224. Application of the Equivalent Bond Orbital Model to the C_{2s}-Ionization Energies of Saturated Hydrocarbons

by **Gerhard Bieri, James D. Dill, Edgar Heilbronner** and **Andreas Schmelzer**

Physikalisch-chemisches Institut der Universität,
Klingelbergstrasse 80, CH-4056 Basel, Switzerland

(25.VII.77)

Summary

It is shown that the *ab initio* STO-3G treatment applied to simple saturated linear, branched and cyclic hydrocarbons, assuming standard geometries, yields orbital energies ε_j^{STO-3G} for their canonical orbitals φ_j which correlate perfectly with the observed C_{2s} ionization energies I_j^m, if *Koopmans'* approximation is accepted.

Applying the *Foster-Boys* localization procedure to these canonical orbitals φ_j leads to localized orbitals λ_μ and their corresponding *Hartree-Fock* matrix $\mathbf{F}_\lambda = (F_{\lambda,\mu\nu})$. An examination of the matrix elements $F_{\lambda,\mu\nu}$, *i.e.* of the self-energies $A_\mu = F_{\lambda,\mu\mu}$ of the localized CC- and CH-orbitals λ_μ and of the cross terms $F_{\lambda,\mu\nu}$ $(\mu \neq \nu)$ between them, leads to the conclusion that a satisfactory approximation should be obtained by setting $A_\mu = A$ for all μ, $F_{\lambda,\mu\nu} = B$ if λ_μ and λ_ν are vicinal and neglecting all other cross terms. The resulting model is nothing but the well-known equivalent bond orbital model of *Lennard-Jones & Hall*, which however can now be calibrated using the known C_{2s}-ionization energies of hydrocarbons. Due to the discrete structure and the wider range (~ 8 eV) of the C_{2s} band systems in the photoelectron spectra of these molecules this leads to a more satisfactory parametrization than using the narrower and badly resolved C_{2p} band system.

Comparison of calculated band positions using the calibrated model with observed C_{2s}-band ionization energies for a series of hydrocarbons reveals that the simple equivalent bond orbital model is better than one might have expected.

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1. Introduction. - In a series of classical papers *Lennard-Jones & Hall* [1] introduced into molecular orbital theory the concept of 'equivalent orbitals' (EO), *e.g.* orbitals χ_{xy} localized between two bonded atoms x, y of a hydrocarbon. The EO's χ_{xy} form the basis for an LCBO description of the delocalized molecular orbitals

$$\varphi_j = \sum_{xy} c_{xy,j}\,\chi_{xy} \tag{1}$$

(LCBO = Linear Combination of (equivalent) Bond Orbitals). The relevant matrix elements with respect to a defined hamiltonian $\mathscr{H}$ are the self-energies $H_{xy,xy} \equiv A_{xy}$ of the EO's χ_{xy}, the interaction elements $H_{xy,x'y'}$ between pairs of EO's χ_{xy}, $\chi_{x'y'}$ and their overlap integrals $S_{xy,x'y'}$:

$$\begin{aligned} H_{xy,xy} &= \langle \chi_{xy} | \mathscr{H} | \chi_{xy} \rangle \equiv A_{xy} \\ H_{xy,x'y'} &= \langle \chi_{xy} | \mathscr{H} | \chi_{x'y'} \rangle \\ S_{xy,x'y'} &= \langle \chi_{xy} | \chi_{x'y'} \rangle \end{aligned} \tag{2}$$

For the latter the *Hückel*-approximation $S_{xy,x'y'} = \delta_{xy,x'y'}$ is often introduced. For a detailed description of the model the reader is referred to the original papers [1], the reviews by *Daudel* [2] and by *Klopman* [3], and to the references given therein.

