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Semi-Empirical Approximations for the Coulomb and Bond Integrals in Simple LCAO-MO Methods

I. Alternant and Non-Alternant Hydrocarbons*

By

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It is suggested that the Coulomb integral in simple LCAO-MO methods is given by $\alpha_r = -(I_r + N_{\max}\overline{E}_s)$, where I_r is the valence state ionization potential of atom r, $\overline{E}_s$ is the average of the valence state electron-affinities of the nearest neighbors of r, and $N_{\max}$ is the maximum π-bond order of atom r. It is assumed that a parabolic relation holds between the bond integral β_{rs} and the overlap integral S_{rs}. All bond integrals and overlap integrals are included. Bond orders and π-electron densities are calculated for a representative number of alternant and non-alternant hydrocarbons. Comparison with values obtained by other simple LCAO-MO methods and by advanced MO calculations suggests that the proposed parametrization introduces some electron-electron interaction in the Hückel methods.

Für die Coulomb-Integrale der einfachen LCAO-MO-Theorie wird der Ansatz $\alpha_r = -(I_r + N_{\max}\overline{E}_s)$ vorgeschlagen, wobei I_r das Ionisationspotential des Valenzzustandes von Atom r, $\overline{E}_s$ der Mittelwert der Elektronenaffinitäten der nächsten Nachbarn und $N_{\max}$ die maximale Bindungsordnung von r ist. Alle Resonanzintegrale werden in die Rechnung einbezogen. Für sie wird eine parabolische Abhängigkeit vom Überlappungsintegral angenommen. Bindungsordnungen und π-Elektronendichten werden für eine Anzahl konjugierter und nicht-konjugierter Kohlenwasserstoffe berechnet. Vergleiche sowohl mit anderen einfachen MO-Theorien als auch mit solchen komplizierterer Natur lassen den Schluß zu, daß ein Teil der Elektronenwechselwirkung bei der vorgeschlagenen Parameterisierung erfaßt wird.

L'expression $\alpha_r = -(I_r + N_{\max}\overline{E}_s)$ est proposée pour l'intégrale de Coulomb dans les méthodes simples LCAO-MO, où I_r signiefie l'énergie d'ionisation de l'état de valence de l'atome r, $\overline{E}_s$ le moyen des affinités électroniques des états de valence des atomes voisins de r, et $N_{\max}$ l'indice de valence maximale de l'atome r. Toutes les intégrales de résonance β_{rs} et de recouvrement S_{rs} sont inclus au calcul, et une relation parabolique entre β_{rs} et S_{rs} adoptée. Les indices de liaison et densités électroniques π sont calculés pour quelques hydrocarbures représentatifs, alternants et non-alternants. La comparaison à d'autres méthodes simples LCAO-MO et à de calculs MO élaborés suggère que la paramétrisation proposée introduit une certaine interaction électronique aux méthodes de Hückel.

Introduction

Interest in simple LCAO-MO calculations has been recently revived by the papers of Hoffmann [9] and of Orloff and Fitts [15]. As pointed out by these authors, the fundamental difficulty of the simple methods is the choice of the one-electron energy integrals,

$\alpha_r = H_{rr}(i) = \int \psi_r^*(i)\,\mathscr{H}(i)\,\psi_r(i)\,d\tau_i$, and $\beta_{rs} = H_{rs}(i) = \int \psi_r^*(i)\,\mathscr{H}(i)\,\psi_s(i)\,d\tau_i$,

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where the Hamiltonian is the exact operator including all many-body interactions [*2*, *10*]. Since these integrals at present cannot be computed reasonable numerical values must be assigned to them.

Because the Hamiltonian in α_r is the molecular Hamiltonian α_r cannot be measured solely in terms of parameters pertaining to the isolated atom r, as done by HOFFMANN [*9*] and by PRITCHARD and SUMMER [*19*]. For the bond integrals, the usual parametrizations due to MULLIKEN [*13*] and to WOLFSBERG and HELMHOLTZ [*23*] are now believed to be not particularly good ones [*16*]. RUEDENBERG [*20*] on the other hand has shown that a parabolic relation between β_{rs} and the overlap integral S_{rs} is a better approximation.

