

Commentationes

Some Comments on the Parameter Choices for S.C.M.O. Calculations on Five Membered Heteroatomic π -Electron Systems

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It has been reported [1] that the usual semi-empirical S.C.M.O. treatments of heteroatomic π -electron systems yield unexpected dependencies of charge distribution on the β_{core} terms involving the heteroatoms. Other workers [2] have claimed that the most usual choices of parameters yield chemically unreasonable charge densities in furan and pyrrole. It is shown here that the first effect is related to the relative magnitudes of the diagonal elements of the Fock matrix and that the second depends very strongly on the nonnearest neighbor F matrix elements but can be overcome with certain parameter choices by the inclusion of non-nearest neighbor β_{core} terms in the calculations.

Bei den üblichen semiempirischen SCMO-Rechnungen an Heteroaromaten ergeben sich unerwartete Abhängigkeiten der Ladungsverteilung von den β_{Rumpf} -Termen [1]. Die gebräuchlichste Parameterwahl führt zu chemisch unverständlichen Ladungsverteilungen bei Furan und Pyrrol [2]. Es wird gezeigt, daß der erste Effekt mit der relativen Größe der Diagonalelemente der Fockmatrix zusammenhängt; der zweite Effekt hängt sehr stark von den Nichtnachbarelementen ab: Bei Einschluß von Nichtnachbar- β_{Rumpf} -Termen und entsprechender Parameterwahl erhält man befriedigende Ladungsverteilungen.

Il a été indiqué [1] que le traitement semi-empirique S.C.M.O. habituel des systèmes d'électrons π dans les hétérocycles comporte des relations inattendues entre la distribution de charge et les termes β_{coeur} impliquant les hétéroatomes. D'autres chercheurs [2] ont affirmé que les choix les plus communs de paramètres fournissent des densités de charge dans le furane et le pyrrole déraisonnables sur le plan chimique. On montre ici que le premier effet est lié aux grandeurs relatives des éléments diagonaux de la matrice de Fock et que le second effet dépend fortement des éléments non immédiatement voisins de cette matrice, mais peut être annulé avec certains choix de paramètres par introduction des termes non voisins β_{coeur} dans les calculs.

Introduction

The effect of a single heteroatom in a six-membered ring π -electron system on such properties as orbital energies, charge densities etc. can be fairly well understood by considering the heteroatoms as a perturbation on the parent homoatomic system. Analytical expressions for the effects of such perturbations on alternant hydrocarbon systems have been derived by Coulson and Longuet-Higgins [3, 4] and have been thoroughly exploited by Dewar [5]. No such simple relationships have been established for non-alternant systems, however. Rings containing an odd number of atoms are non-alternant systems. The five membered ring is chemically the most important of these. A good deal of work has been done in an effort to determine the "best" parameter values for such systems, both within the context of Hückel theory [2, 6] and the S.C.M.O. theory [7, 7a], however there has

been no extensive systematic study of the effect of parameter variation within the S.C.M.O. theory. We have here undertaken a study of the effect of various parameter choices on such systems within the Pariser-Parr-Pople self-consistent molecular orbital (S.C.M.O.) method [8, 9]. Particular emphasis will be placed on charge densities and orbital energies since these are the quantities most often compared in the alternant aromatic systems.

S.C.M.O. Equations

The S.C.M.O. equations as used by Pariser and Parr [8] and Pople [9] may be expressed, within the zero differential overlap (Z.D.O.) approximation, as in Eqs. 1—3.

$$\varepsilon_n = \sum_{\mu} c_{n\mu}^2 F_{\mu\mu} + 2 \sum_{\mu \neq \nu} c_{n\mu} c_{n\nu} F_{\mu\nu}, \quad (1)$$

$$F_{\mu\mu} = (\mu|f|\mu) + R_{\mu\mu}(\mu\mu|\mu\mu) + 2 \sum_{\nu \neq \mu} R_{\mu\nu}(\mu\mu|\nu\nu), \quad (2)$$

$$F_{\mu\nu} = (\mu|f|\nu) - R_{\mu\nu}(\mu\mu|\nu\nu) \quad (3)$$

In Eq. 1, ε_n is the energy of the n -th molecular orbital and the $c_{n\mu}$ are the coefficients of the μ -th atomic orbital in the n -th molecular orbital. In Eqs. 2 and 3, f represents the part of the Fock operator which is a function of the coordinates of only one electron. The $R_{\mu\nu}$'s are the elements of the first order density matrix obtained from the final iteration of the S.C.M.O. problem. (The $R_{\mu\mu}$ and $R_{\mu\nu}$ are one half of the atomic charge density (q_{μ}) and the bond order ($p_{\mu\nu}$) respectively.)

