

An Improved LCAO-MO-SCF π -Electron Method

II. Hydrocarbons and Nitrogen and Oxygen Heterocycles

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Received February 23, 1968

Using the method of a previous paper a modified technique is used to calculate the core parameters for carbon, nitrogen and oxygen atoms. The one-center core parameters H_{pp}^0 , are identified with conventional atomic valence state ionization potentials. The two-center core parameters are given by the equation $H_{pq}^0 = (H_{pp}^0 + H_{qq}^0)/2 (S_{pq} - 0.0855 R_{pq} + 0.24639) - n_p(S_{pq}/4) (\gamma_{pp}^\lambda + \gamma_{pq}^\lambda) - n_q(S_{pq}/4) (\gamma_{qq}^\lambda + \gamma_{pq}^\lambda)$.

It is shown that these parameters, along with the electron repulsion integrals adopted earlier allow one to calculate with reasonable accuracy the singlet spectra and ionization potentials (within Koopmans' approximation) of a large number of unsaturated hydrocarbons as well as the heterocycles pyridine, *p*-benzoquinone (PBQ), pyrrole and furan.

Unter Benutzung einer früheren Methode wird ein modifiziertes Verfahren zur Berechnung der Rumpfp Parameter von C-, N- und O-Atomen vorgeschlagen. Die Einzentren-Rumpfp Parameter H_{pp}^0 werden den üblichen Ionisationspotentialen für die atomaren Valenzzustände gleichgesetzt. Die Zweizentren-Rumpfp Parameter werden nach $H_{pq}^0 = (H_{pp}^0 + H_{qq}^0)/2 (S_{pq} - 0.0855 R_{pq} + 0.24639) - n_p(S_{pq}/4) (\gamma_{pp}^\lambda + \gamma_{pq}^\lambda) - n_q(S_{pq}/4) (\gamma_{qq}^\lambda + \gamma_{pq}^\lambda)$ berechnet.

Auf diese Weise und unter Verwendung der schon früher benützten Coulombintegrale lassen sich die Singulett-Spektren und Ionisationspotentiale einer großen Anzahl ungesättigter Kohlenwasserstoffe sowie der Heterocyclen Pyridin, *p*-Benzochinon, Pyrrol und Furan mit der üblichen Genauigkeit berechnen.

Calcul des paramètres de coeur du carbone, de l'azote et de l'oxygène, en utilisant la méthode d'un article précédent techniquement modifiée. Les paramètres de coeur monocentriques H_{pp}^0 sont identifiés avec les potentiels d'ionisation de l'état atomique de valence conventionnel. Les paramètres de coeur bicentriques sont donnée par l'équation $H_{pq}^0 = (H_{pp}^0 + H_{qq}^0)/2 (S_{pq} - 0,0855 R_{pq} + 0,24639) - n_p(S_{pq}/4) (\gamma_{pp}^\lambda + \gamma_{pq}^\lambda) - n_q(S_{pq}/4) (\gamma_{qq}^\lambda + \gamma_{pq}^\lambda)$. On montre que ces paramètres utilisés avec les intégrales de répulsion précédemment adoptées permettent de calculer avec une précision raisonnable le spectre singulet et les potentiels d'ionisation (dans l'approximation de Koopmans) pour un grand nombre d'hydrocarbures non saturés et des hétérocycles comme la pyridine, la *p*-benzoquinone (PBQ), le pyrrole et le furane.

Introduction

Experience with semiempirical π -theory has demonstrated that the task of deriving suitable parameters is not difficult as long as one is content to deal with a limited series of similar molecules. However, to derive a single consistent set of parameters suitable to the prediction of several properties of a large number of different types of molecules is a difficult problem. This problem has in fact never been adequately solved within π -theory.

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This investigation, as well as an earlier one [1], represents the beginning of an attempt to systematically investigate the parameters in semiempirical theories. LCAO-MO-SCF π -theory has been chosen as the starting point of this investigation. There is the possibility that for certain properties of some classes of compounds a general core description can be derived which makes a further elucidation of the electronic structure by more complicated σ/π -methods unnecessary.

As indicated in Ref. [1] it was felt necessary to introduce a modification into LCAO-MO-SCF π -theory in order to allow a meaningful examination of the basic parameters. This modification included the use of an orthogonalized basis set of atomic functions and a core treatment that allows one to deal with atomic core parameters instead of molecular core parameters. In the original application of this method to some hydrocarbons a calibration procedure was adopted, using ethylene and benzene as reference molecules the essential feature of which was an empirical determination of the orbital exponent ζ in the carbon $2p_\pi$ Slater Type Orbitals (S.T.O.). To extend the calculations to molecules containing heteroatoms, as we intend to do here, it would be necessary first to determine the orbital exponents in the appropriate heteroatom S.T.O.'s. Unfortunately few heteroatom analogues of ethylene and benzene are available for this purpose and for these reliable experimental data are lacking.

In this study the same method is used as was used earlier, but the calibration procedure is modified. It allows one to identify the one-center atomic core parameters with valence state ionization potentials (VSIP) and also to calculate the two-center parameters as a function of the VSIP of the bonded atoms. The simple equation which allows this to be accomplished is tested on a large number of hydrocarbons as well as the heterocycles pyridine, *p*-benzoquinone (PBQ), pyrrole and furan. The primary objective is the calculation of singlet electronic spectra, but molecular ionization potentials are also considered.

Method and Calibration

The method set forth in Paper I is employed with three modifications. First, a more extended configuration interaction (C.I.) treatment is used. Provision is made for including up to 25 configurations resulting from all the possible one-electron excitations involving the ground state 5 highest occupied and 5 lowest unoccupied molecular orbitals. Second, non-nearest-neighbor core integrals H_{pq}^λ are not artificially zeroed before the SCF calculation as was done in the earlier work. The remaining change involves calibrating the off diagonal core parameters H_{pq}^0 . For convenience the entire core treatment is summarized below with these changes included.

