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An Improved LCAO–MO–SCF π-Electron Method. I. Hydrocarbons

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Abstract: A modified semiempirical π-electron method based on an LCAO–MO–SCF formulation is presented. This method differs from conventional Pariser–Parr–Pople SCF calculations in that the core integrals over atomic orbitals involve orthogonalized Slater-type orbitals. Furthermore, the one-electron core operators are expressed in such a manner that core parameters depend only on the kind of atom involved and the distance to its nearest neighbors. The parameters required for hydrocarbon molecules are systematically derived from ethylene and benzene as reference molecules. The parameters are tested by calculating several properties of naphthalene, anthracene, phenanthrene, and a series of polyenes of the type $H—(CH{=}CH)_n—H$. This test constitutes an attempt, therefore, to derive a single set of parameters common to both aromatics and polyenes. Comparison of the results with those achieved by Pariser–Parr–Pople calculations and with experiment indicate that an improvement over conventional calculations has been achieved.

There have been a number of basic parameters, and methods of obtaining parameters, suggested for use in semiempirical π-electron calculations.[1,2] If one selects a particular property and molecule (or restricted class of molecules), it has been possible to obtain reasonable agreement with experiment by the proper choice of the parameters that enter with the LCAO–MO–SCF method. However, it has been noted repeatedly that those parameters applicable to some property and molecules may not be readily generalized to other situations. For this reason the method, the parameters, and the results are often treated with suspicion.

In this investigation we propose to examine the parameter problem using both aromatic hydrocarbons and linear conjugated polyenes as test systems. We wish to show that it is possible to develop an internally consistent method that does lead to results that may be used with confidence. During the course of this investigation, it was recognized that the conventional method for dealing with the core integrals was inadequate. Thus a new method of evaluation will be considered as well.

Method

In this section the important features of the present SCF method are outlined.

1. The π-electron approximation is adopted.

2. The molecular orbitals are taken as a linear combination of Löwdin atomic orbitals. The Löwdin orbitals[3] are related to Slater-type orbitals (S.T.O.'s) as shown in eq. 1, where λ is the array of Löwdin

$$\lambda = \chi \mathbf{S}^{-1/2} \tag{1}$$

orbitals, χ is the array of S.T.O.'s, and $\mathbf{S}^{-1/2}$ is derived from the overlap matrix over S.T.O.'s.

3. The Hamiltonian operator is written as

$$H = \sum_i H_{\text{core}}(i) + \sum_{i>j} e^2/r_{ij} \tag{2}$$

The operators $H_{\text{core}}(i)$ are further expanded using the Goeppert-Mayer and Sklar[4] approximation. In its usual form the Goeppert-Mayer and Sklar expansion of $H_{\text{core}}(i)$ leads to the following expression for $\langle\psi_p(i)|H_{\text{core}}(i)|\chi_q(i)\rangle$. For $p = q$

$$H_{pp} = \langle\chi_p(i)|T(i) + U_p^+(i)|\chi_p(i)\rangle - \sum_{r\neq p}(pp/rr) + \sum_{r\neq p}(U_r^0:pp) \tag{3}$$

and for $p \neq q$

$$H_{pq} = \langle\chi_p(i)|T(i) + U_q^+(i)|\chi_q(i)\rangle - \sum_{r\neq q}(pq/rr) + \sum_{r\neq q}(U_r^0:pq) \tag{4}$$

In eq. 3 and 4 the integrals (pp/rr), more compactly designated γ_{pr} below, and (pq/rr) are two- or three-center, two-electron repulsion integrals (over S.T.O.'s). The integrals $(U_r^0:pp)$ and $(U_r^0:pq)$ are neutral atom penetration integrals including hydrogen atoms.

Equation 3 can be simplified by neglecting those neutral atom penetration integrals where r refers to those carbon and hydrogen atoms which are nearest neighbor to atom p. For a nonbridge, nonterminal

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(1) P. G. Lykos, "Advances in Quantum Chemistry," Vol. 1, P. O. Löwdin, Ed., Academic Press Inc., New York, N. Y., 1964, p. 171.

(2) I. Fischer-Hjalmars in "Molecular Oribtals in Chemistry, Physics and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p. 361.

(3) P. O. Löwdin, *J. Chem. Phys.*, 18, 365 (1950).

(4) M. Goeppert-Mayer and A. L. Sklar, *ibid.*, 6, 645 (1938).

aromatic carbon, we can write

$$H_{pp} = \langle \chi_p(i) | T(i) + U_p{}^{+}(i) | \chi_p(i) \rangle - \sum_{r \neq p} \gamma_{pr} + (U_{q_1}{}^0:pp) + (U_{q_2}{}^0:pp) + (U_{\mathrm{h}p}{}^0:pp) \quad (5)$$

where q_1 and q_2 are carbon atoms adjacent to atom p and hp is the proton attached to p. A new parameter $H_{pp}{}^0$ can then be defined including the first integral and the neutral atom penetrations to give

$$H_{pp} = H_{pp}{}^0 - \sum_{r \neq p} \gamma_{pr} \quad (6)$$

Similarly eq. 4 is simplified by combining the neutral atom penetration integrals with the first term to a constant, $H_{pq}{}^0$, so that

$$H_{pq} = H_{pq}{}^0 - \sum_{r \neq q} (pq/rr) \quad (7)$$

The repulsion integrals here are over S.T.O.'s and are evaluated using the Mulliken approximation so that

$$H_{pq} = H_{pq}{}^0 - \sum_{r \neq q} (S_{pq}/2)(\gamma_{pr} + \gamma_{qr}) \quad (8)$$

4. The π-electronic wave functions are represented as Slater determinants in the usual manner.[5]

5. The basic SCF method is a closed-shell calculation derived from the work of Roothaan[6] as simplified by Pople.[7] The elements of the Fock matrix **F** are given by

$$F_{pp} = H_{pp}{}^{\lambda} + \Sigma_i[2\Sigma_s c_{si}{}^2\gamma_{sp}{}^{\lambda} - c_{pi}{}^2\gamma_{pp}{}^{\lambda}] \quad (9a)$$

and

$$F_{pq} = H_{pq}{}^{\lambda} + \Sigma_i c_{pi} c_{qi} \gamma_{pq}{}^{\lambda} \quad (9b)$$

In eq. 9, i spans the occupied molecular orbitals and s spans the atomic orbitals, λ_s. The superscript λ is adopted to indicate integrals over Löwdin orbitals.

In deriving eq. 9, the more complicated electron repulsion integrals that would otherwise appear are usually neglected on the basis of the zero differential overlap (z.d.o.) approximation.[8] In the present method the same result is achieved by assuming that these integrals are negligibly small when taken over an orthogonalized set of atomic orbitals. This assumption has been shown valid for benzene by McWeeny[9] and has been discussed further by Fischer-Hjalmars.[10] A consequence of this argument is that the two-center integrals, γ_{pq}, over S.T.O.'s or over Löwdin orbitals are very nearly equal.