The $(\mu|f|\mu)$ integral, the so-called α_{core} term, may be expressed in terms of the Goeppert-Mayer and Sklar approximation [10] as in Eq. 4.

$$(\mu|f|\mu) = W_{\mu} - \sum_{\nu \neq \mu} [N_{\nu}(\mu\mu|\nu\nu) - (\mu|\nu\nu)] \quad (4)$$

Here, W_{μ} represents the valence state ionization potential, the energy required to remove an electron from the μ -th atomic orbital with the atom in its appropriate valence state, N_{ν} is the number of electrons that orbital ν formally donates to the π -system and the $(\mu|\nu\nu)$ are the neutral atom penetration integrals. The entire bracketed term represents the interaction of an electron in orbital μ with the other atomic centers in the molecule, assuming each atom in the core is formally neutral. The first term in the brackets is an approximation of the attraction the bare core of atom ν (here atomic orbital labels are also applied to the atoms on which they originate) would exert on an electron on atom μ while the penetration integrals correct for the fact that the ν -th core center is not bare, but rather has the required number of electrons in its π -orbital to make it formally neutral. (Actually, penetration integrals should also be included for neutral atoms which do not enter the conjugated system, such as the hydrogens in a system.) The magnitudes of the neutral atom penetration integrals are relatively small (0.5—0.85 eV for two adjacent carbon atoms, depending upon the choice of the effective nuclear charge) and fall off essentially exponentially with distance. Also, the molecular environment of a given atom in a conjugated hydrocarbon system does not vary greatly from atom to atom. Thus the sum of neutral atom penetration integrals for any given atom in a hydrocarbon system should be relatively small and relatively constant. For this reason they are most often

neglected in π -electron calculations. It should be pointed out that this near constancy of the penetration integrals is not in general valid when heteroatoms are introduced into the system, particularly when the heteroatom bears a double charge in the core of the molecule. The effect of this in the case of pyrrole has been pointed out by Brown and Heffernan [7a] and by Dahl and Hansen¹ [11]. Since a meaningful way to evaluate these in semi-empirical calculations has yet to be found, they are ignored in the calculations reported here. The effect of including them would be to alter the magnitude of the diagonal matrix elements.

If $(\mu|f|\mu)$ is expanded according to Eq. 4 and the neutral atom penetration integrals are neglected, Eq. 2 may be expressed as in Eq. 5

$$F_{\mu\mu} = W_{\mu} + R_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{v \neq \mu} [2R_{vv} - N_v] (\mu\mu|vv). \quad (5)$$

(Certain authors [1, 12] express this in terms of δW_{μ} with reference to the quantity $W_C + 1/2 \gamma_{CC}$, γ_{CC} being the one-center, two-electron repulsion integral for carbon.) The term in the square brackets equals zero for any alternant hydrocarbon system when non-nearest-neighbor β_{core} terms are neglected. If, however, there is appreciable charge separation in a molecule, this can have appreciable magnitude. Land and Pilar suggest that in order to get charge distributions in certain heterocyclic molecules, such as furan, which agree with comparable Hückel calculations this term should be neglected [1].

If the $(\mu|f|v)$ integral (β_{core}) were to be expanded analogously to Eq. 4, rigorously enforcing the Z.D.O. approximation and requiring $(\mu|f|v)$ to equal $(v|f|\mu)$, Eq. 6 would result,

$$(\mu|f|v) = \frac{S_{\mu v}}{2} (W_{\mu} + W_v). \quad (6)$$

$S_{\mu v}$ being the overlap integral. Although functions where β_{core} is proportional to the overlap integral have frequently been used in molecular calculations, more satisfactory results are usually obtained by using some empirical function for

Table 1. S.C.M.O. F matrices for pyrrole, with and without all β_{core} terms included^a