1. The core integrals used in the SCF calculations are

$$H_{pq}^\lambda = \langle \lambda_p | H_{\text{core}}(i) | \lambda_q \rangle$$

where the λ_i are Löwdin orbitals [3],

$$\lambda = \chi S^{-\frac{1}{2}}. \quad (1)$$

In (1) χ is an array of S.T.O.'s, $S^{-\frac{1}{2}}$ is related to the overlap matrix over S.T.O.'s and λ is an array of Löwdin orbitals.

The above core integrals are clearly dependent on all the atomic centers in a molecule, both in the λ_i and in $H_{\text{core}}(i)$. A set of such integrals is thus unique to a particular molecule and cannot in principle be carried over to a different molecule.

2. Given Eq. (1), the relationship between the core integrals over Löwdin orbitals and over S.T.O.'s is

$$H^\lambda = S^{-\frac{1}{2}} H S^{-\frac{1}{2}}, \quad (2)$$

where H^λ and H are the corresponding arrays of core integrals and $S^{-\frac{1}{2}}$ is the same as in Eq. (1). The integrals in H are $H_{pq} = \langle \chi_p | H_{\text{core}} | \chi_q \rangle$.

3. The geometry dependence of $H_{\text{core}}(i)$ is removed by utilizing the Goepfert-Mayer and Sklar expansion [4]. This leads to the following, neglecting all neutral atom penetration integrals,

$$H_{pp} = \langle \chi_p | T(i) + U_p^{n_p}(i) | \chi_p \rangle - \sum_{r \neq p} n_r \gamma_{rp}^\lambda, \quad (3)$$

$$H_{pq} = \langle \chi_p | T(i) + U_p^{n_p}(i) + U_q^{n_q}(i) | \chi_q \rangle - \sum_{r \neq p, q} n_r (rr|pq)^\lambda. \quad (4)$$

The factors n_i specify the appropriate core charges.

Eq. (4) is now simplified by utilizing the Mulliken approximation to give,

$$H_{pq} = H_{pq}^0 - (S_{pq}/2) \sum n_r [\gamma_{rp}^\lambda + \gamma_{rq}^\lambda], \quad (5)$$

where H_{pq}^0 , the desired two-center core parameter, is given by the first integral in Eq. (4). The one-center core parameter H_{pp}^0 is taken as the first term in Eq. (3).

The calibration of the method follows the calibration of Paper I except that only benzene is used as the reference molecule, and slightly different empirical data is adopted for benzene. As in Paper I the two-center two-electron repulsion integrals, γ_{pq}^λ are evaluated using the formula's of Nishimoto and Mataga [5] and the carbon valence state data of Hinze and Jaffé [6] is adopted.

The calibration procedure with benzene can be outlined as follows:

1. The orbital exponent, ζ_C , is taken as 1.625.
2. Eqs. (15) and (18) of Paper I are used to calculate the benzene core integrals H_{11}^λ and H_{12}^λ for each of the γ_{pp}^λ being considered. This assumes therefore that non-nearest neighbor H_{pq}^λ integrals are zero.
3. The core integrals H_{pp} and H_{pq} are then found from the matrix equation, $H = S^{\frac{1}{2}} H^\lambda S^{\frac{1}{2}}$.
4. The core parameters H_{pp}^0 and H_{pq}^0 are determined using equations (3) and (5).
5. The "best" set of parameters is chosen by determining the γ_{pp}^λ that closely produces the parameter $H_{11}^0 = -11.16$ eV (the negative of the VSIP of carbon).

The calibration data are shown in Tab. 1 for the case $\gamma_{11}^\lambda = 10.80$ eV. It is evident from Tab. 1 that the use of $\gamma_{11}^\lambda = 10.80$ eV does not give $H_{11}^0 = -11.16$ eV exactly. The former integral may therefore be refined slightly, if desired.

Table 1. Calibration of benzene core parameters

Input	${}^1L_b = 4.72 \text{ eV}^a$; $I.P. = 9.25 \text{ eV}^b$; $\gamma_{11}^\lambda = 10.80 \text{ eV}$	
Results (in eV)		
$H_{11}^\lambda = -31.72023$	$H_{11}^0 = -11.14128^c$	
$H_{12}^\lambda = -2.29815$	$H_{12}^0 = -6.13067$	
$H_{11} = -32.84891$	$H_{13}^0 = -1.07433$	
$H_{12} = -10.16628$	$H_{14}^0 = -0.36345$	
$H_{13} = -1.68724$	${}^1L_a = 5.94$ (exptl. = 5.90 ^a)	
$H_{14} = -0.64121$	${}^1B_b = 6.76$ (exptl. = 6.74 ^a)	

^a Ref. [31]. The 1L_a and 1B_b bands are for benzene in heptane solution. The 1L_b band lies at 4.72 eV in the vapour phase and 4.69 eV in heptane solution. The former value was chosen in the calibration because it is more certain experimentally.

^b Ref. [28].

^c In subsequent calculations this parameter was assigned the value -11.16 eV . Table 6 shows the minor effect of this change on the $I.P.$ and 1L_b transition of benzene.

Numerous attempts were made to fit the parameters H_{12}^0 , H_{13}^0 , and H_{14}^0 to a simple equation. For the hydrocarbons ($n_t = 1$) this was achieved by the following¹,

$$H_{pq}^0 = -11.1712 (S_{pq} - 0.0852 R_{pq} + 0.24561) - (S_{pq}/2) [\gamma_{pp}^\lambda + \gamma_{pq}^\lambda]. \quad (6)$$

In Eq. (6), S_{pq} is the overlap integral for the separation R_{pq} . It should be noted that atoms p and q need not be nearest neighbors.