6. A limited configuration interaction treatment is superimposed upon the SCF ground-state solution. The configurations included are those involving the four possible one-electron excitations between the two ground-state highest-occupied and lowest-unoccupied molecular orbitals.

7. Koopmans[11] theorem is adopted; *i.e.*, the energy of the ground-state highest-occupied molecular orbital is taken as the molecular ionization potential.

8. The electron repulsion integrals of eq. 9 are evaluated as follows. The one-center integrals, $\gamma_{pp}{}^{\lambda}$, are evaluated in the conventional manner[8] as the difference between the valence-state ionization potential I_p and electron affinity A_p of atom p.

$$\gamma_{pp}{}^{\lambda} = I_p - A_p \quad (10)$$

The two-center integrals $\gamma_{pq}{}^{\lambda}$ are evaluated using the equations of Mataga,[12] namely

$$\gamma_{pq}{}^{\lambda} = 14.397/(a_{pq} + r_{pq}) \quad (11)$$

where

$$a_{pq} = 28.794/(\gamma_{pp}{}^{\lambda} + \gamma_{qq}{}^{\lambda})$$

The reason for choosing the Mataga formulas for these integrals is discussed in the next section.

9. In evaluating $H_{pp}{}^{\lambda}$ and $H_{pq}{}^{\lambda}$ of eq. 9, the fact that these integrals depend upon the molecular geometry in both the Löwdin orbitals and in the one-electron operators $H_{\mathrm{core}}(i)$[13] is recognized. Because of this complicated geometry dependence, these integrals cannot be taken as empirical parameters. However, $H_{pp}{}^0$ and $H_{pq}{}^0$ are defined so that they may readily be evaluated empirically.

The parameters $H_{pp}{}^0$ and $H_{pq}{}^0$ are related to the $H_{pp}{}^{\lambda}$ and $H_{pq}{}^{\lambda}$ integrals by a two-step process. (a) Using eq. 6 and 8, the intermediate integrals H_{pp} and H_{pq} are derived. These new integrals are equivalent to core integrals over S.T.O.'s and formally add to the initial parameters the geometry dependence inherent in the operators $H_{\mathrm{core}}(i)$. (b) The desired core integrals over Löwdin orbitals are then given as[3]

$$\mathbf{H}^{\lambda} = \mathbf{S}^{-1/2}\mathbf{H}\mathbf{S}^{-1/2} \quad (12)$$

In eq. 12, $\mathbf{H}^{\lambda}$ is the matrix containing elements $H_{pq}{}^{\lambda}$, $\mathbf{H}$ is the matrix with elements H_{pq}, and $\mathbf{S}^{-1/2}$ is the same as in eq. 1.

Selection of Parameters

Within the framework of the present method, the following equations can be written for some experimental properties of ethylene and benzene.[14,15] For ethylene

$$^1\Delta E_1 = -2H_{12}{}^{\lambda} + (\gamma_{11}{}^{\lambda} - \gamma_{12}{}^{\lambda})/2 = 7.60 \text{ e.v.} \quad (13)$$

$$\mathrm{IP} = -H_{11}{}^{\lambda} - H_{12}{}^{\lambda} - (\gamma_{11}{}^{\lambda} + \gamma_{12}{}^{\lambda})/2 = 10.62 \text{ e.v.} \quad (14)$$

for benzene

$$^1\Delta E_1 = -2H_{12}{}^{\lambda} + (\gamma_{12}{}^{\lambda} - 3\gamma_{13}{}^{\lambda} + 2\gamma_{14}{}^{\lambda})/6 = 4.91 \text{ e.v.} \quad (15)$$

$$^1\Delta E_2 = {}^1/_2[(e_1 + e_2 + e_4) \pm (e_1{}^2 + e_2{}^2 + 8e_3{}^2 + e_4{}^2 - 2e_1e_2 - 2e_1e_4 - 2e_2e_4)^{1/2}] = 6.19 \text{ e.v.} \quad (16)$$

$$^1\Delta E_3 = -2H_{12}{}^{\lambda} + (\gamma_{11}{}^{\lambda} + 4\gamma_{12}{}^{\lambda} - 4\gamma_{13}{}^{\lambda} - \gamma_{14}{}^{\lambda})/6 = 7.02 \text{ e.v.} \quad (17)$$

$$\mathrm{IP} = -H_{11}{}^{\lambda} - H_{12}{}^{\lambda} - \gamma_{11}{}^{\lambda}/2 - 5\gamma_{12}{}^{\lambda}/3 - 2\gamma_{13}{}^{\lambda} - 5\gamma_{14}{}^{\lambda}/6 = 9.52 \text{ e.v.} \quad (18)$$

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(5) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

(6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(7) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(8) R. G. Parr and R. Pariser, *J. Chem. Phys.*, **21**, 466, 767 (1953).

(9) R. McWeeny, Quarterly Progress Report, Solid State and Molecular Theory Group, M.I.T., Jan. 15, 1954, p. 25.

(10) I. Fischer-Hjalmars, *J. Chem. Phys.*, **42**, 1962 (1965).

(11) T. Koopmans, *Physica*, **1**, 104 (1933).

(12) N. Mataga and K. Nishimoto, *Z. Physik. Chem.* (Frankfurt), **13**, 140 (1957).

(13) P. G. Lykos, *J. Chem. Phys.*, **35**, 1249 (1961).

(14) R. G. Parr and R. Pariser, *ibid.*, **23**, 711 (1955).

(15) H. E. Simmons, *ibid.*, **40**, 3554 (1964).

where

$$
\begin{aligned}
e_1 &= -2H_{12}^{\lambda} + (\gamma_{11}^{\lambda} - \gamma_{12}^{\lambda}/3 + \gamma_{13}^{\lambda} - 5\gamma_{14}^{\lambda}/3)/4 \\
e_2 &= (\gamma_{11}^{\lambda}/3 - 3\gamma_{12}^{\lambda} + 11\gamma_{13}^{\lambda}/3 - \gamma_{14}^{\lambda})/4 \\
e_3 &= (\gamma_{11}^{\lambda} - 5\gamma_{12}^{\lambda} + 5\gamma_{13}^{\lambda} - \gamma_{14}^{\lambda})/6 \\
e_4 &= -4H_{12}^{\lambda} + (\gamma_{11}^{\lambda} + 2\gamma_{12}^{\lambda} + 2\gamma_{13}^{\lambda} - 5\gamma_{14}^{\lambda})/6
\end{aligned} \qquad (19)
$$

In these equations IP means the molecular ionization potential and $^1\Delta E_i$ refers to the *i*th singlet transition.