A. All β_{core}

$$F = \begin{bmatrix} -12.891 & -4.307 & 0.051 & 0.051 & -4.307 \\ -4.307 & -5.307 & -4.916 & -0.370 & 0.227 \\ 0.051 & -4.916 & -5.392 & -3.808 & -0.370 \\ 0.051 & -0.370 & -3.808 & -5.393 & -4.916 \\ -4.307 & 0.227 & -0.370 & -4.916 & -5.903 \end{bmatrix}$$

B. Nearest-neighbor β_{core}

$$F = \begin{bmatrix} -13.041 & -4.394 & 0.521 & 0.521 & -4.394 \\ -4.394 & -5.943 & -4.789 & 0.201 & 0.803 \\ 0.521 & -4.788 & -5.351 & -3.910 & 0.201 \\ 0.521 & 0.201 & -3.910 & -5.351 & -4.788 \\ -4.394 & 0.803 & 0.201 & -4.788 & -5.943 \end{bmatrix}$$

^a $\beta_{\text{core}}(12) = -3.04$ eV. For other parameter values, see Table 3, footnote a.

¹ Both of these references utilized the variable electronegativity SCF method developed by Brown (Trans. Faraday Soc. **54**, 757(1958)) and are not directly comparable to the present work. However, the general conclusion was that the effect of including penetration integrals was similar to that found here for including non-nearest neighbor β_{core} terms.

β_{core} . In addition, the assumption is usually made that β_{core} equals zero for any two atoms not directly bonded in the chemical sense. The use of an empirical β function can be justified by the expediency of obtaining agreement between calculated and observed molecular properties, however, there is no valid foundation for the neglect of non-nearest-neighbor β_{core} terms. (The self-consistent F matrix, with and without non-nearest-neighbor β_{core} terms are compared for pyrrole in Table 1.) It has recently been demonstrated that the inclusion of all β_{core} terms has important consequences in the calculated spectral transitions and charge densities of conjugated hydrocarbon [13] and heteroatomic systems [14].

Calculations

The calculations reported in this work were performed on an I.B.M. 1620 computer with disk pack. The program and basic parameters were as described in reference [13], except for the calculations on pyrrole, where the β_{core} function was as described in reference [14]. The effective electronegativity of the heteroatom was varied by altering the W_x of Eq. 5. The β_{core} function was varied by altering W_μ in Eq. 7 [13].

$$\beta_{\mu\nu} = \frac{(2 - S_{\mu\nu})S_{\mu\nu}}{2 - S_{\mu\nu}^2} (W_\mu W_\nu)^{1/2} \quad (7)$$

The program was set up so that these could be varied independently. For a given calculation only the W_x pertaining to the integral under consideration was varied. All others were maintained at the appropriate value as obtained from valence state data. The two center repulsion integrals were calculated by the Nishimoto-Mataga approximation [15]. The valence state data were taken from the work of Hinze and Jaffé [16].

Charge Density on the Heteroatom

The charge density on the heteroatom is most strongly dependent upon the magnitude of the F_{xx} matrix element for the heteroatom. The more negative this element is, the greater will be the charge on the heteroatom. From Eq. 5 we see that the predominant effects on $F_{\mu\mu}$ come from W_μ and the $(\mu\mu|\mu\mu)$ integral. Making the value of either of these smaller in the absolute sense (making W_μ more negative or $(\mu\mu|\mu\mu)$ less positive) will thus increase the charge density on the heteroatom. This is illustrated in Table 2.

The charge density on the heteroatom also depends upon the magnitude of the β_{CX} term. This is also illustrated in Table 2. Both the magnitude and the sign of this dependence vary with the magnitude of F_{xx} .

Land and Pilar argue that the summation in Eq. 5 should be neglected because the variation of the charge density on the oxygen atom in furan with the magnitude of the carbon-oxygen β_{core} changes sign as the effective electronegativity of the oxygen α_{core} is increased. This is in contrast with what is found for five membered heterocyclics in simple Hückel theory, where, for all heteroatom parameter values more electronegative than carbon, the charge on the heteroatom decreases as the magnitude of the β_{CX} parameter increases. If, on the other hand, the heteroatom is considerably less electronegative than carbon, the charge on the heteroatom will increase as the magnitude of the β_{CX} parameter increases. This is illustrated for Hückel calculations in Fig. 1. Here, the heteroatom parameters are expressed