If the leading term is now identified with $H_{pp}^0 (= H_{qq}^0)$, then for the carbon-carbon bond,

$$H_{pq}^0 = (H_{pp}^0/2) (S_{pq} - 0.0855 R_{pq} + 0.24639) - (S_{pq}/2) [\gamma_{pp}^\lambda + \gamma_{pq}^\lambda]. \quad (7)$$

In obtaining this equation, Eq. (6) was refitted to the benzene data with $H_{pp}^0 = -11.16 \text{ eV}$ instead of -11.1712 eV . In applying Eq. (7) the equation is used as written for $R_{pq} \leq 2.882 \text{ \AA}$. For $R_{pq} > 2.882 \text{ \AA}$ the last two terms in the bracket are neglected to insure that $H_{pq}^0 \leq 0$. For the cases where centers p and q differ Eq. (7) suggests the following relation

$$H_{pq}^0 = [(H_{pp}^0 + H_{qq}^0)/2] (S_{pq} - 0.0855 R_{pq} + 0.23469) - n_p (S_{pq}/4) (\gamma_{pp}^\lambda + \gamma_{pq}^\lambda) - n_q (S_{pq}/4) (\gamma_{qq}^\lambda + \gamma_{pq}^\lambda). \quad (8)$$

One of the primary purposes of this investigation is to test the utility of Eq. (8) for heteroatomic bonds. In these cases the heteroatom one-center core parameter H_{pp}^0 would be the VSIP of the heteroatom and the overlap integral would be an integral over S.T.O.'s where the orbital exponent for the heteroatom orbital is determined from Slater's rules. The heteroatom valence state data and orbital

¹ The last term in Eq. (6) is suggested if Eq. (4) is written in an alternative fashion

$$H_{pq} = \langle \chi_p | T(i) + U_q^{n_q}(i) | \chi_q \rangle - (pp|pq)^\lambda - \sum_{r \neq p,q} (rr|pq)^\lambda$$

or,

$$H_{pq} = \langle \chi_p | T(i) + U_q^{n_q}(i) | \chi_q \rangle - (S_{pq}/2) [\gamma_{pp}^\lambda + \gamma_{pq}^\lambda] - (S_{pq}/2) \sum_{r \neq p,q} [\gamma_{pr}^\lambda + \gamma_{qr}^\lambda].$$

Table 2. *Heteroatomic data*

Atom ^a	VSIP ^b	VSEA ^c	$\gamma_{ii}^{\lambda d}$	ζ^e
\dot{N}	14.12	1.78	12.34	1.95
\ddot{N}	28.775	12.305	16.47	2.125
\dot{O}	17.70	2.47	15.24	2.275
\ddot{O}	34.07	15.22	18.85	2.45

^a The number of dots refer to the number of π -electrons contributed by the hetero core atom.

^b Valence state ionization potential in eV (Ref. [6]).

^c Valence state electron affinity in eV (Ref. [6]).

^d $\gamma_{ii}^{\lambda} = \text{VSIP} - \text{VSEA}$ (eV).

^e Orbital exponent in S.T.O.'s.

exponents used are shown in Tab. 2 along with the values of their one center electron repulsion integrals.

Oscillator strengths f , are calculated in this study using the equations of Pariser [7].

Input Geometries

The geometries chosen for the all-trans polyenes are based on an extension of the Shoemaker and Pauling [8] geometry for butadiene. For the α,ω -diphenyl polyenes $\phi-(\text{CH}=\text{CH})_n-\phi$, the cases $n=1$ to $n=5$ are included. These are assigned a planar, all-trans geometry. The rings are assumed to be regular hexagons with carbon-carbon bond distances of 1.397 Å. For the chains, alternating bond lengths of 1.45 Å and 1.33 Å are used [9].

The alternant hydrocarbons naphthalene, anthracene, naphthacene, pentacene, phenanthrene, chrysene and pyrene are assumed planar with regular hexagon rings and carbon-carbon bond lengths of 1.397 Å.

The geometry adopted for azulene is based upon an X-ray study of the azulene-s-trinitrobenzene complex [10]. This data is used because X-ray work on azulene itself gives a poor structure due to a highly disordered crystal structure [11].

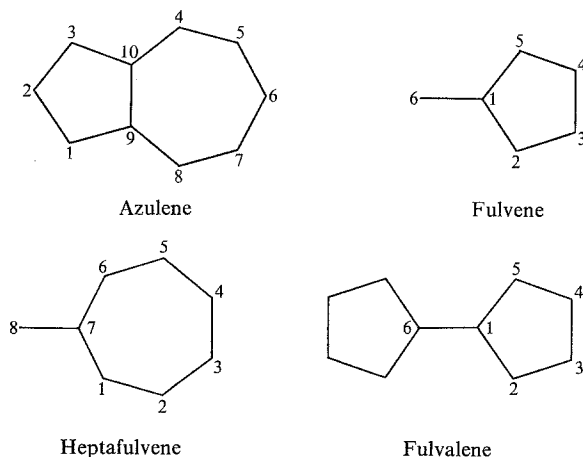


Fig. 1. Numbering systems for the non-alternant hydrocarbons

The remaining nonalternant hydrocarbons fulvene, heptafulvene and fulvalene are assigned carbon-carbon bond distances as calculated from the theoretical analysis of Nakajima and Katagiri [12]. For these molecules the bond angles used to estimate the non-nearest neighbor distances are: fulvene and fulvalene, 108° ; heptafulvene $1-2-3=2-3-4 = 130^\circ$, which implies $7-1-2 = 119.5^\circ$ and $6-7-1 = 141^\circ$ (see Fig. 1).

The geometries adopted for pyridine, pyrrole and furan are based upon the studies of Bak and his coworkers [13, 14, 15] of their microwave spectra. For PBQ the data of Swingle [16] is used.

Hydrocarbon Results

Singlet Transitions

Calculated and experimental results [17] for the all trans polyenes $H-(CH=CH)_n-H$ are presented in Tab. 3. The calculated values are in good agreement with experiment although there is very limited data available for the 1C , 1D and 1F bands. The increase in oscillator strengths of the 1B bands as n increases is in accord with experiment.