Table I. Valence-State Data for the Carbon Atom

Quantity	a, b	a, c	d, e	d, f
I_p	11.54	11.42	11.22	11.16
A_p	0.46	0.58	0.62	0.03

[a] For the valence state, $C^{-}(sx^2yz, V_3)$, $C^0(s, xyz, V_4)$, $C^{+}(syz, V_3)$. [b] H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953). [c] H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955). [d] For the trigonal valence states. [e] G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962). [f] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

Table II. Core Integrals for Ethylene and Benzene and Calculated Higher Singlets for Benzene (e.v.)

		Ethylene		Benzene		Singlets	
γ_{pq}^{λ} [a]	Valence-state data[b]	H_{11}^{λ}	H_{12}^{λ}	H_{11}^{λ}	H_{12}^{λ}	$^1\Delta E_2$	$^1\Delta E_3$
1	1	−17.1199	−3.0199	−40.3104	−2.3521	4.71	7.39
1	2	−16.9184	−3.0584	−39.9958	−2.3556	4.69	7.32
1	3	−16.7162	−3.0962	−39.6725	−2.3592	4.68	7.25
1	4	−17.1617	−3.0117	−40.3748	−2.3513	4.72	7.40
2	1	−17.0261	−2.9261	−40.0683	−2.3857	5.25	7.14
2	2	−16.8261	−2.9661	−39.8063	−2.3904	5.24	7.06
2	3	−16.6261	−3.0061	−39.5354	−2.3939	5.22	6.98
2	4	−17.0677	−2.9177	−40.1336	−2.3863	5.26	7.15
3	1	−16.4947	−2.3947	−32.2400	−2.3916	6.20	7.02
3	2	−16.3000	−2.4400	−31.9449	−2.3929	6.15	6.97
3	3	−16.1049	−2.4849	−31.6452	−2.3943	6.10	6.92
3	4	−16.5352	−2.3852	−32.3010	−2.3913	6.21	7.03
					Exptl.[c]	(6.19)	(7.02)

[a] The two-center electron-repulsion integrals given by (1) Roothaan, (2) Pariser and Parr equation, and (3) Mataga equation. [b] The one-center electron-repulsion integrals given by eq. 10 using the valence-state data of (see footnotes, Table I) (1) Skinner and Pritchard, (2) Pritchard and Skinner, (3) Pilcher and Skinner, and (4) Hinze and Jaffé. [c] See eq. 16 and 17.

In deriving eq. 13 to 19, it has been assumed that the integrals H_{13}^{λ} and H_{14}^{λ} for benzene are negligible. Lykos[13] has derived expressions corresponding to these which explicitly contain all nonnearest-neighbor core integrals. As this author has pointed out, the neglected integrals may be significant in magnitude and perhaps need to be included in the final analysis. The neglect of these quantities here is based on the fact that no suitable equations, relating H_{13}^{λ} to a physical observable, are known. In principle it is possible to find H_{14}^{λ} from a knowledge of the diamagnetic anisotropy of benzene, but it is doubtful that an integral determined in this way would be very reliable.

We now wish to evaluate the integrals in eq. 13 to 19 so that the best possible agreement can be achieved in relation to experimental results. We assume initially that H_{11}^{λ} may be different for the calibration molecules, ethylene and benzene.

The first step in selecting the integrals involves adopting the atoms-in-molecules approximation for evaluating the one-center electron-repulsion integrals, γ_{11}^{λ}. Several sets of valence-state data can be used in this connection and these will be discussed later.

The next step consists in examining the various ways of evaluating the repulsion integrals γ_{pq}^{λ}: (1) these integrals can be evaluated exactly by assuming that they are over $2p\pi$ S.T.O.'s; (2) the integrals can be evaluated according to the uniformly charge sphere method of Pariser and Parr;[8] and, finally, (3) the integrals can be evaluated according to the approximations of Mataga.[12] The three methods will all be considered.

To evaluate the integrals over S.T.O.'s exactly, the equations of Roothaan[16] are used. In the S.T.O.'s the appropriate orbital exponent is fixed by determining its value from the corresponding value of the one-center integral determined from valence-state data.

These considerations require an examination of the four sets of valence-state data shown in Table I. Thus four different values of γ_{11}^{λ} are possible. For each of these values we consider three kinds of two-center repulsion integrals; hence there are a total of twelve sets of electron-repulsion integrals to consider.

To obtain the necessary core integrals for ethylene and benzene, one of the twelve possible sets of electron-repulsion integrals is substituted into eq. 13 and 15 to find H_{12}^{λ}; then the corresponding molecular ionization potentials, *i.e.*, from eq. 14 and 18, are used to find the H_{11}^{λ}. The selection of a given set of integrals and core parameters is then made by calculating the two highest singlet transitions in benzene. The carbon–carbon distances in these calculations are: r_{12} in ethylene = 1.338 Å., r_{12} in benzene = 1.397 Å., which for a regular hexagon model gives r_{13} = 2.420 Å. and r_{14} = 2.794 Å.[17] The results are shown in Table II, as are the calculated highest singlets of benzene. The calculated singlets for benzene are poorly reproduced when using either the exact repulsion integrals or those calculated from the Pariser and Parr equation. On the other hand, the results achieved by the use of Mataga integrals are within 1.5% of the experimental values

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(16) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

(17) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

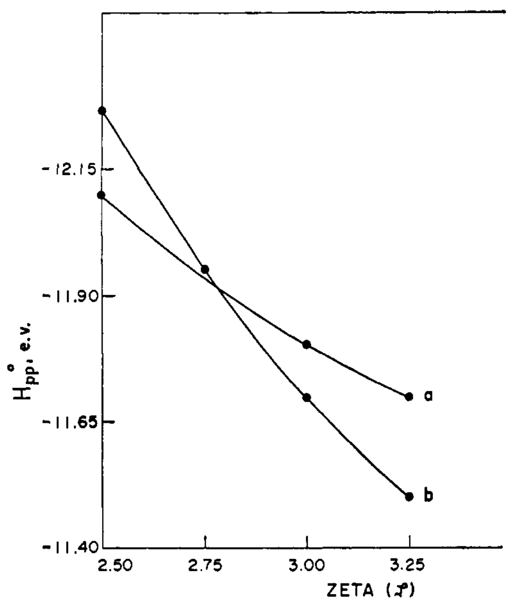

Figure 1. H_{pp}^{0} as a function of ζ: a, ethylene carbon; b, benzene carbon.

and are to a first approximation independent of the carbon valence-state data used.[18] For this reason it was decided to adopt the Mataga equation for evaluating all two-center repulsion integrals γ_{pq}^{λ}. Also, quite arbitrarily, the valence-state data of Hinze and Jaffé[19] was adopted for all subsequent calculations.