Table 2. Variation of total π -electron density with β_{core} (CX)^a

β_{12}	β_{13}	q_x	q_2	q_3	A_{23} ^c
A. All β_{core} [in eV]					
$\delta W_x^b = 4.0$ eV					
-2.07	-0.44	0.7654	1.3985	1.2188	0.1797
-2.59	-0.55	0.7804	1.3858	1.2239	0.1619
-3.21	-0.68	0.7948	1.3783	1.2288	0.1450
-3.68	-0.78	0.8040	1.3664	1.2316	0.1348
$\delta W_x = 0$					
-2.07	-0.44	1.2488	1.1888	1.1868	0.0020
-2.59	-0.55	1.2000	1.2000	1.2000	0.0000
-3.21	-0.68	1.1539	1.2108	1.2123	-0.0015
-3.68	-0.78	1.1236	1.2175	1.2194	-0.0019
$\delta W_x = -2.0$ eV					
-2.07	-0.44	1.4714	1.0985	1.1658	-0.0673
-2.59	-0.55	1.4001	1.1171	1.1828	-0.0657
-3.21	-0.68	1.3303	1.1355	1.1994	-0.0639
-3.68	-0.78	1.2871	1.1472	1.2092	-0.0620
$\delta W_x = -6.0$ eV					
-2.07	-0.44	1.7744	0.9851	1.1277	-0.1326
-2.59	-0.55	1.7012	1.0020	1.1474	-0.1454
-3.21	-0.68	1.6190	1.0214	1.1691	-0.1477
-3.68	-0.78	1.5626	1.0353	1.1834	-0.1481
$\delta W_x = -12.0$ eV					
-2.07	-0.44	1.9296	0.9361	1.0991	-0.1630
-2.59	-0.55	1.8939	0.9397	1.1133	-0.1736
-3.21	-0.68	1.8448	0.9455	1.1321	-0.1866
-3.68	-0.78	1.8046	0.9510	1.1467	-0.1957
B. Nearest-neighbor β_{core} only					
$\delta W_x = 4.0$ eV					
-2.07		0.7978	1.3833	1.2178	0.1655
-3.21		0.8366	1.3568	1.2249	0.1319
$\delta W_x = 0$					
-2.07		1.2372	1.1905	1.1909	-0.0004
-3.21		1.1658	1.2084	1.2087	-0.0003
$\delta W_x = -2.0$ eV					
-2.07		1.4386	1.1061	1.1746	-0.0685
-3.21		1.3234	1.1402	1.1981	-0.0579

^a The following parameters were used for these calculations: $W_C = -11.16$ eV, $\gamma_{11} = 11.13$ eV, Nishimoto-Mataga integrals for the homoatomic case were used throughout. For the geometry, a regular pentagon with benzene bond lengths was used.

^b Change in W_x from the carbon value.

^c $q_2 - q_3$.

Table 2 (continued)

	q_x	q_2	q_3	A_{23}^c
$\delta W_x = -6.0 \text{ eV}$				
-2.07	1.7285	0.9908	1.1449	-0.1541
-3.21	1.5362	1.0466	1.1853	-0.1387
$\delta W_x = -12.0 \text{ eV}$				
-2.07	1.9044	0.9277	1.1201	-0.1924
-3.21	1.8085	0.9485	1.1472	-0.1987

in the usual manner for Hückel calculations (Eqs. 8 and 9).

$$\alpha_x = \alpha_c + h_x \beta_{CC}, \quad (8)$$

$$\beta_{CX} = k_{CX} \beta_{CC}. \quad (9)$$

Land and Pilar report that if the summation in Eq. 5 is retained, a heteroatom parameter value 8.5 eV more electronegative than carbon yields a π -electron charge density on oxygen which is independent of the magnitude of the β_{core} para-

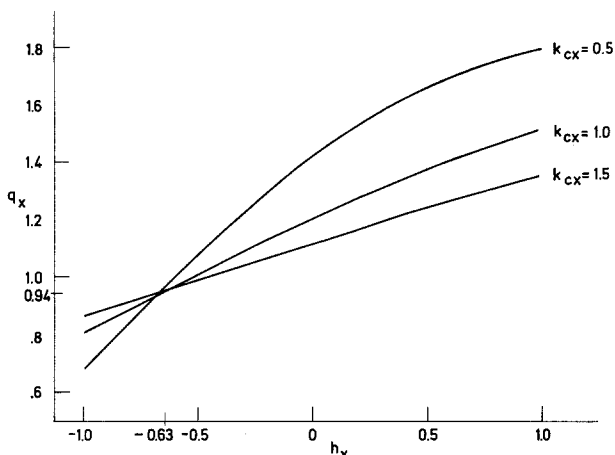


Fig. 1. Variation of heteroatom charge as a function of heteroatom parameters in the Hückel approximation