This model has already been used by *Hall* [4] to explain, among other things, the dependence of the first ionization potential I_1 of an alkane C_NH_{2N+2} on its size (N) and its type of branching. However, one of the difficulties that arose in the practical application of the LCBO treatment was that the number of necessary parameters, *i.e.* the self-energies A_{CC}, A_{CH} of the EO basis functions χ_{CC}, χ_{CH} and the various interaction elements $H_{CC,C'C'}$, $H_{CC,C'H'}$, ... between pairs of EO's exceeded by far the number of available experimental data. Therefore a calibration of these matrix elements could only be achieved if a certain number of *ad hoc* assumptions were introduced. Nevertheless, it was a notable success of the theory that it explained the observed trends in the first ionization energies I_1 of saturated hydrocarbons, and in particular that it introduced and stressed the importance of 'delocalized' molecular orbitals in saturated systems, a concept which, at the time, must have appeared rather strange to chemists.

With the advent of UV-photoelectron spectroscopy [5] the experimental background for an LCBO-model changed dramatically, because much more detailed information concerning the higher ionization energies I_j of molecules became available. In particular the He(Iα) photoelectron spectra of hydrocarbons [6] [7] yielded reasonably safe estimates of the ionization energies corresponding to electron ejection from orbitals belonging to what is now known as the C_{2p}-valence-shell. Although it is true that the assignment of even the simplest representatives, *e.g.* of ethane, met with difficulties [8-10] it became now possible to use this detailed information for a recalibration of the LCBO-model. In this connection the work of *Brailsford & Ford* [9], and that of *Murrell & Schmidt* [10] should be mentioned. In both cases the number of different types of equivalent interaction elements $H_{xy,x'y'}$ (*e.g.* $H_{CH,CH}$ between two vicinal EO's χ_{CH} involving the same carbon atom) has been restricted to only a few and the basis orbitals χ_{xy} have been assumed to form an orthonormal set. A simplified version of the LCBO model, based on topological and symmetry properties of the EO's χ_{xy} and their linear combinations has been proposed by *Herndon* [11] and an extension for qualitative studies by *Gimarc* [12]. Finally, *Pauzat, Ridard & Millié* [13] described an LCBO model which includes estimates for the changes in ionization energy due to electron reorganization in the radical cation and to electron correlation effects.

The major difficulty underlying all these studies is, that the C_{2p} band system in the photoelectron spectrum of an alkane consists of a series of broad, unresolved and strongly overlapping bands (in the interval from ~9 eV to ~16 eV) which it is almost impossible to deconvolute, except in the simplest cases. Notwithstanding this handicap the numerical values derived for a limited set of matrix elements by *Brailsford & Ford* [9] and by *Murrell & Schmidt* [10] are in rather good agreement with each other and they have been used with success for the interpretation of the photoelectron spectra of other hydrocarbons [14].

Thanks to the availability of efficient sources for He(II) radiation ($h\nu = 41$ eV) [15] it became possible to record photoelectron spectra of hydrocarbons which include the higher energy bands due to the ejection of electrons from orbitals of the C_{2s}-valence-shell [7] [16–18]. These bands, which occupy the spectral region from ~16 eV to ~26 eV, are well separated from each other, at least in the spectra of the lower members of the alkanes C_NH_{2N+2} and cycloalkanes C_NH_{2N}, *i.e.* those with $N \leqslant 6$. In addition there is little doubt concerning their assignment, because the irreducible representations to which the corresponding doublet states of the radical cation belong, can be deduced unambiguously on a purely qualitative level by symmetry arguments and from the nodal properties of the vacated molecular orbital. Thus the additional information now available should provide an ideal and much safer means for the recalibration of simple LCBO models. In this communication we wish to pursue this idea and to present such a reparametrized model in its simplest form.

2. Justification for a Simple Equivalent Bond Orbital Model. - To begin with we note that *ab initio* models, *e.g.* the STO-3G model [19] which we shall use here, yield rather satisfactory predictions for the photoelectron spectra of alkanes and cycloalkanes, in particular for their C_{2s} band systems, under the implicit assumption

Table 1. *Comparison of STO-3G orbital energies $\varepsilon_j^{STO\text{-}3G}$ of saturated hydrocarbons with the observed ionization energies I_j^m* (all values in eV)

$\Delta = -\varepsilon_j^{STO\text{-}3G} - I_j^m$

$I_j^{STO\text{-}3G}$ = Ionization energy obtained from the $\varepsilon_j^{STO\text{-}3G}$-value according to the regression function (3)