All these parametrizations [*9*, *13*, *19*, *23*] have been proposed on the basis of physical intuition as to the meaning of α_r and β_{rs}. However, in most simple LCAO-MO calculations it has been found convenient to represent the Coulomb and the bond integrals by expressions of the type:

$$\alpha_r = \alpha_0 + h_r \beta_0 \tag{1}$$

and:

$$\beta_{rs} = k_{rs} \beta_0 \tag{2}$$

where α_0 and β_0 are standard parameters, usually those of benzene, and h_r and k_s are arbitrary constants chosen in such a way as to reproduce the experimental value of a molecular property. Thus, these are essentially two variables approximations. Electron-electron interaction can be incorporated within the framework of these procedures by the use of an iterative calculation such as the ω-technique [*21*, *22*], but this requires the introduction of a third variable.

Within the limitations of all independent particle models, simple LCAO-MO methods can be explored along these two main lines. On one hand it will possibly be rewarding to examine statistically which values of α_r and β_{rs} reproduce best a group of molecular properties for the largest possible number of molecules. This has been done in the past [*21*], although perhaps not in the systematic way that would be desirable. On the other hand, following the fundamental contributions of MULLIKEN [*13*] we could try to eliminate as far as possible the arbitrary character of the choice of α_r and β_{rs} by analysing these integrals and partitioning them in terms of experimental atomic parameters. In this first communication we are concerned with the latter type of approach.

The Coulomb Integral

The validity of the σ-π separability conditions will be assumed. Deviations from these conditions can be serious [*9*, *12*] and should be particularly so in heterocyclics, but we will neglect them since we are confined to an analysis of the performance of a certain parametrization within the simple LCAO-MO methods. Overlap integrals between adjacent as well as non-adjacent atoms will be included and accordingly atomic charges and bond orders are those defined by CHIRGWIN and COULSON [*4*].

Consider a two-electron localized bond between atoms r and s, and let the two electrons be i (centered in r) and j (centered in s). The Coulomb integral is:

$$\alpha_r(i) = \int \psi_r^*(i)\left(-\frac{1}{2}\nabla_i^2 - \frac{1}{R_{ir}} - \frac{1}{R_{is}} + V_{av}(ij)\right)\psi_r(i)\, dt_i \tag{3}$$

where $V_{av}(ij)$ is the electron-electron interaction operator averaged in a certain way*. This integral can be written

$$\alpha_r(i) = \int \psi_r^*(i)\left(-\frac{1}{2}\nabla_i^2 - \frac{1}{R_{ir}}\right)\psi_r(i)\,dt_i + \int \psi_r^*(i)\left(-\frac{1}{R_{is}} + V_{av}(ij)\right)\psi_r(i)\,dt_i \qquad (4)$$

If $\psi_r(i)$ in the isolated atom obeys the virial theorem, then:

$$\alpha_r(i) = -I_r + \int \psi_i^*(i)\left(-\frac{1}{R_{is}} + V_{av}(ij)\right)\psi_r(i)\,dt_i \qquad (5)$$

where I_r is the valence state ionization potential (VSIP) of atom r. This usual partitioning [*6*] entails an approximation, since in order for the molecular eigenfunction to obey the virial theorem the atomic orbitals of the linear combination must be scaled differently from the isolated atoms. In spite of this error, equation (5) will hold approximately. The integral

$$\int \psi_r^*(i)\left(-\frac{1}{R_{is}} + V_{av}(ij)\right)\psi_r(i)\,dt_i$$

measures the interaction of the core of atom s plus electron j with electron i centered in r (since we are dealing with only the Coulomb integral we can treat electron i as a point charge centered in r, neglecting overlap). If the bond distance is