For the diphenylpolyenes, $n = 1,5$ the four lowest allowed singlet transitions (${}^1B_u \leftarrow {}^1A_g$) for each molecule are shown in Tab. 4. These are designated as the A , ${}^1G^-$, B and C bands, although the ${}^1G^-$ transition is presumed to be a part of the A band in all cases [18]. The spectrum of stilbene ($n = 1$) has been studied in detail by Beveridge and Jaffé [18]. The correspondance between their results and

Table 3. Results for the polyenes, $H-(CH=CH)_n-H$, singlet transitions (eV)

n		1B -band		1C -band		1D -band		1F -band	
		ΔE	f	ΔE	f	ΔE	f	ΔE	f
2	calc.	5.48	1.054	6.47	0.0	7.79	0.0	9.32	0.286
	expt.	5.71 ^a							
3	calc.	4.49	1.516	6.50	0.003	7.78	0.026	8.31	0.328
	expt.	4.63 ^a							
4	calc.	3.90	1.945	5.96	0.004	6.97	0.112	7.33	0.213
	expt.	4.08 ^a		5.84					
5	calc.	3.50	2.344	5.48	0.004	6.31	0.198	6.64	0.156
	expt.	3.71 ^a							
6	calc.	3.24	2.747	5.12	0.004	5.80	0.277	6.12	0.127
	expt.	3.41 ^a							
7	calc.	3.04	3.115	4.84	0.004	5.37	0.352	5.72	0.112
	expt.	3.18 ^a							
8	calc.	2.88	3.474	4.61	0.004	5.02	0.408	5.40	0.107
	expt.	3.02 ^a							
9	calc.	2.76	3.813	4.43	0.004	4.73	0.461	5.16	0.108
	expt.								
10	calc.	2.68	4.154	4.29	0.003	4.48	0.507	4.95	0.110
	expt.	2.77 ^a		4.17 ^b		4.60 ^b			

^a Ref. [17]. — ^b Ref. [23].

Table 4. Results for diphenylpolyenes $\phi-(CH=CH)_n-\phi$, lowest singlet transitions (eV)

n		A-band		¹ G ⁻ -band		B-band		C-band	
		ΔE	f	ΔE	f	ΔE	f	ΔE	f
1	calc.	4.06	1.402	4.36	0.006	5.70	0.646	6.13	0.656
	expt. ^a	4.22				5.56		6.17	
2	calc.	3.66	1.889	4.33	0.003	5.53	0.576	5.95	0.254
	expt. ^b	3.58				5.37			
3	calc.	3.37	2.342	4.35	0.002	5.45	0.587	5.65	0.056
	expt. ^b	3.36				5.19			
4	calc.	3.16	2.762	4.41	0.002	5.41	0.482	5.33	0.151
	expt. ^b	3.14				5.39			
5	calc.	3.00	3.155	4.49	0.002	5.39	0.528	5.05	0.127
	expt. ^b	2.92				5.14			

^a Suzuki, H.: Bull. chim. Soc. (Japan) 33, 379 (1960).

^b Zechmeister, L.: Cis-Trans Isomeric Compounds, Vitamin A, and Acryl-polyenes. New York, N.Y.: Academic Press, Inc. 1962.

the present results is shown in Tab. 5 which compares most of the singlet transitions calculated in both cases. As indicated in Tab. 4 the agreement between the calculated and experimental [17] values is good for the higher diphenylpolyenes.

The calculated and experimental singlet transitions for the linear acenes benzene, naphthalene, anthracene, naphthacene and pentacene are shown in Tab. 6. The corresponding values for phenanthrene, chrysene and pyrene are given in Tab. 7. In both tables the transitions are designated using the notation of Platt [19] and the experimental data is taken from Klevens and Platt [20] with the exception of that for pyrene [17].

Agreement between the calculated and experimental values for the linear acenes is good, the worst cases being for pentacene and the ¹C_b bands of anthracene and naphthacene. It is probable that for these cases the use of 25 excited configurations in the C.I. treatment is becoming inadequate. The singlets predicted for phenanthrene, chrysene and pyrene are acceptable on the whole but get worse for the higher singlets of the larger molecules indicating again a limitation in the C.I. treatment.

Table 5. Results of calculations on trans-stilbene (singlets), eV

State	Symmetry	Ref. [18]		Present work		Expt. ^a
		ΔE	f	ΔE	f	
¹ B	B _u	4.194	0.571	4.061	1.402	4.22
¹ G ⁻	B _u	4.674		4.351	0.006	
¹ G ⁻	A _g	4.679		4.361	0.0	
¹ (C, H) ⁺	A _g	5.114		5.529	0.0	
¹ H ⁺	B _u	5.662	0.558	5.695	0.646	5.56
¹ G ⁺	A _g	6.336		5.633	0.0	
¹ C ⁻	A _g	6.426		5.637	0.0	
¹ G ⁺	B _u	6.459	0.831	6.129	0.656	6.17

^a See Ref. [18], Tab. 3.

Table 6. Results for the linear polyacenes, lowest singlet transitions (eV)

Molecule		1L_b		1L_a		1B_b		1C_b	
		ΔE	f	ΔE	f	ΔE	f	ΔE	f
Benzene	calc. ^a	4.71	0.0	5.94	0.0	6.76	1.156		
	expt. ^b	4.72	0.002	5.90	0.10	6.76	0.69		
Naphthalene	calc.	4.01	0.016	4.33	0.235	5.72	2.113	6.21	0.562
	expt. ^c	3.97	0.002	4.29	0.18	5.64	1.70	6.53	0.20
Anthracene	calc.	3.64	0.071	3.34	0.288	5.09	2.954	6.10	0.294
	expt. ^c			3.28	0.10	4.88	2.28	5.61	0.28
Naphthacene	calc.	3.42	0.186	2.74	0.347	4.65	3.548	6.36	1.246
	expt. ^c			2.62	0.08	4.56	1.85	5.88	0.45
Pentacene	calc.	3.27	0.385	2.33	0.366	4.38	3.949		
	expt. ^c	2.97		2.12	0.08	4.00	2.2		

^a The calculated *I.P.* and 1L_b transition are not exactly equal to calibration values because the parameters used are not identical with the calibration values (e.g. compare Eqs. 6 and 7). See Footnote c, Tab. 1.