The final step in the calibration process involves using eq. 12, 6, and 8 to determine the appropriate values of H_{pp}^{0} and H_{pq}^{0}. The basic problem that arises here is that of determining the orbital exponent ζ to use in the S.T.O.'s involved in the overlap integrals. It is assumed that the same exponent should be used in all equations.

There exists no obvious criterion for selecting a best value of ζ, hence it was decided to derive parameters corresponding to a range of values and attempt to select the best one on the basis of the accuracy of the final results for the hydrocarbons other than ethylene and benzene. Figures 1 and 2 show the plots of H_{pp}^{0} *vs.* ζ and H_{pq}^{0} *vs.* r_{qp} obtained in this manner. In Figure 1, the ethylene and benzene curves intersect at $\zeta = 2.81$.

Application of the appropriate core parameters to various hydrocarbons demonstrated that the results achieved for molecular ionization potentials and singlet transitions were surprisingly independent of the particular ζ value. On the basis of this criterion, there does not appear to be a "best" value of ζ. In view of this conclusion, a value of $\zeta = 2.81$ was adopted for the remainder of the calculations. For this value H_{pp}^{0} for ethylene and benzene are equal.

In Table III are shown the values of the core integrals for ethylene and benzene. The core integrals over S.T.O.'s (*i.e.*, H_{pp} and H_{pq}) are also shown since they demonstrate the geometry dependence of the operators $H_{\text{core}}(i)$.

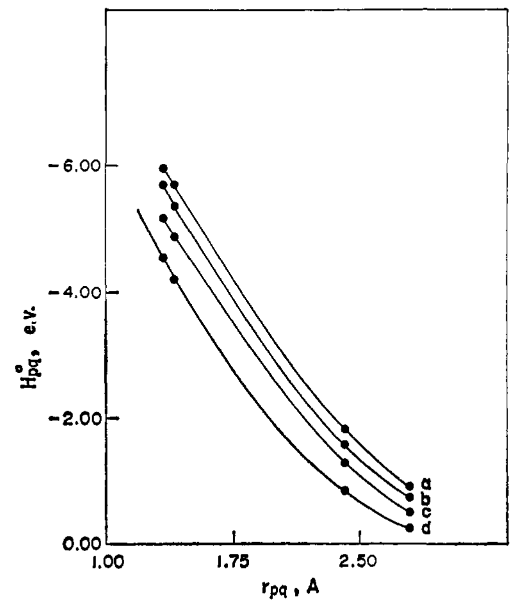

Figure 2. Plots of H_{pq}^{0} *vs.* r_{pq} for various ζ values: a = 2.50, b = 2.65, c = 2.90, d = 3.30.

It is important to note that although nonneighbor values of H_{pq}^{λ} are neglected, the corresponding nonneighbor values of H_{pq} and H_{pq}^{0} are not negligible and must be retained. That the use of nonneighbor H_{pq}^{0} values leads, in general, to small values of H_{pq}^{λ} between nonneighbors is justified by several typical examples in the Appendix. In our calculations the H_{pq}^{λ} values between nonneighbors were set equal to zero before the SCF calculation.

Table III. Core Integrals (in e.v.) for Ethylene and Benzene[a]

Ethylene		Benzene	
Integral	Value	Integral	Value
H_{11}^{λ}	−16.5352[b]	H_{11}^{λ}	−32.3010[b]
H_{12}^{λ}	−2.3852[b]	H_{12}^{λ}	−2.3913[b]
H_{11}	−17.3958	H_{11}	−33.8963
H_{12}	−8.3504	H_{12}	−13.3268
H_{11}^{0}	−11.9248	H_{13}	−3.0590
H_{12}^{0}	−5.3560	H_{14}	−1.4404
		H_{11}^{0}	−11.9183
		H_{12}^{0}	−5.0321
		H_{13}^{0}	−1.3320
		H_{14}^{0}	−0.5482

[a] Calculated for $\zeta = 2.81$. [b] See Table II.

Results

All calculations were performed on the IBM 7040 and IBM 7094 electronic digital computers using programs written in FORTRAN IV. Input to the program consists essentially of the number and kind of atoms in the molecule, the parameters discussed earlier, the molecular geometry, and a matrix defining a Hückel molecular orbital calculation from which a starting set of wave functions for the SCF calculation is obtained. All integrals are calculated internally and the entire SCF iteration scheme proceeds automatically to convergence, which is chosen as a difference of 10^{-4} in successive sets of linear coefficients.

Geometries. Only the all-*trans* geometry was used in the case of the polyenes. The geometry suggested

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(18) O. W. Adams and R. L. Miller, *J. Chem. Phys.*, **41**, 2948 (1964).

(19) See footnote *f*, Table I.

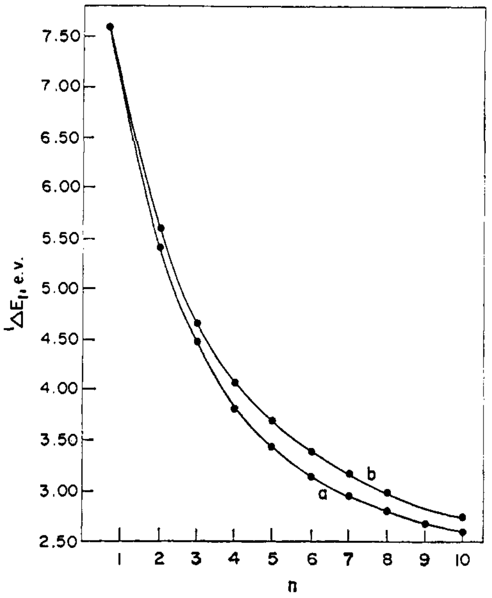

Figure 3. Lowest singlet transitions of the polyenes H—(CH=CH)$_n$—H: a, calcd.; b, exptl.

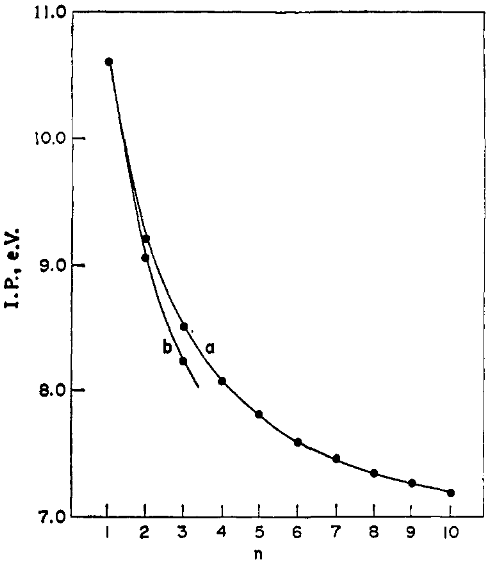

Figure 4. Ionization potentials of the polyenes H—(CH=CH)$_n$—H: a, calcd.; b, exptl.

by Shoemaker and Pauling[20] for the planar model of butadiene was adopted and used as a basis for all the subsequent higher polyenes. The regular alternation of bond lengths implied has been discussed by Longuet-Higgins and Salem,[21] Dixon,[22] Ooshika[23] and more recently by Dewar and Gleicher.[24] While no experimental structural determinations exist for the higher polyenes, some support for the above model follows from the results of Bastiansen,[25] *et al.*, for the bond lengths in 1,3,5,7-cyclooctatetraene. Here alternating bonds of 1.334 and 1.462 Å. are observed.