meter involving the heteroatom and which has a value of about 0.94. If a more electronegative value is used, the charge on oxygen decreases with an increasing β_{core} as expected, while for a less electronegative value the charge increases with increasing β_{core} . (Obviously, for a given value of the β_{core} term, the more electronegative the heteroatom the greater will be its π -electron charge density). From Fig. 1, we can see that in the Hückel case this same thing would occur for a h_x parameter having a value of about -0.63 .

If a heteroatom W_x 8.5 eV more electronegative than carbon and a charge density on oxygen of 0.94 are used with Eq. 5 to calculate a diagonal F matrix element for oxygen, assuming that the remaining electron density is essentially equally distributed about the four carbons and using the Pariser and Parr integral values [8], a value near, but slightly more positive than that for the diagonal

element for a carbon in the cyclopentadienyl anion is obtained (12.3 eV relative to the V.S.I.P. of carbon versus a value of 11.7 eV for the cyclopentadienyl anion). This suggests that, for a heteroatom W_X less electronegative than this, the situation will be analogous to a Hückel treatment with a heteroatom less electronegative than carbon (see entries in Table 2 for $\delta W_X = 4.0$ eV). Hence, the change in dependency of the charge on oxygen with the magnitude of β_{CX} should not be surprising.

Relative Charge Density in Positions 2 and 3

The relative charge densities in the 2 and 3 positions in heteroatomic five membered rings is also dependent upon both the F_{XX} term for the heteroatom and the β_{core} term involving the heteroatom. For a given β_{core} value the charge on the 2 position decreases as the F_{XX} term for the heteroatom becomes more negative. On the other hand, the charge on the 3 positions is much less sensitive to F_{XX} for a given β_{core} value. This is shown in Table 2. For a given value of F_{XX} the relative charges in all three positions are dependent upon the magnitude of β_{CX} . This is shown in Table 2 for arbitrary parameter values and in Table 3 for the specific case

Table 3. π -Charge distribution in pyrrole as a function of β_{CN} ^a

β_{12}	β_{13}	q_1	q_2	q_3	A_{23}
All β_{core} [in eV]					
-2.36	-0.37	1.7898	1.0638	1.0411	0.0227
-2.61	-0.41	1.7693	1.0686	1.0513	0.0173
-3.04	-0.48	1.7125	1.0760	1.0678	0.0082
-3.24	-0.51	1.6912	1.0793	1.0752	0.0041
-3.90	-0.61	1.6237	1.0900	1.0983	-0.0083
Nearest-Neighbor β_{core} only					
-2.36		1.7524	1.0581	1.0657	-0.0076
-2.61		1.7231	1.0641	1.0744	-0.0103
-3.04		1.6770	1.0734	1.0881	-0.0147
-3.24		1.6570	1.0774	1.0941	-0.0167
-3.90		1.5955	1.0900	1.1123	-0.0223

^a Nitrogen parameters: $W_N = -28.71$ eV, $\gamma_{NN} = 16.75$ eV; Carbon β_{core} values: $\beta_{23} = -2.67$ eV, $\beta_{24} = -0.53$ eV, $\beta_{34} = -2.44$ eV; other parameters as before.

of pyrrole. The absolute magnitudes of the charge changes on the 2 and 3 positions as a function of β_{CX} are relatively small, but the trends are important. Qualitatively, in the cases where F_{XX} is as negative as or more negative than F_{CC} , an increase in β_{CX} decreases the π -charge on position 1 and increases the charge on both positions 2 and 3. The converse is true when F_{XX} is less electronegative than F_{CC} . In all but one of the studied cases, the charge build-ups, with increasing magnitude of β_{core} , is greater at the 3 position than at the 2 position. When the heteroatom was only slightly more electronegative than carbon ($\delta W_X = -2.0$ eV) the trend was reversed.

