc' + dd') +$ $(de' + ed')(dd' + ee')\}$
B'	$2\{aa'(ab' + ba') + aa'(ae' + ea')\}$
B''	$2\{bb'(ab' + a'b) + ee'(ae' + e'a)\}$
C	$(bc' + eb')^2 + (cd' + c'd)^2 + (ce' + c'e)^2$
C'	$(ab' + ba')^2 + (ae' + ea')^2$

If any particular γ_{μ} or δ_{μ} is to be written in terms of atomic integrals, the coefficients of the latter, given in Tables 2 and 3, are to be evaluated. Further work on this problem involving the evaluation of all the integrals is in progress and will be presented in a subsequent communication.

ABSTRACT

The contribution of the electronic repulsion to the energy of the ground and two of the excited states in case of Furan, Pyrrole and Thiophene is evaluated in terms of the atomic integrals using the method of the antisymmetrised molecular orbitals.

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