^b See Tab. 1. — ^c Ref. [20].

Table 7. Results for the non-linear polyacenes, lowest singlet transitions (eV)

Molecule		1L_b		1L_a		1B_b		1C_b	
		ΔE	f	ΔE	f	ΔE	f	ΔE	f
Phenanthrene	calc.	3.74	0.006	4.22	0.345	4.94	1.692	5.75	0.347
	expt. ^a	3.76	0.003	4.23	0.18	5.09	1.09	5.84	0.60
Chrysenes	calc.	3.64	0.021	3.83	0.545	4.81	2.264	5.81	0.688
	expt. ^a	3.41	0.005	3.74	0.36	4.61	1.29	5.64	0.69
Pyrene	calc.	3.51	0.011	3.60	0.820	4.83	0.965	5.56	1.538
	expt. ^b	3.34		3.70		4.55		5.15	

^a Ref. [20]. — ^b Ref. [17].

Table 8. Results for the non-alternant hydrocarbons, singlet transitions (eV)

Molecule		${}^1\Delta E_1$		${}^1\Delta E_2$		${}^1\Delta E_3$		${}^1\Delta E_4$		${}^1\Delta E_5$	
		ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE	f
Azulene	calc.	2.07	0.019	3.43	0.015	4.86	2.055	5.60	0.200	6.36	0.686
	expt. ^a	1.96	0.009	3.66	0.08	4.60	1.10	5.24	0.38	6.42	0.65
Fulvene	calc.	3.17	0.034	4.90	0.524	6.38	0.432				
	expt. ^b	3.32	0.012	5.12	0.320						
Heptafulvene	calc.	2.39	0.024	4.29	0.409	5.80	1.073				
	expt. ^c	2.91	0.02	4.43	0.3	5.71					
Fulvalene	calc.	2.64	0.023	3.87	1.103	6.25	0.553				
	expt. ^c	2.94		3.95	0.4						

^a Spectroscopic values for ${}^1\Delta E_3$, ${}^1\Delta E_4$, and ${}^1\Delta E_5$ are from Kleven, H. B.: J. chem. Physics 18, 1063 (1950), as are the oscillator strengths of ${}^1\Delta E_1$ and ${}^1\Delta E_2$. The energies for the two lowest transitions: Hunt, G. R., and I. G. Ross: Molecular Spectroscopy 9, 50 (1962).

^b Thiec, J., and J. Wiemann: Bull. chim. Soc. [France] 1956, 177.

^c Ref. [21].

Tab. 8 presents the results for the non-alternant hydrocarbons azulene, fulvene, heptafulvene and fulvalene. The only large errors noted are for the lowest singlets of heptafulvene and fulvalene and these may not be as serious as they seem since the experimental peaks [21] are very broad making a comparison of theory and experiment very difficult. The higher energy peaks are better defined and the agreement between theory and experiment is improved.

There are several variants of LCAO-MO-SCF π -theory which have now been applied successfully to the calculation of the singlet spectra of a wide range of unsaturated hydrocarbons. Most notable are the recent studies of Nishimoto and Forster [22] and Bloor, Gilson and Brearley [23], both groups using β -variation modifications. A successful treatment of the spectra of unsaturated hydrocarbons is therefore not a sufficient test of the utility of the present method and its parameters. However, it is certainly a necessary test of the method.

Ionization Potentials

The *I.P.* calculated for all of the hydrocarbons considered in the previous section are displayed in Tab. 9 along with experimental values. The calculated values are, as explained earlier, uncorrected energies of the respective highest occupied molecular orbitals, as demanded by Koopmans' approximation [2].

For the polyenes and diphenylpolyenes agreement between the calculated and experimental values is quite good.

For all of the alternant hydrocarbons of Tab. 9 except chrysene, the calculated values are within the estimated probable errors quoted by the experimentalists [25, 26] namely ± 0.3 eV for each molecule except naphthalene where the figure ± 0.15 eV is quoted [27]. For benzene and naphthalene experimental values determined by Watanabe [28] from photoionization measurements are also shown, the benzene value being that used in the calibration procedure discussed earlier.

Table 9. Ionization potentials (eV) of the hydrocarbons

Molecule ^a	calc.	expt.	Molecule	calc.	expt.
H-(CH=CH) _n -H			DPP, <i>n</i> = 4	7.41	7.5 ^c
<i>n</i> = 2	8.99	9.07 ^b	DPP, <i>n</i> = 5	7.32	7.4 ^c
<i>n</i> = 3	8.37	8.26 ^b	benzene	9.26	9.25 ^d
<i>n</i> = 4	7.98	7.8 ^b	naphthalene	8.14	8.12 ^d , 8.26 ^e
<i>n</i> = 5	7.73		anthracene	7.45	7.55 ^f
<i>n</i> = 6	7.55		naphthacene	7.01	6.95 ^g
<i>n</i> = 7	7.41		pentacene	6.71	
<i>n</i> = 8	7.31		phenanthrene	8.00	8.03 ^f
<i>n</i> = 9	7.23		chrysene	7.69	8.01 ^g
<i>n</i> = 10	7.17		pyrene	7.44	7.72 ^g
DPP, <i>n</i> = 1	7.95	7.9–8.0 ^c	azulene	7.51	7.43 ^h , 7.72 ^e
DPP, <i>n</i> = 2	7.71	7.75 ^c	fulvene	8.52	
DPP, <i>n</i> = 3	7.54	7.6 ^c	heptafulvene	7.45	
			fulvalene	8.54	

^a DPP = diphenylpolyene.