Table 1

Method	q_1	q_2	q_9
	a) Trans-Butadiene		
HMO	1.0000	1.0000	
Pople[a]	1.0000	1.0000	
Parr and Mulliken[b]	0.9552	1.0448	
Berry LCAO-SCF[c]	0.9216	1.0784	
Berry AIM[c]	1.0638	0.9362	
Moser[d]	0.9388	1.0612	
Takekiyo VB[e]	0.9882	1.0118	
Present Paper	1.0097	0.9903	
	b) Naphthalene		
HMO	1.0000	1.0000	1.0000
Pople[a]	1.0000	1.0000	1.0000
Pritchard and Summer[f]	1.004	1.008	0.976
Moser[g]	0.967	1.003	1.062
Kolboe and Pullman[h]	0.9998	0.9998	1.0008
Present Paper	1.0072	1.0009	0.9839

[a] Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).

[b] Parr, R. G., and R. S. Mulliken: J. chem. Physics **18**, 1338 (1950).

[c] Berry, R. S.: J. chem. Physics **26**, 1660 (1057).

[d] Moser, C. M.: J. chem. Soc., 3455 (1954).

[e] Takeyiko, S.: Bull. chem. Soc. Japan **35**, 355 (1962).

[f] Pritchard, H. O., and F. H. Sumner: Reference [**19**].

[g] Moser, C. M.: J. chem. Physics **52**, 24 (1955).

[h] Kolboe, S., and A. Pullman: Colloq. Internat. Calc. Fonction d'onde Mol., C. N. R. S., Paris, 1958, p. 213.

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* The nuclear repulsion term $1/R_{rs}$ is included as part of the total energy of the π-electronless framework.

equal to the double of the radius of atoms s, this interaction is clearly given by E_s, the valence state electron affinity (VSEA) of atom s. Hence:

$$\alpha_r\,(i) = -\,(I_r + E_s)\ . \tag{6}$$

Equation (6) is valid for a bonding localized orbital between atoms r and s. For the delocalized π-electrons in poly-atomic systems, we write

$$\alpha_r\,(i) = -\,(I_r + N_{\max}\,\overline{E}_s) \tag{7}$$

where $N_{\max}$ is the maximum π-bond order [3, 11] of atom r, and $\overline{E}_s$ is the average of the VSEA of the nearest neighbors of r [7]. To antecipate briefly, we checked equation (7) with a number of alternant hydrocarbons and the expectation of uniform charge distribution in those molecules is closely met. This can be seen from Tab. 1 where the charge distribution for transbutadiene and naphthalene is compared with the distributions calculated by other methods. Although this hardly is a proof of the validity of equation (7), it gives us confidence in the internal self-consistency of the method.

The Bond Integral

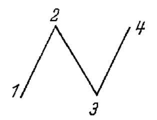
It will be assumed [20] that the bond integral is given by a parabolic relation:

$$\beta_{rs} = a\,S_{rs} + b\,S_{rs}^2\ . \tag{8}$$

The constants a and b are determined in the following way: for $R_{rs} = \infty$, $S_{rs} = 0$ and $\beta_{rs} = 0$. Also, for $R_{rs} = 0$. $S_{rs} = 1$ and $\beta_{rs} = \alpha_{(r+1)}$, where $\alpha_{(r+1)}$ is the Coulomb integral of electron i in an atom of $Z = Z_r + 1$*. The value of β_{rs} for $R = R_e$ can be obtained from the barycenter of the singlet and triplet $\pi \rightarrow \pi^*$ transitions of a standard molecule. In the case of the C-C π-bond the standard molecule was chosen to be ethylene, where $R_e = 1.334$ A [1]. $S_{\mathrm{CC}} = 0.273$ [14], and $\Delta\varepsilon = 6.1$ eV [17]. From the three points ($S = 0$, $S = 0.273$, and $S = 1.000$) we draw the parabola:

$$\beta_{\mathrm{CC}} = -0.951\,S + 0.388\,S^2 \text{ (in a. u.)} \tag{9}$$

The value of -6.08 eV for β_{CC} of the ethylene π-bond in certainly larger than the usual values, but it is close to HOFFMANN's, -5.45 eV [9].