For naphthalene and anthracene the geometries adopted are those of Ahmed and Cruickshank[26] and Robertson.[27,28] For phenanthrene the geometry is based upon that derived by Coulson and Haigh[29] from the calculations of Pritchard and Sumner.[30]

Final Calculations. Results of the final calculations are shown in Tables IV and V for the polyenes, and Tables VI and VII for the aromatic hydrocarbons. Experimental results, where known, are also shown.

For the polyenes the lowest singlet transitions ($^1\Delta E_1$), in solution, are known for all except the C_{18} case.[31] The difference between calculated and experimental results vary from 0.26 to 0.15 e.v., with an average deviation of 0.21 e.v. This agreement is best illustrated in Figure 3, in which the calculated and experimental results are plotted against the length of the polyene chain. Unfortunately there are no experimental data for the higher singlets of these molecules.

Table IV. Results for the Polyenes H—(CH=CH)$_n$—H and Electronic Transitions (e.v.)

n		IP	Singlets $^1\Delta E_1$	$^1\Delta E_2$	$^1\Delta E_3$	Triplets $^3\Delta E_1$
1	Calcd.	(10.62)	(7.60)			
	Exptl.[a]	10.62	7.60			
2	Calcd.	9.23	5.49	6.60	7.98	1.20
	Exptl.	9.07	5.71			
3	Calcd.	8.52	4.48	5.75	6.64	1.25
	Exptl.	8.23	4.63			
4	Calcd.	8.10	3.86	5.14	5.75	1.23
	Exptl.		4.08			
5	Calcd.	7.82	3.45	4.73	5.13	1.23
	Exptl.		3.71			
6	Calcd.	7.62	3.17	4.44	4.67	1.24
	Exptl.		3.41			
7	Calcd.	7.47	2.97	4.23	4.34	1.26
	Exptl.		3.18			
8	Calcd.	7.36	2.82	4.02	4.13	1.29
	Exptl.		3.02			
9	Calcd.	7.28	2.71	3.81	4.01	1.33
	Exptl.					
10	Calcd.	7.20	2.62	3.63	3.93	1.37
	Exptl.		2.77			

[a] Experimental spectroscopic data shown in this table are taken from ref. 31. Ionization potentials are taken from ref. 32.

The calculated ionization potentials of the polyenes are shown in Table IV and are plotted against the length of the polyene chain in Figure 4. The only experimental data available here are for the C_4 and C_6 cases.[32] For these two cases the difference between calculated and experimental results are 0.22 and 0.15 e.v., which is about the same as the deviation noted for the singlets. The tendency for the calculated ionization potentials to level off in the higher polyenes seems entirely reasonable.

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(20) V. Shoemaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939).

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(22) W. T. Dixon, *Tetrahedron*, 18, 875 (1962).

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(32) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (London), **A185**, 182 (1946).

Table V. Results for the Polyenes H—(CH=CH)$_n$—H, Charge Densities and Bond Orders[a]

n	q_1	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	q_{10}	p_{12}	p_{23}	p_{34}	p_{45}	p_{56}	$p_{6,7}$	$p_{7,8}$	$p_{8,9}$	$p_{9,10}$
1	1.00										2.000								
2	1.045	0.955									1.938	1.346							
3	1.053	0.958	0.990								1.928	1.366	1.872						
4	1.055	0.959	0.996	0.990							1.926	1.370	1.862	1.388					
5	1.056	0.960	0.999	0.990	0.996						1.926	1.372	1.860	1.394	1.852				
6	1.056	0.960	1.000	0.990	0.998	0.995					1.924	1.372	1.858	1.396	1.848	1.400			
7	1.057	0.961	1.001	0.990	0.999	0.995	0.998				1.924	1.372	1.858	1.396	1.848	1.402	1.846		
8	1.057	0.961	1.001	0.990	1.000	0.995	0.999	0.998			1.924	1.372	1.858	1.396	1.846	1.402	1.844	1.404	
9	1.057	0.961	1.001	0.990	1.000	0.995	0.999	0.998	0.997		1.924	1.372	1.858	1.396	1.846	1.402	1.844	1.404	1.844
10	1.056	0.961	1.002	0.990	1.000	0.995	1.000	0.997	0.999	0.999	1.924	1.372	1.858	1.396	1.846	1.402	1.844	1.404	1.842

[a] The numbering proceeds from a terminal carbon atom serially to the opposite end of the chain. Only the unique value of the densities and orders are shown.

Table VI. Results for the Aromatic Hydrocarbons, Ionization Potentials and Electronic Transitions (e.v.)

Property	Naphthalene Calcd.	Naphthalene Exptl.[a]	Anthracene Calcd.	Anthracene Exptl.[a]	Phenanthrene Calcd.	Phenanthrene Exptl.[a]
IP	8.39	8.26	7.68	7.55	8.24	8.03
$^1\Delta E_1$ (^{1}L$_b$)	4.39	3.97	3.68		4.23	3.62
$^1\Delta E_1$ (^{1}L$_a$)	4.68	4.33	3.92		4.54	4.23
$^1\Delta E_3$ (^{1}B$_b$)	5.95	5.61	5.20	4.88	5.36	4.94
$^3\Delta E_1$	2.71	2.64	1.94	1.84	3.01	2.70

[a] Experimental values for the ionization potentials are taken from ref. 34. This article also contains a convenient summary of ionization potentials reported by earlier workers. Experimental values for the singlet spectra are taken from ref. 31. Triplet values are taken from ref. 37 and 38.