^b Price, W. C., and A. D. Walsh: Proc. Roy. Soc. (London) A 185, 182 (1946).

^c Ref. [24]. — ^d Ref. [28]. — ^e Ref. [27]. — ^f Ref. [25]. — ^g Ref. [26]. — ^h Ref. [29].

For azulene, the only non-alternant hydrocarbon for which experimental data are available, the calculated value is closely bracketed by a higher electron impact value [27] (est. probable error ± 0.15 eV) and a lower value obtained from the ultraviolet spectrum [29].

On the basis of the fact that photoionization measurements almost invariably give lower *I.P.* than electron impact measurements [30], it is not surprising that our calculated values, being based upon a benzene photoionization value, are in almost every case lower than the electron impact results.

The ability of the present method to calculate *I.P.* within Koopmans' approximation is significant and encouraging, although these quantities can be obtained within the β -variation methods by applying suitable correction factors to the energies of the highest occupied molecular orbitals [22].

A much more severe and definitive test of a method and its parameters lies in its ability to calculate the spectra and *I.P.* of unsaturated systems containing heteroatoms while at the same time using a set of parameters systematically related to those used for the hydrocarbons. The success of the present method in this regard will now be considered.

Heterocycle Results

Singlet Transitions

The calculated and experimental singlet transitions for pyridine, PBQ, pyrrole and furan are presented in Tab. 10.

The pyridine experimental data is that derived by Petruska [31] from the spectrum of pyridine in isooctane. This author expresses the pyridine transitions as frequency shifts from the benzene reference spectrum. Since Petruska's benzene data has been chosen for our calibration (however, see footnote a to Tab. 1), the choice of his pyridine values seems logical. The 1L_b and 1L_a transitions calculated for pyridine are both lower in energy than experiment (0.12 eV and 0.14 eV, respectively). If the calculated 1B_a and 1B_b bands are averaged, the resulting value deviated from experiment by 0.15 eV. The calculated transitions are, therefore, slightly low in energy, but the energy differences between the excited states are faithfully reproduced.

Two $\pi \rightarrow \pi^*$ transitions have been identified for PBQ. The lowest energy transition involves an excited state of $^1B_{1g}$ symmetry and the higher one an excited state of $^1B_{3u}$ symmetry [32]. In Tab. 10 the experimental data for PBQ are taken from Brand and Goodwin [33] for PBQ in cyclohexane. The calculated values for both transitions are too low by about the same amount (~ 0.3 eV) but as in the pyridine case the energy difference between the excited states is correct.

The singlet transitions calculated for pyrrole and furan are in excellent accord with the experimental assignment made by Pickett, *et al.* [34] for pyrrole and Watanabe and Nakayama [35] and Price and Walsh [36] for furan.

It appears that the present method is capable of calculating the singlet spectra of the four key heteroatomic molecules chosen for this test with a reasonable accuracy. This has furthermore been done without adding any new empirical parameters except conventional valence state data (Tab. 2) and S.T.O.'s with orbital exponents determined from Slater's rules.

Table 10. Results for heteroatomic molecules – singlet transitions (eV)

Molecule	A ^a		B		Exp.	
	ΔE	f	ΔE	f	ΔE	f
Pyridine	4.67	0.067	4.994 ^b	0.058 ^b	4.79 ^e	0.04 ^e
	5.96	0.030	6.30 ^b	0.038 ^b	6.10 ^e	0.10 ^e
	6.86	0.944	7.170 ^b	1.125 ^b	7.04 ^e	1.30 ^e
	6.91	1.105	7.241 ^b	1.138 ^b		
PBQ	4.12	0.0	3.787 ^b	0.0 ^b	4.30 ^f	
	4.77	0.893	4.839 ^b	1.420 ^b	4.96 ^f	
	7.28	0.199	6.444 ^b	0.0 ^b		
	7.43	1.276				
Pyrrole	5.84	0.0	5.985 ^c	0.135 ^c	5.88 ^g	
	6.66	0.151	6.735 ^c	0.255 ^c	6.77 ^g	
	7.21	0.726	7.326 ^c	0.347 ^c	7.21 ^g	
	7.56	0.796	8.201 ^c	0.979 ^c		
Furan	5.74	0.0	5.8 ^d	0.38 ^d	5.88 ^h	
	6.39	0.347	7.2 ^d	0.48 ^d	6.47 ^h	
	7.29	0.842	7.5 ^d	0.39 ^d	7.38 ^h	
	7.58	0.419	7.9 ^d	0.47 ^d	7.55 ^h	

^a Present results. — ^b Ref. [37], NM integrals. — ^c Ref. [38]. — ^d Ref. [40]. — ^e Ref. [31]. — ^f Ref. [33]. — ^g Ref. [34]. — ^h Refs. [35] and [36].

Nishimoto and Forster [37] have applied their β -variation method to the spectra of pyridine and PBQ (Tab. 10). The results are at least as adequate as the present results for pyridine although they adopt different experimental values. Their results for PBQ give a much lower value than the present method for the lowest singlet transition. No calculations are available for furan and pyrrole by the β -variation method. Tab. 10 shows the singlet results for pyrrole as calculated by Dahl and Hansen [38]. This is a variable electronegativity calculation with the inclusion of neutral atom penetration integrals. The present results are in better agreement with experiment. Also shown in Tab. 10 are the furan results of Pujol and Julg using an Improved L.C.A.O. Theory [40]. This is one of the few available π calculations for this molecule.

Ionization Potentials

In Tab. 11 three sets of *I.P.* are presented for the heterocycles. Col. 1 shows the results from the present calculations. Col. 2 shows the energies of the highest occupied molecular orbitals found from other π -electron calculations. For pyridine and PBQ these are calculated using the β -variation method. For pyrrole and furan the values are taken from the work of Dahl and Hansen [39] and Pujol and Julg [40].