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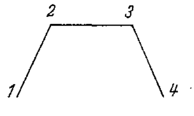

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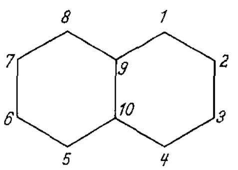

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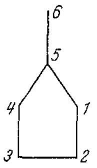

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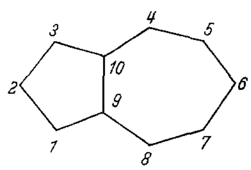

V

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* This is rigorous for H_2^+, since $\lim\limits_{R\to 0}\beta_{H_2^+} = \alpha_{He^+}$. For many-electrons systems we can imagine the formation of a united pseudo-atom of nuclear charge $Z + 1$.

Results and Discussion

Overlap integrals are from the tables of Mulliken, Rieke, Orloff, and Orloff [*14*]. Valence state ionization potential (C $[t_1\, t_2\, t_3\, z] \rightarrow \mathrm{C}^+ [t_1\, t_2\, t_3]$) and electron-affinity (C $[t_1\, t_2\, t_3\, z] \rightarrow \mathrm{C}^- [t_1\, t_2\, t_3\, z^2]$) are from Pilcher and Skinner: $I_C = 11.22$eV and $E_C = 0.62$ eV [*18*]. Tab. 2 shows the calculated M. O.s, orbital energies, bond orders, charge distributions and π dipole moments for a representative number of alternant and non-alternant hydrocarbons.

Butadiene. The high value for the π-bond order between carbons 2 and 3 must be pointed out. The π-electron energies are -56.76 eV for the *trans* form and -56.60 eV for the *cis* form, corresponding to a potential barrier of 3.7 kcal.

Table 2

Molecule	Bond	Bond Order	π-Electron Distribution
Trans-Butadiene (I)	1,2	0.923	$q_1 = q_4 = 1.0097$
	2,3	0.385	
	1,3	0.004	$q_2 = q_3 = 0.9903$
	1,4	−0.385	
Cis-Butadiene (II)	1,2	0.934	$q_1 = q_4 = 1.0064$
	2,3	0.357	
	1,2	0.003	$q_2 = q_3 = 0.9936$
	1,4	−0.3333	
Benzene	1,2	0.6666	$q_1 = q_2 = q_3 = q_4 =$
	1,3	0.0000	$q_5 = q_6 = 1.0000$
	1,4	−0.3333	
Naphthalene (III)	1,2	0.745	$q_1 = 1.0072$
	2,3	0.574	
	1,9	0.541	$q_2 = 1.0009$
	9,10	0.545	$q_9 = 0.9839$
Fulvene (IV)	1,2	0.840	$q_1 = 1.068$
	2,3	0.423	$q_2 = 1.027$
	1,5	0.386	$q_5 = 1.000$
	5,6	0.835	$q_6 = 0.811$
Azulene (V)	1,2	0.643	$q_1 = 1.146$
	1,9	0.613	$q_2 = 0.999$
	9,10	0.345	$q_4 = 0.898$
	4,10	0.613	$q_5 = 1.007$
	4,5	0.650	$q_6 = 0.918$
	5,6	0.643	$q_9 = 0.993$