Table 3 presents the charge densities in pyrrole as calculated by a typical π -electron method, but varying the value of β_{CN} . It is seen that for all except the

most negative value of β_{CN} , the all β_{core} calculations yield $q_2 > q_3$; while for all values tried, the nearest-neighbor β_{core} calculations yielded $q_3 > q_2$. The former situation is more in agreement with the chemists intuition, since pyrrole undergoes electrophilic substitution in the 2 position. There is, however, still some doubt about the validity of charge density as a criterion for determining reactivity. More disconcerting is the fact that the π -electron part of the recent non-empirical, all electron calculations of Clementi [17] yielded a greater π -density at the 3 position. In fact, his π -densities are almost identical with the present nearest-neighbor calculations with a β_{CN} value of -3.24 eV (Table 4).

Table 4. *Non-empirical π -electron densities on pyrrole^a*

$q_1 = 1.6589$
$q_2 = 1.0752$
$q_3 = 1.0953$

^a Ref. [17].

The source of the inversion of the charge density, depending on whether or not all β_{core} terms is included, in the pyrrole calculations (it also occurs for certain β_{core} functions in furan) can be explained from an examination of Table 1. The primary differences in the F matrices when all β_{core} are included and when they are not are, as would be expected, in the elements corresponding to non-nearest neighbor interactions. (In fact, if the two matrices are normalized to F_{34} in each case, the other elements all are within 5% of each other.) The non-neighbor terms differ in relative magnitude and, more importantly, in sign. To find the dependence of the charge on each of these, the F matrix for the all β_{core} case was diagonalized after deletion of each of the non-neighbor elements in succession (Table 5). F_{13} and its symmetry related elements had relatively little effect, due to its small size, however its deletion caused a slight increase in charge in positions 1 and 3 and a slight decrease in charge in position 2. Deletion of F_{24} , the only element which differed in sign in the two matrices caused a significantly greater charge shift (due to its greater magnitude) with a decrease in charge in position 1 and 2 and an increase in position 3. Deletion of F_{25} again caused a decrease in charge in positions 1 and 2 and an increase in position 3. This implied that a reversal of the sign of F_{24} in the F matrix for the nearest neighbor only β_{core} case would cause a situation

Table 5. *Charge distribution in pyrrole as a function of F matrix elements deleted (all β_{core})^a*

	Elements deleted							
	None	F_{13}	F_{24}	F_{25}	F_{13}, F_{24}	F_{13}, F_{25}	F_{24}, F_{25}	All N.N. ^b
q_{N}	1.7164	1.7180	1.7012	1.7126	1.7028	1.7144	1.6970	1.6988
q_2	1.0734	1.0716	1.0524	1.0708	1.0504	1.0690	1.0502	1.0482
q_3	1.0682	1.0690	1.0968	1.0726	1.0978	1.0736	1.1012	1.1022

^a $(\beta_{\text{core}})_{12} = -3.04$ eV. These matrices were diagonalized by a less accurate method than the one in the S.C.M.O. program, consequently column 1 here differs slightly from the corresponding values in Table 3. The elements which are symmetry related to those indicated were also deleted.

^b All non-nearest neighbor $F_{\mu\nu}$ terms deleted.

where position 2 had a greater charge than position 3, and that a reversal of the sign of F_{13} and F_{25} would increase the already present excess charge on position 3. This was verified (Table 6).

Since the values of the non-neighbor F matrix elements depend both on β_{core} and the two center repulsion integrals (Eq. 3), these results suggest that the relative charge distribution in molecules could be strongly dependent on both the geo-

Table 6. Charge distribution in pyrrole as a function of non-neighbor F matrix elements (nearest-neighbor β_{core} only)^a

	Original	Sign of F_{24} changed	Sign of F_{13} and F_{25} changed	All non-neighbor β_{core} deleted
q_N	1.6783	1.6932	1.6809	1.6887
q_2	1.0743	1.0978	1.0187	1.0590
q_3	1.0864	1.0555	1.1408	1.0968

^a See Table 5, footnote a.

Table 7. Charge distribution in pyrrole with regular pentagon geometry^a

	Nishimoto-Mataga Integrals ^b	Pariser-Parr Integrals ^c
q_n	1.7003	1.6105
q_2	1.0874	1.1454
q_3	1.0625	1.0494

^a All bond lengths 1.39 Å; β_{core} values: $\beta_{12} = -2.82$ eV, $\beta_{13} = -0.44$ eV, $\beta_{23} = -2.34$ eV, $\beta_{24} = -0.50$ eV; other parameters as previously described.