Hydrocarbon	$-\varepsilon_j^{STO\text{-}3G}$	I_j^m	Δ	$I_j^{STO\text{-}3G}$	$-\varepsilon_j$
CH_4	24.72	22.9	1.82	22.2	25.66[c]
C_2H_6	26.82	23.9	2.92	23.8	27.66[c]
	21.89	20.4	1.49	20.0	22.74[c]
C_3H_8	27.80	24.7	3.10	24.5	28.75[c]
	24.16	22.1	2.06	21.7	25.25[c]
	20.82	19.5	1.32	19.2	21.84[c]
n-C_4H_{10}	28.27	24.7	3.57	24.9	29.06[c]
	25.71	23.0	2.71	22.9	26.63[c]
	22.32	20.7	1.62	20.3	23.37[c]
	20.57	18.8	1.77	19.0	21.53[c]
i-C_4H_{10}	28.55	24.8	3.75	25.1	
	24.22[a]	21.9	2.32	21.8	
	19.91	18.4	1.54	18.5	
n-C_5H_{12}	28.54	24.8	3.74	25.1	28.22[d]
	26.67	23.7	2.97	23.7	26.35[d]
	23.95	21.7	2.25	21.6	23.63[d]
	21.20	19.9	1.30	19.5	20.88[d]
	20.54	18.7	1.84	19.5	20.19[d]

Hydrocarbon	$-\varepsilon_j^{STO\text{-}3G}$	I_j^m	Δ	$I_j^{STO\text{-}3G}$
i-C_5H_{12}	28.89	24.9	3.99	25.1
	25.97	23.3	2.67	23.1
	24.24	22.0	2.24	21.8
	22.17	20.4	1.77	20.2
	19.79	18.3	1.49	18.4
neo-C_5H_{12}	29.19	25.1	4.09	25.6
	24.30[b]	21.9	2.40	21.9
	18.80	17.8	1.00	17.7
cyclo-C_3H_6	29.27	26.5	2.77	25.6
	21.30[a]	19.5	1.80	19.6
cyclo-C_4H_8	29.23	25.5	3.73	25.6
	23.35[a]	21.0	2.35	21.1
	19.13	18.2	0.93	17.9
cyclo-C_5H_{10}	29.32	-	-	25.6
	25.25[a]	22.2	3.05	22.6
	19.92[a]	18.3	1.62	18.5
cyclo-C_6H_{12}	29.49	25.7	3.79	25.8
	26.26[a]	23.1	3.16	23.4
	21.47[a]	19.5	1.97	19.7
	19.76	18.1	1.66	18.4

[a] Doubly degenerate level.

[b] Triply degenerate level.

[c] Orbital energies calculated by an *ab initio* procedure using a 4.31 G basis set [18].

[d] STO-3G orbital energies obtained by *Pireaux et al.* [18].

of the validity of *Koopmans'* approximation. As an example we have listed in *Table 1* the STO-3G orbital energies $\varepsilon_j^{\text{STO-3G}}$ for the lower members of the alkanes and cycloalkanes (assuming standard geometries [20]) together with the experimentally determined ionization energies [16–18]. For the sake of comparison we have included in *Table 1* the theoretical results obtained recently by *Pireaux et al.* [18] for the same molecules, who have used a 4.31G basis set for the molecules methane to butane and the STO-3G basis for pentane. (Presumably a slightly different geometry has been assumed which accounts for the constant difference of 0.3 eV in their orbital energies relative to ours.) The linear regression function which correlates the two sets of data is:

$$\begin{aligned}-\varepsilon^{\text{STO-3G}} &= (-4.338\pm0.531)\ \text{eV} + (1.310\pm0.024)\ \text{I}_j^m \\ \text{r} &= 0.9927\end{aligned} \tag{3}$$

The standard deviations given for slope and intercept relate to 43 degrees of freedom, degenerate orbital energies having been given the appropriate weight. Note that the large standard deviation of the constant term is due to the fact that the sample ranges from 30 to 20 eV, whereas the constant relates to $\text{I}_j^m = 0$ eV.