Molecule Occupied MO. s	Energies of Occupied and Lowest Non-occupied MO. s (a. u.)
Trans-Butadiene (I)	
$\Psi_{\mathrm{I}} = 0.3269\,(\psi_1 + \psi_4) + 0.4929\,(\psi_2 + \psi_3)$	$\varepsilon_{\mathrm{I}} = -0.5582;$
$\Psi_{\mathrm{II}} = 0.5487\,(\psi_1 - \psi_4) + 0.3624\,(\psi_2 - \psi_3)$	$\varepsilon_{\mathrm{II}} = -0.4852;$
	$\varepsilon_{\mathrm{III}} = -0.3331$
Cis Butadiene (II)	
$\Psi_{\mathrm{I}} = 0.3333\,(\psi_1 + \psi_4) + 0.4873\,(\psi_2 + \psi_3)$	$\varepsilon_{\mathrm{I}} = -0.5594;$
$\Psi_{\mathrm{II}} = 0.5445\,(\psi_1 - \psi_4) + 0.3740\,(\psi_2 - \psi_3)$	$\varepsilon_{\mathrm{II}} = -0.4813;$
	$\varepsilon_{\mathrm{III}} = -0.3405$

Table 2 (Continued)

Molecule Occupied M. O. s	Energies of Occupied and Lowest Non-occupied MO. s (a. u.)
Benzene	
$\Psi_{\mathrm{I}} = 0.3255\,(\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6)$	$\varepsilon_{\mathrm{I}} = -0.5879$;
$\Psi_{\mathrm{II}} = 0.0165\,(\psi_1 - \psi_4) + 0.4652\,(\psi_2 - \psi_5) + 0.4487\,(\psi_3 - \psi_6)$	$\varepsilon_{\mathrm{II}} = \varepsilon_{\mathrm{III}} = -0.5036$;
$\Psi_{\mathrm{III}} = 0.5277\,(\psi_1 - \psi_4) + 0.2495\,(\psi_2 - \psi_5) - 0.2781\,(\psi_3 - \psi_6)$	$\varepsilon_{\mathrm{IV}} = \varepsilon_{\mathrm{V}} = -0.3058$
Naphthalene (III)	
$\Psi_{\mathrm{I}} = 0.2317\,(\psi_1 + \psi_4 + \psi_5 + \psi_8) + 0.1902\,(\psi_2 + \psi_3 + \psi_6 + \psi_7)$	$\varepsilon_{\mathrm{I}} = -0.6063$;
$+ 0.3439\,(\psi_9 + \psi_{10})$	$\varepsilon_{\mathrm{II}} = -0.5609$;
$\Psi_{\mathrm{II}} = 0.2280\,(\psi_1 + \psi_4 - \psi_5 - \psi_8) + 0.3497\,(\psi_2 + \psi_3 - \psi_6 - \psi_7)$	$\varepsilon_{\mathrm{III}} = -0.5257$;
$\Psi_{\mathrm{III}} = 0.3567\,(\psi_1 - \psi_4 - \psi_5 + \psi_8) + 0.1586\,(\psi_2 - \psi_3 - \psi_6 + \psi_7)$	$\varepsilon_{\mathrm{IV}} = -0.4999$;
$+ 0.2959\,(\psi_9 - \psi_{10})$	$\varepsilon_{\mathrm{V}} = -0.4720$;
$\Psi_{\mathrm{IV}} = 0.0091\,(\psi_1 + \psi_4 + \psi_5 + \psi_8) + 0.3644\,(\psi_2 + \psi_3 + \psi_6 + \psi_5)$	$\varepsilon_{\mathrm{VI}} = -0.3429$
$+ 0.3981\,(\psi_9 + \psi_{10})$	
$\Psi_{\mathrm{V}} = 0.4004\,(\psi_1 - \psi_4 + \psi_5 - \psi_8) + 0.2601\,(\psi_2 - \psi_3 + \psi_6 - \psi_7)$	
Fulvene (IV)	
$\Psi_{\mathrm{I}} = 0.3373\,(\psi_1 + \psi_4) + 0.3176\,(\psi_2 + \psi_3)$	$\varepsilon_{\mathrm{I}} = -0.5944$;
$+ 0.3955\,\psi_5 + 0.1904\,\psi_6$	$\varepsilon_{\mathrm{II}} = -0.5047$;
$\Psi_{\mathrm{II}} = 0.0341\,(\psi_1 + \psi_4) + 0.4090\,(\psi_2 + \psi_3)$	$\varepsilon_{\mathrm{III}} = -0.4743$;
$- 0.4599\,\psi_5 - 0.5308\,\psi_6$	$\varepsilon_{\mathrm{IV}} = -0.3747$
$\Psi_{\mathrm{III}} = 0.5621\,(\psi_1 - \psi_4) + 0.3678\,(\psi_2 - \psi_3)$	
Azulene (V)	
$\Psi_{\mathrm{I}} = 0.2607\,(\psi_1 + \psi_3) + 0.2348\,\psi_2 + 0.2125\,(\psi_4 + \psi_8)$	$\varepsilon_{\mathrm{I}} = -0.6069$
$+ 0.1478\,(\psi_5 + \psi_7) + 0.1300\,\psi_6 + 0.3556\,(\psi_9 + \psi_{10})$	
$\Psi_2 = -0.2232\,(\psi_1 + \psi_3) - 0.2703\,\psi_2 + 0.1762\,(\psi_4 + \psi_8)$	$\varepsilon_{\mathrm{II}} = -0.5611$
$+ 0.3638\,(\psi_5 + \psi_7) + 0.4311\,\psi_6 - 0.0831\,(\psi_9 + \psi_{10})$	$\varepsilon_{\mathrm{III}} = -0.5327$
$\Psi_3 = -0.1719\,(\psi_1 - \psi_3) + 0.4329\,(\psi_4 - \psi_8) + 0.3222\,(\psi_5 - \psi_7)$	$\varepsilon_{\mathrm{IV}} = -0.4907$
$-0.2506\,(\psi_9 - \psi_{10})$	$\varepsilon_{\mathrm{V}} = -0.4545$
$\Psi_4 = 0.2244\,(\psi_1 + \psi_3) + 0.5136\,\psi_2 - 0.2376\,(\psi_4 + \psi_8)$	$\varepsilon_{\mathrm{VI}} = -0.3715$
$+ 0.1507\,(\psi_5 + \psi_7) + 0.3687\,\psi_6 - 0.3256\,(\psi_9 + \psi_{10})$	
$\Psi_5 = 0.5352\,(\psi_1 - \psi_3) + 0.1169\,(\psi_4 - \psi_8) + 0.3322\,(\psi_5 - \psi_7)$	
$+ 0.2647\,(\psi_9 - \psi_{10})$	

