

# THEORETICAL STUDY OF $\pi$ -SYSTEMS WITH HETEROATOMS

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## INTRODUCTION

The number of theoretical studies of  $\pi$ -electron systems is rapidly growing. The most frequently adopted method of investigation has been the molecular orbital (MO) method in the simple Hückel approximation (HMO method) (Streitwieser<sup>1</sup>). Self-consistent field (SCF) calculations including the zero differential overlap (ZDO) approximation<sup>2,3</sup> have also been carried out both for hydrocarbons and for molecules with heteroatoms. In both these methods certain integral values are determined by semi-empirical procedures. When only a limited class of molecules is considered, the parameters can be chosen to give a very good fit to experimental data (Pariser<sup>4</sup>). On the other hand it can also be desirable to choose the parameters on rather general grounds to make possible an extension of the calculations to less well-known molecules. In the case of SCF semi-empirical theories such attempts have been made previously (Fischer-Hjalmars<sup>5</sup>) and are now extended to molecules with nitrogen and oxygen atoms in different valence states.

## PARAMETER CHOICE

In SCF theories the semi-empirical parameters are both one-electron integrals:

$$W_{\mu} = \int \chi_{\mu}^{*}(T + U_{\mu}^{+})\chi_{\mu} d\tau \quad (1)$$

$$\beta_{\mu\nu} = \int \chi_{\mu}^{*}H^{\text{core}}\chi_{\nu} d\tau \quad (2)$$

and two-electron integrals:

$$\gamma_{\mu\nu} = \int \chi_{\mu}^{*}(1)\chi_{\mu}(1)1/r_{12}\chi_{\nu}^{*}(2)\chi_{\nu}(2) d\tau_1 d\tau_2 \quad (3)$$

$\chi_{\mu}$  is an atomic space orbital (AO), centred on atom  $\mu$ ,  $T$  is the kinetic energy operator,  $U_{\mu}^{+}$  the potential from the singly charged core of the atom  $\mu$  and  $H^{\text{core}}$  the sum of the kinetic energy and the potential energy from all nuclei and all  $c$  electrons.

The two-electron integrals  $\gamma_{\mu\nu}$  of equation (3) can easily be evaluated when the AO's are  $2p\pi$  Slater orbitals. However, as is well known, the introduction of theoretical  $\gamma$  values in an unsophisticated SCF calculation will not lead to agreement with experiments, (Parr<sup>6</sup>). This concerns especially the one-centre integral  $\gamma_{\mu\mu}$ . Pariser and Parr<sup>2</sup> suggested that the

value of  $\gamma_{\mu\mu}$  should be determined from experimental values of the appropriate valence state ionization potential,  $\text{IP}(\mu)$ , and electron affinity,  $\text{EA}(\mu)$ , using the relation:

$$\text{IP}(\mu) - \text{EA}(\mu) = \gamma_{\mu\mu} \quad (4)$$

The present author<sup>5</sup> has suggested that  $\gamma_{\mu\mu}$  should be determined from experimental values of the Slater-Condon parameters  $F_0$  and  $F_2$  and the relation:

$$\gamma_{\mu\mu} = F_0 + 4F_2 \quad (5)$$

The connection between equations (4) and (5) has been discussed previously<sup>5,7</sup>. In the present investigation equation (5) has been used.

In the discussion of two-centre two-electron integrals,  $\gamma_{\mu\nu}$ , it is suitable to distinguish between two different regions of the internuclear distance  $R_{\mu\nu}$ . For large values of  $R_{\mu\nu}$ ,  $R_{\mu\nu} > 4 \text{ \AA}$ , the value of  $\gamma_{\mu\nu}$ , obtained from a straightforward, theoretical computation, can be adopted also in the semi-empirical approach. The region  $0 < R_{\mu\nu} < 4 \text{ \AA}$  is, however, of considerable interest. Pariser and Parr<sup>2</sup> suggested that for  $0 < R < 2.8 \text{ \AA}$  the value of  $\gamma_{\mu\nu}$  should be determined by an interpolation procedure using second-degree polynomials. Other procedures have also been suggested (*see* Fischer-Hjalmar<sup>8</sup>). The procedure used here is that used by Fischer-Hjalmar<sup>7</sup>.

The one-electron one-centre parameters  $W_\mu$  of equation (1) have often been determined from experimental values of ionization potentials, either from the atomic ionization potential or from the ionization potential of a selected reference molecule. When heteroatoms are involved and when the valence states are similar, *e.g.*, C(tr tr tr  $\pi$ ) and N(tr<sup>2</sup> tr tr  $\pi$ ), it has often been assumed that:

$$W_C - W_\mu = -c[\text{IP}(C) - \text{IP}(\mu)] \quad (6)$$

In many cases the value  $c = 1$  has been used. However, McWeeny and Peacock<sup>9</sup> found that  $W_C - W_N = 1.68 \text{ eV}$ , corresponding to  $c \approx 0.5$ , gives better agreement between experimental and theoretical data for pyridine and diazines than  $c = 1$ . In recent years many authors have adopted the McWeeny-Peacock value of  $W_C - W_N$ .