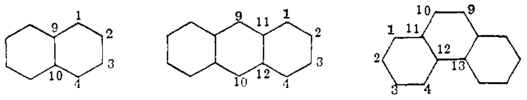
Table VII. Results for the Aromatic Hydrocarbons, Charge Densities and Bond Orders[a]

	q_1	q_2	q_9	p_{12}	p_{23}	p_{19}	$p_{9,10}$
Naphthalene	1.013	1.001	0.971	1.756	1.570	1.526	1.566

	q_1	q_2	q_9	q_{11}	p_{12}	p_{23}	$p_{1,11}$	$p_{9,11}$	$p_{11,12}$
Anthracene	1.012	1.000	1.021	0.978	1.778	1.540	1.496	1.618	1.502

	q_1	q_2	q_3	q_4	q_9	q_{11}	q_{12}	p_{12}	p_{23}	p_{34}	$p_{4,12}$	$p_{11,12}$	$p_{1,11}$	$p_{9,10}$	$p_{10,11}$	$p_{12,13}$
Phenanthrene	1.010	1.005	0.999	1.021	1.010	0.977	0.979	1.724	1.604	1.722	1.576	1.590	1.568			

[a] The numbering systems used are



An interesting result of the present calculations is shown in the π-electron charge densities of Table V for the polyenes. The terminal carbon atoms are seen to possess an appreciable negative charge. This charge is almost balanced by a positive charge on the second and next to last carbon atoms, and the interior carbons are almost neutral. It is difficult to assess this predicted charge-distribution pattern. The closest physical evidence rests upon chemical shift data obtained by Goldstein and Hobgood[33] from the proton magnetic resonance spectrum of 1,3-butadiene. These workers found the chemical shift for the terminal carbon atoms to be −298.7 c.p.s. and for the internal carbons −220.6 c.p.s. (relative to internal cyclohexane), indicating a greater shielding for the terminal carbon atom. To the extent to which this greater shielding reflects a higher π charge density, these experimental results are consistent with the patterns calculated here.

The calculated results for the singlet transitions in the three aromatic hydrocarbons studied are shown in Table VI. The naphthalene results for the three lowest singlets all deviate from experiment by about 0.37 e.v. but all in the same direction. It thus appears that the calculated results predict the proper spacings between the excited levels even though the levels are raised.

The best indication of the accuracy of the anthracene calculation is the ^{1}B$_b$ band which is a pronounced maximum in the spectrum. The calculated result is in error here by 0.32 e.v., similar to the error noted with naphthalene. The experimental ^{1}L$_a$, ^{1}L$_b$ bands of anthracene lie in the region 4.01 to 3.31 e.v.[31] The calculated results do lie in this region although their accuracy cannot be readily assessed.

For phenanthrene the errors between experiment and calculation are about those noted above except for the ^{1}L$_b$ transition, where the error is 0.61 e.v. if the experimental value of Table VI is adopted. However, the ^{1}L$_b$ band in phenanthrene actually shows[31] five distinct peaks in the region 3.90–3.62 e.v., and it is not clear which of these represents the 0–0 transition.

It is worth noticing that for the aromatic hydrocarbons the predicted transitions are always higher than experiment (*i.e.*, in energy terms). For the polyenes the reverse is true.

The ionization potentials predicted for the aromatic hydrocarbons are shown in Table VI along with the recent experimental results of Wachs and Dibeler.[34] The differences between experimental and calculated

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(33) R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectry.*, **12**, 76 (1964).

(34) M. E. Wachs and V. H. Dibeler, *J. Chem. Phys.*, **31**, 1557 (1959).

results for naphthalene, anthracene, and phenanthrene are 0.13, 0.13 and 0.21 e.v., respectively. It is interesting to note that the value of the ionization potential of benzene obtained by these authors is 9.38 e.v. which differs from our benzene calibration value of 9.52 e.v. by 0.14 e.v., which is almost the same as the errors in the naphthalene and anthracene calculations.

The present method leads to charge densities that are not uniform in the aromatic hydrocarbons. A slight excess of π charge is predicted at the 1-position in naphthalene, the 2-position being almost neutral. This is the opposite effect to that obtained by Moser[35] in a more conventional LCAO-MO-SCF calculation, but agrees qualitatively with results obtained by Ruedenberg using the augmented tight-binding approximation.[36] Similar results are noted for anthracene and phenanthrene. Perhaps the most significant feature here is that in all three molecules the tertiary-type carbon has an appreciable deficiency of π electrons.

In Tables IV and VI, results are shown for the ground-state–lowest-triplet transitions. No experimental information is known concerning these transitions for the polyenes. For the aromatic hydrocarbons, however, the agreement between calculated and experimental[37,38] results for this property is good. The errors for naphthalene, anthracene, and phenanthrene are 0.07, 0.10, and 0.31 e.v., respectively. The results for naphthalene and anthracene suggest that is may be possible to calculate accurate singlet and triplet transition energies simultaneously using the same basic parameters and method.

Discussion

In this section we shall compare the results of calculations using the parameters suggested here and those based on the values most frequently used. We shall then summarize the essential features in the present method and attempt to correlate our parameters with values obtained from experiment.

In comparing the present method with conventional studies, only our own computer programs are used. These programs contain several optional ways of handling the parameters and allow for a wide range of different calculations by merely changing a few input words. This approach ensures that all of the calculations involve exactly the same amount of configuration interaction.

We shall focus particular attention on, first, the way of calculating the electron-repulsion integrals and, second, on the technique for evaluating the core integrals. For the electron-repulsion integrals, those of Roothaan and of Pariser and Parr will be used. In using the Roothaan integrals the orbital exponent is determined as described in Selection of Parameters. The technique of handling the off-diagonal core integrals involves using the equation[8]

$$H_{pq} = -2517.5e^{-5.007r_{pq}} \qquad (20)$$

Here the superscript λ is omitted to avoid confusion with the integrals, H_{pq}^{λ}. The integrals of eq. 20 should, in fact, rightly be considered as purely empirical parameters. The core integrals H_{pp} are handled by the conventional equation

$$H_{pp} = -I_p - \sum_{p \neq q} \gamma_{pq} \qquad (21)$$

where I_p is the valence-state ionization potential. Since Hinze and Jaffé valence-state data have been used in the earlier work, these values will also be used in eq. 10 and 21.

Based on these differences in the evaluation of repulsion integrals, the three possibilities are (1) Roothaan repulsion integrals (method A), (2) Pariser and Parr repulsion integrals (method B), and (3) Mataga repulsion integrals (method C). The results of method C indicate the effect of the variation of core integrals, since Mataga integrals have been used in previous calculations.

For each of these methods, calculations are made only for the molecules butadiene and naphthalene, chosen as typical of the rest. Results of the calculations are shown in Tables VIII and IX. In the tables

Table VIII. Comparison of Butadiene Calculations[a]

Result	Method A	B	C	Previous[b]	Exptl.[b]
H_{11}	−28.0227	−27.8401	−23.2930	−23.1182	
H_{22}	−31.9509	−31.4253	−25.6499	−24.9234	
H_{12}	−2.920	−2.920	−2.920	−2.424	
H_{23}	−1.683	−1.683	−1.683	−2.277	
IP	11.51	11.34	10.34	9.23	9.07
$^1\Delta E_1$	6.28	6.44	6.60	5.49	5.71
$^1\Delta E_2$	7.94	7.89	7.47	6.60	
$^1\Delta E_3$	8.41	8.05	8.96	7.98	
$^3\Delta E_1$	3.66	3.46	2.51	1.20	
q_1	1.000	1.000	1.000	1.045	
q_2	1.000	1.000	1.000	0.955	
p_{12}	1.978	1.978	1.974	1.938	
p_{23}	1.204	1.210	1.228	1.346	

[a] All quantities are in electron volts except for the charge densities q_i and bond orders p_{ij}. [b] Previous results refer to the calculations shown in Table IV.