mole^{-1} favorable to the *trans* form. As can perhaps be expected from the use of spectral data to compute β_{CC}, the calculated $\pi \rightarrow \pi^*$ transition for *trans*-butadiene is 4.14 eV, in good agreement with the experimental value for the barycenter of the singlet and triplet transitions, 4.0 eV [*8*].

Benzene. The experimental value for the barycenter of the $\pi \rightarrow \pi^*$ singlet and triplet transitions is 5.50 eV [*5*]. Our results give 5.38 eV but the significance of the agreement should not also be overemphasized. We should note again [*7*] that the sum of the π-bond orders around a given carbon atom in benzene is exactly 1 if we include the bond orders with the non-adjacent atoms.

Naphthalene. We have seen already (Tab. 1) that the charge distribution in naphthalene is uniform. The bond orders are given in Tab. 3, and a number of bond orders calculated by differing methods are included for comparison.

Table 3. *Bond Orders in Naphthalene*

Bond	Method							
	I[a]	II[b]	III[c]	IV[d]	V[e]	VI[f]	VII[g]	VIII[h]
1,2	0.725	0.713	0.798	0.738	0.756	0.87	0.815	0.745
2,3	0.603	0.607	0.514	0.580	0.570	0.40	0.668	0.574
1,9	0.555	0.548	0.487	0.529	0.526	0.41	0.656	0.541
9,10	0.518	0.456	0.624	0.514	0.563	0.73	0.627	0.545

[a] HMO.