It should be pointed out, however, that  $\gamma_{\mu\mu}$  and the constant  $c$  in equation (6) are not completely independent parameters. Whether the value of  $\gamma_{\mu\mu}$  is determined from (4) or from (5) the following approximate relationship holds:

$$\gamma_{\mu\mu} - \gamma_{\nu\nu} \approx k[\text{IP}(\mu) - \text{IP}(\nu)] \quad (7)$$

where  $k \approx 2/3$  in connection with equation (4) and  $k \approx 1$  in connection with equation (5). The present author has shown<sup>10</sup> that it is necessary to choose:

$$c > \frac{1}{2}k \quad (8)$$

If the inequality (8) is violated, the computed polarity will be inconsistent with the assumptions.

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When lone pairs are involved in the conjugated system, *e.g.*  $N(\text{tr tr tr } \pi^2)$ , the parameter  $W_\mu$  should be chosen in a different way. In the present investigation the lone pair  $W_\mu$  values have been determined from ionization potentials of aliphatic compounds (Fischer-Hjalmar<sup>5,7</sup>).

The one-electron, two-centre parameter  $\beta_{\mu\nu}$  of equation (2) has been exhaustively analysed by Mulliken<sup>11</sup>. In that investigation he also suggested the approximate relationship:

$$\beta_{\mu\nu} = \text{const. } S_{\mu\nu} \quad (9)$$

which since then has been adopted in a multitude of cases. In the present investigation we have assumed that  $\beta_{\mu\nu}$  should have the same value for each *pure* double bond independent of the kind of atoms involved. A similar assumption has been made previously by Sidman<sup>12</sup>. To obtain the dependence of  $\beta$  on the distance we have put:

$$\beta_{\mu\nu} = k_{\mu\nu} S_{\mu\nu} \gamma_{\text{theor}, \mu\nu} \quad (10)$$

Equation (10) is a simplification of a previously derived formula<sup>7</sup>.

All standard parameter values, used in the present investigation, are collected in *Table 1*.

*Table 1.* Values† of semi-empirical parameters adopted in the present investigation

<i>Parameter</i>	<i>Value</i>	<i>Remark</i>
$\gamma_{\text{CC}}$	11.76	Equation (5)
$\gamma_{\text{NN}}$	15.49	Equation (5)
$\gamma_{\text{OO}}$	18.79	Equation (5)
$W_{\text{C}}, n_\pi = 1$	-9.40	Fitted to $\text{IP}(\text{C}_6\text{H}_6) = 9.247$
$W_{\text{N}}, n_\pi = 1$	-12.68	$c = 1$ in Equation (6)
$W_{\text{N}}, n_\pi = 2$	-8.51	$\text{IP}(\text{R}_1\text{R}_2\text{NH})$
$W_{\text{O}}, n_\pi = 2$	-9.61	$\text{IP}(\text{R}_1\text{R}_2\text{O})$
$\beta_{\text{CC}}(R = 1.397 \text{ \AA})$	-2.32	Fitted to spectrum of $\text{C}_6\text{H}_6$

† Energy values in electron volts.

## RESULTS

Semi-empirical SCF calculations with the parameter choice, described above, have been carried out for several molecules on the UNIVAC 1107 computer in Oslo. The programme used for these calculations has been written in Stockholm by Eisenberger and extended to include superposition of several configurations by Alm.

The present report will be limited to the discussion of pyridine, pyrrole and furan. It is particularly appropriate to choose these molecules, since their complete structures have been determined in Copenhagen by Bak *et al.*<sup>13-15</sup>.

The calculated lower electronic excitation energies and the corresponding oscillator strengths are listed in *Table 2*. For comparison the values obtained for benzene are also given. It should be remembered that only one parameter,  $\beta_{\text{CC}}(R = 1.397 \text{ \AA})$ , is chosen to obtain a reasonable fit of the benzene spectrum. As pointed out above, a parameter choice on less general grounds

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 Table 2. Excitation energies,†  $E - E_0$ , and oscillator strengths,  $f$ , calculated by superposition of configurations