Table IX. Comparison of Naphthalene Calculations[a]

Result	Method A	B	C	Previous[b]	Exptl.[b]
H_{11}	−58.1501	−58.1428	−45.3553	−44.4418	
H_{22}	−54.9508	−55.0264	−43.3300	−42.3740	
H_{99}	−65.2471	−65.0301	−49.6505	−48.2738	
H_{12}	−2.709	−2.709	−2.709	−2.451	
H_{23}	−2.228	−2.228	−2.228	−2.388	
$H_{1,9}$	−2.006	−2.006	−2.006	−2.386	
$H_{9,10}$	−2.354	−2.354	−2.354	−2.495	
IP	10.68	10.58	9.69	8.39	8.26
$^1\Delta E_1$	4.90	4.87	4.62	4.39	3.97
$^1\Delta E_2$	5.01	5.04	5.22	4.68	4.33
$^1\Delta E_3$	6.59	6.37	5.95	5.95	5.61
$^3\Delta E_1$	4.36	4.15	3.43	2.71	2.64
q_1	1.000	1.000	1.000	1.013	
q_2	1.000	1.000	1.000	1.001	
q_9	1.000	1.000	1.000	0.971	
p_{12}	1.834	1.828	1.820	1.756	
p_{13}	1.466	1.474	1.486	1.570	
p_{19}	1.442	1.448	1.460	1.526	
$p_{9,10}$	1.692	1.684	1.668	1.566	

[a] All quantities are in electron volts except for the charge densities and bond orders. [b] Previous results refer to calculations shown in Table VI.

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(35) C. M. Moser, *J. Chim. Phys.*, **52**, 24 (1955).

(36) K. Ruedenberg, *J. Chem. Phys.* **34**, 1861, 1878, 1884, 1892, 1897, 1907 (1961).

(37) G. Porter, *Proc. Chem. Soc.*, 291 (1959).

(38) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 4537 (1964).

Table X. Typical Elements, H_{pq}^{λ} (e.v.), for Polyene H—(CH=CH)$_5$—H (A) and Naphthalene (B) before Zeroing the Nonnearest-Neighbor Elements[a]

Element	Value A	Value B	Element	Value A	Value B
H_{12}^{λ}	−2.4278	−2.4509	H_{23}^{λ}	−2.2752	−2.3882
H_{13}^{λ}	−0.0189	−0.0129	H_{24}^{λ}	−0.0507	. . .
H_{14}^{λ}	−0.2249	−0.0130	H_{25}^{λ}	−0.2026	. . .
H_{15}^{λ}	−0.0538	−0.2138	H_{26}^{λ}	−0.0555	−0.0083
H_{16}^{λ}	−0.0072	−0.0088	H_{27}^{λ}	−0.0060	−0.0647
H_{17}^{λ}	−0.0002	−0.2393	H_{28}^{λ}	−0.0030	−0.2393
H_{18}^{λ}	−0.0003	−0.0078	H_{29}^{λ}	−0.0003	−0.0730
H_{19}^{λ}	−0.0001	−2.3859	$H_{2,10}^{\lambda}$	−0.0001	−0.0116
$H_{1,10}^{\lambda}$	0.0	−0.0177	$H_{9,10}^{\lambda}$	. . .	−2.4955

[a] See footnote *b* to Tables V and VII for atom subscript designation.

the columns labeled "Previous" refer to the results shown in the Results section.

The improvement achieved in the present method, as compared to methods A, B, and C, is clear from the tables. It is interesting to note that one effect of this method of evaluating the off-diagonal integrals H_{pq} is to smooth out the differences between these integrals for different bonds. This factor undoubtedly has much to do with the improved spectroscopic results.

In summary, the present attempt to deduce a set of parameters useful in LCAO-MO-SCF calculations has led to an improvement over the conventional method as judged by the calculation of ionization potentials and spectroscopic properties in two different kinds of unsaturated hydrocarbons, the aromatics, and the polyenes. This improvement rests both in basic modifications in the method and in a systematic approach to deriving empirical parameters.

The modifications of the conventional method had to do primarily with the use of an orthogonal basis set of atomic orbitals and the implications in using such a set for the core parameters in particular. Further, the molecular geometry inherent in the one-electron core operators $H_{\text{core}}(i)$ is explicitly taken into account in the treatment here.

One conclusion of the determination of empirical parameters is that the two-center electron-repulsion integrals are best handled by the use of the Mataga formulas. Use of these formulas is not new in LCAO-MO-SCF calculations. They were first used by Mataga and Nishimoto[12] in some very successful calculations on N-heterocycles. Bloor[39] has also used them quite successfully in calculations on aniline.

The Mataga integrals γ_{pq} are plotted as a function of r_{pq} in Figure 5, along with comparable values for the integrals calculated exactly according to Roothaan. The most significant difference in the Mataga integrals is their comparatively low value in the important region where r_{pq} corresponds to normal nearest-neighbor and next nearest-neighbor internuclear separations. This behavior suggests that these integrals may, in some way, be taking two-electron correlation into account.

The treatment of core integrals made here is a consequence of earlier suggestions by Löwdin[3] and Lykos.[13] Fischer-Hjalmars[2] has also recently discussed this problem. The present treatment shows that the integrals H_{pp}^{λ} and H_{pq}^{λ} have about the same value as is commonly used in most LCAO-MO-SCF calculations. However, the extreme sensitivity of the H_{pq}^{λ} to the internuclear separation r_{pq} has been removed.

An interesting similarity exists between the core integrals of this work and the framework integrals discussed by Ruedenberg[39] in the tight binding approximation. Ruedenberg derived a Coulomb integral, which he designated γ, which like our parameter H_{pq}^{λ} is relatively insensitive to the internuclear separation r_{pq}. However, this integral is the difference between two terms, $\gamma = \beta - S\alpha$, each of which strongly depends on r_{pq}. Our parameter H_{pq}^{0} is somewhat analogous to β. Ruedenberg obtains an empirical value of $\gamma = -2.398$ e.v. from the spectrum of benzene which is almost identical with the values derived earlier for H_{12}^{λ} for ethylene and benzene, namely −2.3852 and −2.3913 e.v., respectively (see Table II).