[b] HMO with variation in α.

[c] Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).

[d] SCF with variation in α; H. O. Pritchard, and F. H. Sumner: Trans Faraday Soc. **51**, 457 (1955).

[e] Modified SCF, (reference d).

[f] Kolboe, S., and A. Pullman: Colloq. Internat. Calc. fonct. onde molec., C. N. R. S., Paris **1958**, p. 213

[g] ASMO-CI, H. Ito, and Y. I'Haya: Theoret. chim. Acta **2**, 247 (1964).

[h] Present Paper.

Fulvene. The charge distribution of fulvene, shown in Tab. 2, is repeated in Tab. 4, together with values calculated by other methods. Tab. 4 also shows the charge distribution calculated by a refinement in our procedure, namely, an ω-technique treatment starting with our original charge distribution. We also tried an iterative calculation based on a parabolic relation between α_C and q_C [19] but the calculation does not converge. It is seen that our method, without iteration, gives results intermediate between those obtained by the ω-technique and those from advanced MO methods. The iteration gives still better results, but the improvement perhaps does not justify the introduction of a new arbitrary parameter.

Table 4. *Charge Distribution in Fulvene*

	$q_1 = q_4$	$q_2 = q_3$	q_5	q_6	μ (D)
HMO	−0.092	−0.073	−0.047	+0.378	4.7
Modified HMO[a]	−0.060	−0.052	−0.036	+0.260	3.25
ω-Technique[b]	−0.055	−0.029	−0.138	+0.306	3.03
SCF-MO[c]	−0.040	+0.007	−0.053	+0.119	1.0
Present Paper	−0.068	−0.027	0.000	+0.189	2.3
Present Paper[d]	−0.060	−0.025	−0.003	+0.173	2.1
Experimental					1.2

[a] Different βs for differing bond distances.

[b] Streitwieser, Jr., A. Heller, and M. Feldman: J. Phys. Chem. 68 1224 (1964). The reported dipole moments are evidently in error.

[c] Francois, P., and A. Julg: J. Chim. Physique **57**, 490 (1960).

[d] Iterative calculation included.

Azulene. Tab. 5 shows the charge distribution of azulene calculated by our approach and by a number of other methods. Our calculated dipole moment is in better agreement with the experimental value than the one calculated by the conventional ω-technique. Although in this case we did not make any iterative calculation, there is little doubt that the result could be improved by such refinement.

Table 5. *Charge Distribution in Azulene*

	$q_1 = q_4$	q_2	$q_8 = q_9$	$q_4 = q_7$	q_6	$q_9 = q_{10}$	μ (D
Modified HMO[a]	−0.139	−0.047	+0.145	+0.014	+0.130	−0.027	5.2
ω-Technique[b]	−0.118	−0.048	+0.095	+0.025	+0.084	−0.020	3.8
VESCF[c]	−0.061	−0.021	+0.063	−0.009	+0.039	+0.009	2.3
Modified SCF[d]	−0.049	+0.003	+0.092	−0.034	+0.062	−0.042	1.7
Present Paper	−0.145	+0.001	+0.102	−0.007	+0.082	+0.007	3.5
Experimental							1.1

[a] Differing β_S for different bond distances.
[b] STREITWIESER, A., Jr.: Reference [**21**].
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General Conclusions

Our calculations of alternant and non-alternant hydrocarbons* give results which are at least comparable with those obtained with the ω-technique [*21*, *22*], but involving one arbitrary parameter less. It is thus possible that our parametrization introduces some electron-electron interaction within the framework of the simple LCAO methods.

Preliminary calculations of azobenzenes and other heterocyclics indicate that the polarization of the π-electrons by the asymmetric σ framework must be taken into account. These calculations will be the subject of a forthcoming publication.

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* Results for other hydrocarbons can be secured by writing to the author.

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