Although the correlation is excellent as indicated both by the residual error and the correlation coefficient, it should be noted that the slope of the linear function (3) is not unity, because the difference $\Delta = -\varepsilon_j^{\text{STO-3G}} - \text{I}_j^m$ increases (linearly) with increasing ionization energy I_j^m. This was to be expected, because according to an observation by *Rosmus* [21] *Koopmans'* approximation tends to overestimate higher ionization energies by larger amounts than the lower ones. More or less independent of the theoretical model used for the SCF calculation of the neutral molecule this is due to the fact that with increasing ionization energy the electron correlation energy of the radical cation increases and finally exceeds that of the neutral parent molecule.

From the regression function given in (3) we conclude that a STO-3G treatment yields predictions for the C_{2s} photoelectron spectrum of saturated hydrocarbons which are quite satisfactory for all practical purposes both qualitatively and, within reasonable limits, quantitatively. The question to be answered is, whether such an *ab initio* calculation can be replaced for our purposes by a simple LCBO treatment without signficant loss in quality.

To this end we first transform the set of canonical orbitals $\boldsymbol{\varphi} = (\varphi_j)$ obtained for a given hydrocarbon within the STO-3G formalism into a set of orthonormal localized orbitals $\boldsymbol{\lambda} = (\lambda_\mu)$ using the *Foster-Boys* localization procedure [22]:

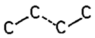
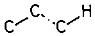
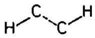
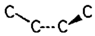
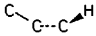
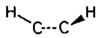
$$\boldsymbol{\lambda} = \boldsymbol{\varphi}\mathbf{L} \tag{4}$$

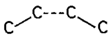
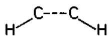
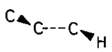
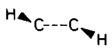
The matrix elements $F_{\lambda,\mu\nu}$ of the corresponding *Hartree-Fock* matrix $\mathbf{F}_\lambda = (F_{\lambda,\mu\nu})$ obtained from the original matrix $\mathbf{F}_\varphi = (F_{\varphi,ij})$ according to

$$\mathbf{F}_\lambda = \mathbf{L}^\dagger\ \mathbf{F}_\varphi \mathbf{L} \tag{5}$$

are listed (in part) in *Table 2*, where the following conventions have been used, $\mathscr{F}$ denoting the Fock operator:

Table 2. *Self energies and interaction matrix elements between localized λ_{CC} and λ_{CH} orbitals obtained by the* Foster-Boys *procedure [22] from* ab initio *STO-3G canonical orbitals of saturated hydrocarbons* (all values in eV). The molecules are assumed with standard geometries [20]: all systems in conformations of lowest energy; cyclobutane and cyclopentane with symmetry D_{4h} and D_{5h} respectively. The values given for each type of self-energy or interaction are the mean of the corresponding terms obtained for the particular molecule

		CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	neo-C_5H_{12}	
C—H	A_{CH}	-16.97	-16.95	-16.94	-16.93	-16.93	-16.92	-16.92	-16.92	-16.97
C—C	A_{CC}		-17.76	-17.77	-17.75	-17.79	-17.73	-17.78	-17.84	-17.80
C—C—C	$B_{CC,CC}$			-2.95	-2.95	-2.94	-2.96	-2.95	-2.93	-2.98
C—C—H	$B_{CC,CH}$		-2.91	-2.91	-2.91	-2.91	-2.91	-2.92	-2.92	-2.91
H—C—H	$B_{CH,CH}$	-2.88	-2.88	-2.88	-2.88	-2.88	-2.88	-2.88	-2.88	-2.86
	$\Gamma_{CC,CC}$[a]				+0.94		+0.94	+0.94		
	$\Gamma_{CC,CH}$[a]			+0.98	+0.98	+0.96	+0.98	+0.96	+0.95	+0.98
	$\Gamma_{CH,CH}$[a]		+1.03	+1.01	+1.01	+0.99	+1.01	+1.01		+0.99
	$\Gamma_{CC,CC}$[b]				-0.56[c]			-0.55		-0.54
	$\Gamma_{CC,CH}$[b]			-0.55	-0.55	-0.54	-0.54	-0.54	-0.53	-0.55
	$\Gamma_{CH,CH}$[b]		-0.58	-0.57	-0.57	-0.56	-0.57	-0.57		-0.56