^b Calculated as in Ref. [15]

^c Calculated as in Ref. [8].

metry used in the calculations and on the type of functions used to calculate the non-neighbor β_{core} terms and the electron repulsion terms. Results showing this are presented in Table 7. (These values should be compared with those of column 1 of Table 5.)

Orbital Energies

The orbital energies are affected by variations in W_{XX} and β_{CX} in the qualitative manner that would be expected. This is shown in Figs. 2, 3, 4 and 5. In each case, those orbitals with nodes passing through the nitrogen atom (the a_2 orbitals in the C_{2v} point group) are those least effected by variations in the parameters. The most interesting feature in these comparisons is actually the difference in the results when all β_{core} are included and when only nearest-neighbor β_{core} terms are included. Although the lowest energy orbital, for a given set of parameters, is lower by roughly 1 eV when all β_{core} terms are included, the converse is true for the pair of bonding orbitals which are degenerate in the cyclopentadienyl case. In the antibonding orbitals, the all β_{core} calculations again yield the lower energies, although the differences are less than half as great. This is the source of the result, reported in

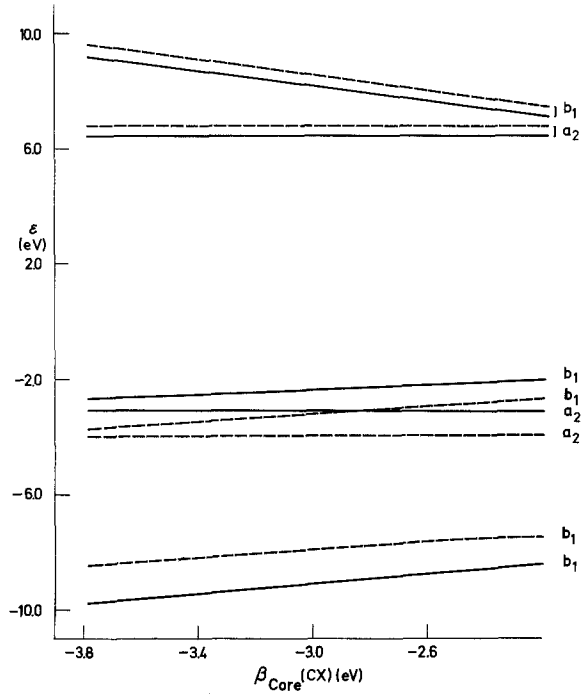


Fig. 2. Dependence of S.C.M.O orbital energies on $\beta_{\text{core}}(\text{CX})$, $\delta W_X = 4.0$ eV. Solid line, all β_{core} ; dashed line, nearest neighbor β_{core} only

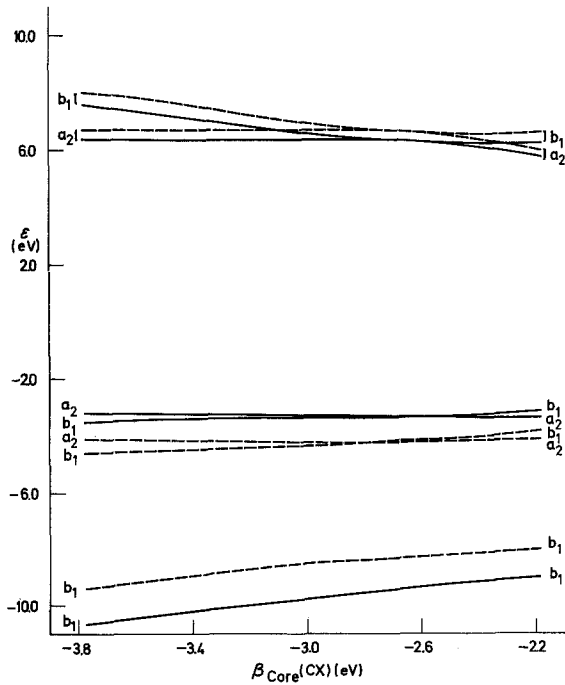


Fig. 3. Dependence of S.C.M.O. orbital energies on $\beta_{\text{core}}(\text{CX})$, $\delta W_X = 0$. Solid line, all β_{core} ; dashed line, nearest neighbor β_{core} only