State	Calculated values		Experimental values		
	$E - E_0$	$f$	$E - E_0$	$f$	Reference
Benzene					
${}^1B_{2u}$	4.79	0	4.89	0.0014	16
${}^1B_{1u}$	5.28	0	6.14	0.10	16
${}^1E_{1u}$	7.25	1.2	6.74	0.69	16
Ion	(9.247)	—	9.247	—	17
Pyridine					
${}^1B_2$	4.82	0.02	4.96	0.03	16
${}^1A_1$	5.21	0.01	6.36	0.20	16
${}^1B_2$	7.31	1.15	7.04	1.36	16
${}^1A_1$	7.54	1.11	9.28	—	18
Ion	9.24	—	—	—	—
Pyrrole					
${}^1B_2$	5.58	0.15	5.7	—	19
${}^1A_1$	5.79	0.05	6.7 Rydb. (?)	—	19
${}^1B_2$	7.55	0.55	7.2	—	19
${}^1A_1$	7.80	0.95	8.9	—	19
Ion	8.72	—	—	—	—
Furan					
${}^1B_2$	4.58	0.11	4.7	Weak	20, 21
${}^1A_1$	6.27	0.03	6.1	—	22
			6.47 Rydb. (?)	—	22
${}^1A_1$	7.60	0.97	7.3	—	22
${}^1B_2$	7.81	0.35	7.4	—	22
Ion	9.52	—	9.01	—	19

† Energy values in electron volts.

than the present will give a much better fit for a limited group of compounds (cf. Pariser<sup>4</sup> and Fischer-Hjalmars<sup>5</sup>).

From the computed bond orders,  $P_{\mu\nu}$ , the bond lengths  $R$  have been determined. As is well-known, Coulson<sup>23</sup> has evaluated a formula for the dependence of  $R$  on  $P$ , valid in the Hückel approximation:

$$R(P) = s - (s - d) \left/ \left[ 1 + K \frac{1 - P}{P} \right] \right. \quad (11)$$

where  $s$  and  $d$  are the lengths of the single and double bonds respectively. (When necessary, the notations  $s(\mu\nu)$ ,  $d(\mu\nu)$  will be used below). When  $K$  is

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determined from the requirement that equation (11) should fit the benzene values,  $R = 1.397$ ,  $P = 2/3$ , the equation for C—C bonds becomes:

$$R(P) = s - (s - d)P \quad (12)$$

when the C—C distances given in *Table 3* are adopted. It is not immediately evident that equation (12) can be used both for Hückel bond orders and SCF bond orders. However, it has been shown by Skancke<sup>24</sup> that equation (12) can be obtained also in the SCF scheme. In the present study the additional, reasonable assumption has been made that equation (12) should be valid also for C—N and C—O bonds. It should be remembered, however, that the experimental values of  $s(\text{CO})$  and of  $s(\text{CN})$  and  $d(\text{CN})$  are less accurate than  $s(\text{CC})$  and  $d(\text{CC})$ . The values of *Table 3* have been adopted for the present study.

*Table 3.* Adopted values of experimental bond distances†

Bond type	Single bond $s(\mu\nu)$	Double bond $d(\mu\nu)$
CC	1.517	1.337
CN	1.470	1.290
CO	1.430	1.216

† Lengths in Ångström units.

The calculated atomic distances are shown in *Table 4*. For comparison the

*Table 4.* Bond distances† calculated by equation (12) with bond orders  $P$  obtained by different computational schemes

Bond type	Calculated bond length value. Bond order calculation according to			Experimental value
	reference 26	references 5 and 25	present scheme	
Pyridine				
NC <sub>1</sub>	1.3514	1.3522	1.3509	1.3402
C <sub>1</sub> C <sub>2</sub>	1.3972	1.3961	1.3981	1.3945
C <sub>2</sub> C <sub>3</sub>	1.3969	1.3975	1.3966	1.3944
Pyrrole				
NC <sub>1</sub>	1.405	1.391	1.380	1.374
C <sub>1</sub> C <sub>2</sub>	1.364	1.369	1.380	1.381
C <sub>2</sub> C <sub>3</sub>	1.431	1.428	1.414	1.417
Furan				
OC <sub>1</sub>	—	—	1.362	1.362
C <sub>1</sub> C <sub>2</sub>	—	—	1.363	1.361
C <sub>2</sub> C <sub>3</sub>	—	—	1.435	1.431

† Lengths in Ångström units.

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values obtained by use of the previously adopted parameter scheme<sup>5,25</sup> are included as well as values computed from the SCF MOs given by Leroy<sup>26</sup>. In the case of pyridine the bond orders in all three schemes are close to the benzene value,  $P = 2/3$ . Consequently, the calculated bond lengths are almost identical and close to the experimental values. In the case of pyrrole all the calculated distances are within 0.03 Å of the experimental values. The parameters of the present investigation obviously give the best fit. It is very gratifying that in the case of furan also the fit is very good. It should be pointed out that apart from the geometry no experimental data for pyridine, pyrrole or furan have been used to determine the parameters. Thus it can be hoped that the application of the present computational scheme will yield acceptable values also when applied to other molecules.

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