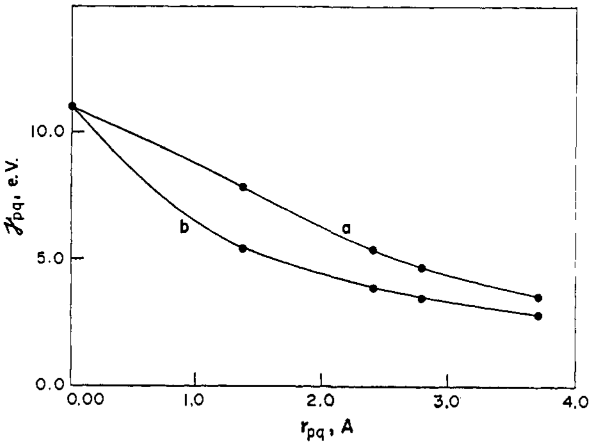

Figure 5. Two-center electron-repulsion integrals: a, exact; b, Mataga.

It is useful to consider the empirical parameter H_{pp}^{0} which appears in eq. 6. In many calculations a similar equation is used in which the valence-state ionization potential I_p, of atom p, is identified with H_{pp}^{0}. The Hinze and Jaffé value of I_p is −11.16 e.v. which differs from our H_{pp}^{0} value by about 0.76 e.v. Referring to eq. 5, however, it is clear that three significant neutral atom penetration integrals appear. If the values 0.82 and 0.60 e.v. are adopted for the carbon penetrations and the hydrogen penetrations, respectively,[40] then

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(39) J. E. Bloor, P. N. Daykin, and P. Boltwood, *Can. J. Chem.*, **42**, 121 (1964).

(40) Values of the carbon penetration integrals are estimated from the tabulations of R. G. Parr, D. P. Craig, and I. G. Ross, *J. Chem. Phys.*, **18**, 1561 (1950). The corresponding value for the hydrogen penetration is taken from R. D. Brown and M. L. Hefferman, *Australian J. Chem.*, **12**, 319 (1959).

$$\langle\psi_p(i)/T(i) + U_p^{+}(i)|\psi_p(i)\rangle = -11.92 + 2.24 \text{ e.v.} = -9.68 \text{ e.v.}$$

The interesting thing to note here is that the experimental ionization potential of methyl radical is 9.80 e.v.,[41] a difference of only 0.12 e.v. from the integral shown above.

What this simplified calculation suggests is that the quantity $\langle\chi_p(i)|T(i) + U_p^{+}(i)|\chi_p(i)\rangle$ should be identified with the experimental ionization potential of the methyl radical!

No detailed discussion has been made of the computer programs used here. Such SCF programs are becoming commonplace in many laboratories, the program of each laboratory being unique in detail only. We, therefore, felt that a description of our programs was unnecessary. A possible unique feature of our program is the way in which the core elements H_{pq}^{λ} and H_{pp}^{λ} are automatically calculated. Details of the program can be obtained from the authors.

Acknowledgment. The authors gratefully acknowledge the suggestions and encouragement of Professor P. G. Lykos. R. L. M. wishes to acknowledge the support of National Institute of Health Grant GM 10826-01.

Appendix

In the description of the method in the Selection of Parameters section, it was mentioned that off-diagonal elements H_{pq}^{λ} for nonnearest neighbors are set equal to zero before forming the Fock matrix. Table X shows the values of these integrals for two typical examples, illustrating that the integrals are in fact small and can be set equal to zero with essentially no effect on the final result.

(41) C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, 41, 2948 (1964).

Electron Spin Resonance Spectra of γ-Irradiated Polycrystalline Alkyl Iodides[1,2]

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin. *Received September 13, 1965*

Abstract: It has been previously shown[3] that polycrystalline C_2H_5I which has been γ-irradiated at 77°K gives an unexpectedly complex esr spectrum with more than 32 lines spread over 1000 gauss. Similar complexity with varying spreads was found for the polycrystalline forms of other normal alkyl iodides having an even number of carbon atoms per molecule, but not for the odd-carbon-number species or for the glassy forms. To assist in determining the cause of the complex signals, spectra have been taken of C_2H_5I prepared from I^{129}, rather than the naturally occurring I^{127}, and of C_2D_5I, to learn whether changes in the spins and nuclear magnetic moments of the iodine and hydrogen atoms affect the pattern. The spectrum of the polycrystalline $C_2H_5I^{129}$ is indistinguishable from that of $C_2H_5I^{127}$, while that of $C_2D_5I^{127}$ has the wide spread of the latter, but fewer and broader lines. These data are interpreted to indicate that the breadth of the spectra results from coupling of the spin of the unpaired electron with orbital angular momentum on the iodine to give radicals with anisotropic apparent g values ranging from about 1.7 to 2.3. The many lines are the result of superposition of the hydrogen hyperfine splitting spectra of radicals oriented to give different apparent g values. Similar complex spectra are produced in $(C_2H_5)_3SnI$ (1000 gauss) and CH_2I_2 (700 gauss). Momentary warming from 77° to a temperature slightly under the melting point, followed by return to 77°, causes the complex spectra of C_2H_5I and i-C_3H_7I to decrease while a simpler spectrum grows. This occurs only in those samples which are frozen to the polycrystalline form following supercooling and not in those frozen slowly from a seed crystal, suggesting that a dissociative neutralization process may be favored by release of strain energy.

We have reported earlier[3] that n-alkyl iodides containing an even number of carbon atoms per molecule give esr spectra with an unexpectedly widespread and large number of lines following γ-irradiation in the polycrystalline state at 77°K. The purpose of the present work has been to seek an explanation of these complex spectra utilizing isotopic substitution, orientation effects, annealing studies, and radiolyses of related systems as sources of information.

Experimental Section

C_2D_5I of stated isotopic purity of $\geqq 99\%$ was obtained from Merck Sharp and Dohme Ltd. It was used both as received and after passage through a preparative gas chromatography column. The results were the same for both types of sample. $C_2H_5I^{129}$ was synthesized by the reaction $(C_2H_5)_4Sn + I_2{}^{129} \rightarrow (C_2H_5)_3SnI^{129} + C_2H_5I^{129}$, in the manner used by Iyer and Martin[4] for the synthesis of $C_3H_7I^{129}$. Research grade tetraethyltin obtained from Peninsular Chemresearch and $I_2{}^{129}$ from the Oak Ridge National

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(1) This work was supported in part by the U. S. Atomic Energy Commission (Contract AT(11-1)-32) and by the W. F. Vilas Trust of the University of Wisconsin. We are indebted to Professor R. N. Dexter of the University of Wisconsin Physics Department for substantial assistance in use of the esr equipment.

(2) Further details of this work are given in the Ph.D. thesis of H. W. Fenrick, University of Wisconsin, 1966, available from University Microfilms, Ann Arbor, Mich.

(3) H. W. Fenrick, S. V. Filseth, A. L. Hanson, and J. E. Willard, *J. Am. Chem. Soc.*, 85, 3731 (1963).

(4) R. M. Iyer and G. R. Martin in "Proceedings of the 1960 Prague Symposium on Chemical Effects of Nuclear Transformations," Vol. I, International Atomic Energy Agency, Vienna, 1961 p 283.