The *I.P.* calculated by the present method agree very well with experiment [28, 39] for the two nitrogen-containing molecules. The situation is less clear for the oxygen containing compounds. There is no experimental value available for PBQ, but for furan the calculated and experimental [39, 40] values disagree by 0.5 eV, an error which dictates the necessity of further theoretical study of this

molecule. A comparison of the results in Columns 1 and 2 of Tab. 11 indicates that the present results are much more consistent with Koopman's approximation than the others. The differences noted between these two columns are particularly large for pyrrole and furan and are much larger than the 0.5 eV error noted above for furan.

Table 11. *Heterocycle results – ionization potentials (eV)*

Molecule	A^a	B	Expt.
Pyridine	9.19	10.399 (9.29) ^b	9.23 ^c
PBQ	10.00	10.994 (9.94) ^b	
Pyrrole	8.29	14.49 ^c	8.22 ^f
Furan	8.31	12.64 ^d	8.77 ^f

^a Present results.

^b Ref. [37]. The first value is the energy of the highest occupied molecular orbital calculated for the β -variation method using our computer program. The second value is that shown in Ref. [37] after correction relative to benzene.

^c Ref. [38]. — ^d Ref. [40]. — ^e Ref. [28]. — ^f Ref. [39].

Discussion

In the present method we have assumed in the benzene calibration that $H_{pq}^\lambda = 0$ where p and q are non-nearest neighbors. The question that needs to be examined now is: Does the use of the present core treatment, based on the benzene calibration, give rise to non-nearest neighbor core integrals H_{pq}^λ of significant magnitude with molecules other than benzene, or on the other hand do these integrals vanish? In particular it may happen that some of these integrals actually become positive in sign, which seems to make no sense physically.²

In order to answer this question the non-nearest neighbor integrals for several typical hydrocarbon molecules will be examined. In Tab. 12 these integrals are shown which, for the particular molecule in question, have the largest absolute magnitudes. The non-nearest neighbor H_{pq}^λ not listed in this table have much smaller magnitudes. Also listed in Tab. 12 for the purpose of comparison are the H_{pq}^λ for bonded atoms. It is clear from these data that for all of the hydrocarbons the non-nearest neighbor H_{pq}^λ are all small in magnitude (i.e. usually <0.1 eV and only occasionally larger than this).

In order to be certain of the influence of these small quantities calculations were performed for the molecules of Tab. 12 wherein the non-nearest neighbor H_{pq}^λ were artificially zeroed before the SCF calculation. The changes that resulted in the calculated *I.P.* and singlet transitions for these molecules are shown in Tab. 13. The changes are seen to be relatively small even in the case of azulene for which the largest positive non-nearest neighbor H_{pq}^λ existed originally. To a good approximation, therefore, the restriction placed on the hydrocarbon core parameters by the benzene calibration holds throughout the calculations. This places our calculation in this sense on the same basis as more conventional LCAO-MO-SCF calculations which neglect non-nearest-neighbor core integrals.

² In Paper I there were several sign errors in Table X. In particular in Column *A* the following elements should have positive signs: $H_{14}^\lambda, H_{16}^\lambda, H_{17}^\lambda, H_{19}^\lambda, H_{25}^\lambda, H_{27}^\lambda, H_{28}^\lambda$, and $H_{2,10}^\lambda$. Similarly in Column *B* the following elements should have positive signs: $H_{15}^\lambda, H_{16}^\lambda, H_{17}^\lambda, H_{1,10}^\lambda, H_{26}^\lambda$, and H_{28}^λ .

Table 12. Core integrals, H_{pq}^λ (eV)

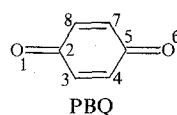
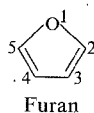
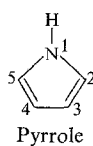
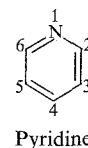
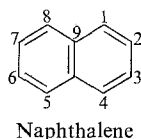
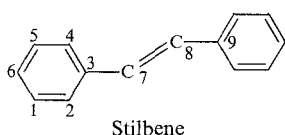
Molecule ^a	Nearest neighbor ^{b,d}	Non-nearest neighbor ^{c,d}
<i>t</i> -Butadiene	$H_{12}^\lambda = -2.386$ $H_{23}^\lambda = -2.164$	$H_{13}^\lambda = 0.045$, $H_{14}^\lambda = 0.060$
Hexatriene	$H_{12}^\lambda = -2.387$ $H_{23}^\lambda = -2.165$	$H_{13}^\lambda = 0.042$, $H_{14}^\lambda = 0.061$, $H_{24}^\lambda = 0.036$ $H_{25}^\lambda = 0.054$
Stilbene	$H_{12}^\lambda = -2.292$ $H_{78}^\lambda = -2.496$	$H_{17}^\lambda = 0.071$, $H_{24}^\lambda = 0.055$, $H_{28}^\lambda = 0.063$ $H_{38}^\lambda = 0.075$, $H_{39}^\lambda = 0.037$, $H_{57}^\lambda = 0.067$
Naphthalene	$H_{12}^\lambda = -2.292$ $H_{9,10}^\lambda = -2.359$	$H_{15}^\lambda = 0.073$, $H_{17}^\lambda = 0.080$, $H_{18}^\lambda = 0.021$ $H_{29}^\lambda = -0.030$
Azulene	$H_{12}^\lambda = -2.248$ $H_{9,10}^\lambda = -2.136$	$H_{13}^\lambda = -0.022$, $H_{14}^\lambda = 0.046$, $H_{17}^\lambda = 0.053$ $H_{18}^\lambda = 0.077$, $H_{1,10}^\lambda = -0.046$, $H_{24}^\lambda = 0.119$ $H_{29}^\lambda = -0.256$, $H_{46}^\lambda = 0.116$, $H_{29}^\lambda = -0.194$ $H_{37}^\lambda = 0.108$, $H_{5,10}^\lambda = 0.061$
Pyridine	$H_{12}^\lambda = -2.436$ $H_{23}^\lambda = -2.295$	$H_{13}^\lambda = -0.058$, $H_{14}^\lambda = 0.021$, $H_{24}^\lambda = -0.023$ $H_{25}^\lambda = -0.040$, $H_{35}^\lambda = -0.016$
Pyrrole	$H_{12}^\lambda = -3.728$ $H_{23}^\lambda = -2.263$	$H_{13}^\lambda = -0.586$, $H_{24}^\lambda = -0.116$, $H_{25}^\lambda = 0.065$
Furan	$H_{12}^\lambda = -3.960$ $H_{23}^\lambda = -2.293$	$H_{13}^\lambda = -0.646$, $H_{24}^\lambda = -0.143$, $H_{25}^\lambda = -0.110$
PBQ	$H_{12}^\lambda = -2.917$ $H_{23}^\lambda = -2.073$ $H_{34}^\lambda = -2.488$	$H_{13}^\lambda = -0.186$, $H_{14}^\lambda = 0.081$, $H_{15}^\lambda = -0.008$ $H_{16}^\lambda = -0.001$, $H_{24}^\lambda = 0.0$, $H_{25}^\lambda = 0.086$ $H_{26}^\lambda = -0.008$, $H_{35}^\lambda = 0.0$, $H_{36}^\lambda = 0.081$ $H_{37}^\lambda = 0.055$, $H_{38}^\lambda = 0.011$