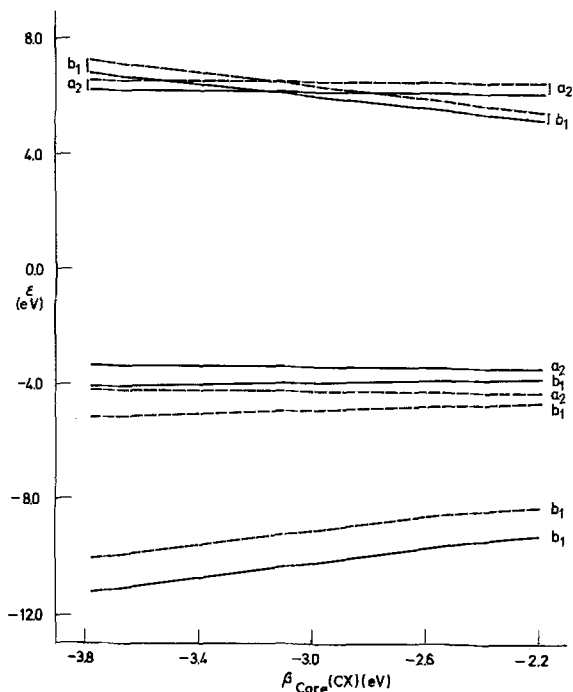


Fig. 4. Dependence of S.C.M.O. orbital energies on $\beta_{\text{core}}(\text{CX})$, $\delta W_x = -2.0$ eV. Solid line, all β_{core} ; dashed line, nearest neighbor β_{core} only

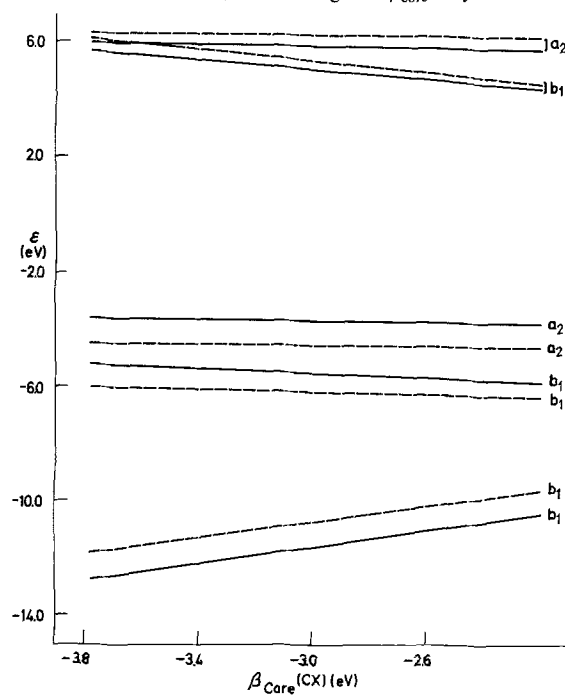


Fig. 5. Dependence of S.C.M.O. orbital energies on $\beta_{\text{core}}(\text{CX})$, $\delta W_x = -6.0$ eV. Solid line, all β_{core} ; dashed line, nearest neighbor β_{core} only

reference [14], that, for a given set of valence state and repulsion integral values, if the calculated spectral transitions for nearest-neighbor β_{core} only and all β_{core} were in agreement, the nearest-neighbor β_{core} calculations predicted the highest ionization potential.

For both the case with all W_{μ} equal and β_{core} varying and the case with all β_{core} equal and W_{X} varying, there is a change in ordering of both the bonding and antibonding pairs of b_1 and a_2 orbitals. This is to be expected since the parameters bracket the cyclopentadienyl case. If W_{X} differs from the other W_{μ} values, this is much less likely to occur within a reasonable range of parameter values. For example, if δW_{X} equals -2.0 eV it occurs for the antibonding pair of orbitals when β_{12} is large, but does not occur at all for the bonding pair, although the trend looks as if the change might occur for very low magnitude β_{core} values. If δW_{X} equals -6.0 eV or $+4.0$ eV the change in order does not occur at all within the range of β_{12} values reported. It could, however, conceivably occur outside the reported range.

Conclusions

Although the work reported here cannot be used to uniquely define a "best" set of parameters for use in semi-empirical S.C.M.O. calculations on five-membered heterocyclics, it does reveal the trends to be expected for various types of parameter variations. The only parameters extensively studied here were W_{X} and β_{core} , however the effects of the variation of other parameters such as penetration integrals and repulsion integrals can be deduced from the manner in which they enter into Eqs. 2 and 3.

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