		cyclo-C_3H_6	cyclo-C_4H_8	cyclo-C_5H_{10}	planar[f] cyclo-C_6H_{12}
C—H	A_{CH}	-17.21	-16.96	-16.86	-16.81
C—C	A_{CC}	-16.90	-17.17	-17.72	-17.70
C—C—C	$B_{CC,CC}$	-4.79	-3.44	-3.00	-2.64
C—C—H	$B_{CC,CH}$	-2.49	-2.76	-2.91	-3.00
H—C—H	$B_{CH,CH}$	-3.00	-2.90	-2.86	-2.85
	$\Gamma_{CC,CC}$[d]		-2.03	-0.98	-0.77
	$\Gamma_{CH,CH}$[d]	-0.69	-0.84	-1.12	-1.31
	$\Gamma_{CC,CH}$[e]	+0.38	+0.45	+0.45	+0.51
	$\Gamma_{CH,CH}$[e]	+0.70	+0.60	+0.54	+0.46

[a] Antiplanar conformation of λ_μ and λ_ν, *i.e.* twist angle $\theta = 180°$.

[b] Gauche conformation of λ_μ and λ_ν, *i.e.* twist angle $\theta = 60°$ or 300°.

[c] This value has been calculated for the gauche conformer of *n*-butane.

[d] Syn-planar conformation of λ_μ and λ_ν, twist angle $\theta = 0°$.

[e] Conformation of λ_μ and λ_ν with twist angle $\theta = 120°$.

[f] This hypothetical planar cyclohexane molecule of symmetry D_{6h} is included for the sake of comparison, to show the dependence of $B_{CC,CC}$ and $B_{CC,CH}$ on the bond angle.

a) The diagonal elements of $\mathbf{F}_\lambda$ are the self-energies A_μ of the localized orbitals λ_μ:

$$A_\mu \equiv F_{\lambda,\mu\mu} = \langle \lambda_\mu | \mathscr{F} | \lambda_\mu \rangle \tag{6}$$

b) The interaction elements between two localized orbitals λ_μ and λ_ν, *i.e.* the matrix elements $F_{\lambda,\mu\nu}$ of $\mathbf{F}_\lambda$, are called $B_{\mu\nu}$ or $\Gamma_{\mu\nu}$ depending on whether λ_μ and λ_ν are vicinal or geminal orbitals respectively.

$$F_{\lambda,\mu\nu} = \langle \lambda_\mu | \mathscr{F} | \lambda_\nu \rangle =: \begin{cases} B_{\mu\nu} \text{ (vicinal)} \\ \Gamma_{\mu\nu} \text{ (geminal)} \end{cases} \tag{7}$$

From the numerical values listed in *Table 2* the following conclusions can be drawn:

1) In agreement with what has been observed in many similar cases [23] all the matrix elements which refer to a certain type of orbital λ_μ or to pairs of orbitals λ_μ, λ_ν in similar relative position, exhibit a high degree of transferability. In our particular case the differences between the values of A_{CC}, of A_{CH} and of the cross-terms of same type are only a few hundreths of an eV, going from one hydrocarbon to the next. Notable exceptions are cyclopropane and to a lesser extent cyclobutane, *i.e.* those cycloalkanes in which the *Walsh* orbitals play an important role.

2) A more important result is the observation that the self-energies A_μ of the localized CC and CH orbitals λ_{CC} and λ_{CH} are roughly the same, the mean value of A_{CH} ($= -16.9$ eV) being only slightly smaller in absolute value than the mean of A_{CC} ($= -17.8$ eV).

3) The interaction matrix elements $B_{\mu\nu}$ between two vicinal localized orbitals, *i.e.* two EO's emanating from a common carbon atom are the same within 0.1 eV (or about 3 percent of their absolute value) independent of the type of λ_μ and λ_ν: $B_{CC,CC} = -2.95$ eV, $B_{CC,CH} = -2.91$ eV and $B_{CH,CH} = -2.88$ eV.