^a Only a few typical hydrocarbons are shown.

^b In some cases all nearest neighbor integrals are given; in other cases only a few typical values.

^c For the hydrocarbons only the integrals of largest magnitude are shown. Those not listed are significantly smaller. For the heterocycles all non-nearest-neighbor integrals are shown regardless of their magnitude.

^d The numbering system for the polyenes is obvious and that for azulene is shown in Fig. 1. The other molecules are numbered as follows:



It is necessary now to examine the non-nearest neighbor H_{pq}^λ for the heterocycle molecules to see if the situation is the same here. Tab. 12 shows all of the integrals H_{pq}^λ for the four heterocycle molecules. For furan there are no H_{pq}^λ with a positive sign and with pyrrole only one, H_{25}^λ , and that is quite small. In a similar fashion only H_{14}^λ integral of pyridine is positive but small in magnitude. For PBQ there are several positive integrals, but in no case does their magnitude exceed 0.09 eV.

Table 13. Changes in results on neglecting non-nearest-neighbor H_{pq}^{λ}

Molecule	ΔIP^a	Singlet Transitions ^b , eV			
		$\Delta(^1\Delta E_1)$	$\Delta(^1\Delta E_2)$	$\Delta(^1\Delta E_3)$	$\Delta(^1\Delta E_4)$
<i>t</i> -Butadiene	-0.08	-0.10	0.0	-0.02	+0.04
Hexatriene	-0.10	-0.10	+0.03	0.0	-0.09
<i>t</i> -Stilbene	+0.02	-0.03	0.0	0.0	-0.01
Naphthalene	-0.05	0.0	0.0	-0.07	+0.05
Azulene	-0.09	-0.05	-0.01	-0.16	-0.0
Pyridine	+0.12	+0.10	+0.06	+0.07	+0.03
PBQ	+0.20	-0.22	-0.06	-0.03	-0.12
Pyrrole	+0.07	+0.40	+0.23	+0.57	+0.40
Furan	+0.22	+0.50	+0.41	+0.57	+0.49

^a Ionization Potential (eV), $(IP)_1 - (IP)_2$; $(IP)_1$ = result of Tab. [9], $(IP)_2$ = result of zeroing.

^b $\Delta(^1\Delta E_2) = (\Delta^1 E_1) - (\Delta^2 E_2)$; $(\Delta^1 E_2)_1 = i$ th singlet transition of Tab. [3], [4], [6], [8] or [10], $(\Delta^1 E_2)_2 = i$ th singlet transition with zeroing.

In order to assess the effect of these non-nearest neighbor integrals (both positive and negative in sign) the heterocycle calculations were repeated with all such integrals artificially set to zero before the SCF calculation. The results of these calculations are shown in Tab. 13 as differences in *I.P.* and singlet transitions from the results of Tab. 10. The results for pyridine and PBQ are different than those presented in Tab. 10, but the differences are only somewhat larger than for the hydrocarbons. For pyrrole and furan on the other hand the results are significantly different, a fact which can be attributed to the existence of rather large negative values of H_{pq}^{λ} where the atoms *p* and *q* are meta to each other. There is no doubt that the success of the present method in these cases rests largely on the existence of significant next-nearest neighbor H_{pq}^{λ} which appear quite naturally from the core treatment that has been adopted.

We have presented here a core treatment which rests largely on conventional valence state data. No attempt has been made to refine the treatment in order to remove deficiencies such as the appearance of rather large positive values of non-nearest neighbor H_{pq}^{λ} with azulene (and other nonalternants), singlet transitions for pyridine and PBQ which are slightly low in energy or an *I.P.* for furan is too small. Such refinements will be the subject of a future communication. Also, no attempt has been made to discuss the calculated ground state properties such as charge densities and bond orders for the molecules considered here. The calculation of such properties within π -theory is of questionable validity [41, 42]. However, a recent study by Baird and Dewar [43] using a valence-shell electron SCF-MO method demonstrates that this method, which includes both σ - and π -electrons, gives results for the π -electrons which are close to those calculated by SCF π -theory. On this basis the ground state results predicted by the present method are being examined relative to several σ , π electron theories. Until such a time as this work is completed the ground state results are available upon request from the authors.

In connection with this work the authors have written a FORTRAN IV computer program for the IBM 7094 which is suitable for many types of closed shell LCAO-MO-SCF π -electron calculations. Listings of the program are available from the authors.

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