4) The interaction matrix elements $\Gamma_{\mu\nu}$ between geminal localized orbitals λ_μ, λ_ν are only $1/3$ of the value of $B_{\mu\nu}$, *i.e.* considerably smaller.

These observations strongly suggest that we should not expect significant changes in the eigenvalues ε_j, if they are obtained by diagonalizing a corresponding matrix $\mathbf{F}'_\lambda$ (and subsequent recalibration of the matrix elements) which incorporates the following simplifications:

a) All self-energies A_{CC} and A_{CH}, as well as all vicinal cross-terms $B_{CC,CC}$, $B_{CC,CH}$ and $B_{CH,CH}$ are set equal, respectively:

$$\begin{gathered} A_{CC} = A_{CH} = A \\ B_{CC,CC} = B_{CC,CH} = B_{CH,CH} = B \end{gathered} \tag{8}$$

b) All other cross-terms, *e.g.* $\Gamma_{\mu,\nu}$ *etc.*, are set equal to zero. This simplification, which at first sight may seem rather drastic, has as a consequence that our model becomes insensitive to configurational and/or conformational changes. As long as we are interested mainly in the C_{2s} molecular orbitals of hydrocarbons, this is indeed what has been observed to first order. The lack of configurational and conformational sensitivity of the C_{2s} band positions is implied in the *Hückel* formalism proposed by *Potts & Streets* [16] who use linear combinations of 2s atomic orbitals for the computation of C_{2s} molecular orbital energies of hydrocarbons, a method on which we shall comment later [24]. With these reservations we have for the 1,3-interaction terms:

$$\Gamma_{CC,CC} = \Gamma_{CC,CH} = \Gamma_{CH,CH} = 0 \tag{9}$$

This also implies that higher terms (*e.g.* the 1,4-interaction terms $\Delta_{CC,CC}$ *etc.*) are neglected *a fortiori.*

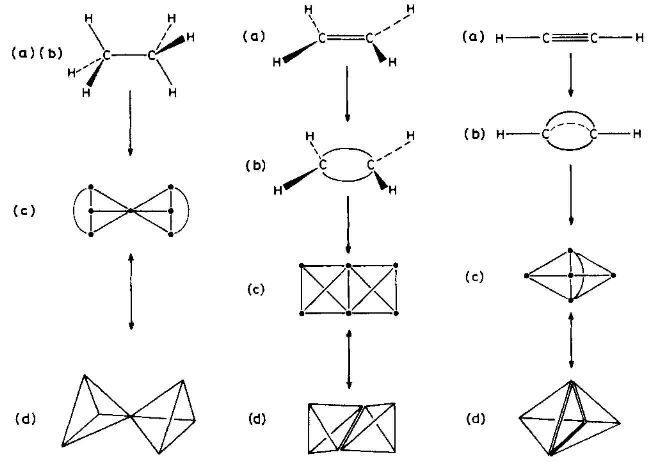
Although we are not concerned with unsaturated hydrocarbons in the present context, a few remarks are in order. If the occupied STO-3G canonical orbitals φ_j of such molecules are localized according to (4), using the *Foster-Boys* localization procedure [22] one obtains a pair of localized 'banana' orbitals λ_b, $\lambda_{b'}$ for each double bond and three 'banana' orbitals λ_b, $\lambda_{b'}$, $\lambda_{b''}$, related by a local threefold axis, for each triple bond. The self-energy A_b of the λ_b lie approximately 1.5 to 2.5 eV above A_{CH} or A_{CC} and the cross-term $B_{bb'}$ for two 'banana' orbitals bridging the same two carbon atoms is over twice as large as $B_{CC,CC}$, $B_{CC,CH}$ and $B_{CH,CH}$ found for saturated hydrocarbons. Under these conditions it becomes rather questionable whether the simplification (8) can be extended to include A_b and $B_{bb'}$, even if the known differences $A_b - A$ and $B_{bb'} - B$ are introduced *a posteriori* by first order pertubation techniques. Nevertheless, for the sake of the following argument, we assume that it is legitimate to replace A_b by A and $B_{bb'}$ by B, and we shall investigate this approximation more closely at a later stage [24].

3. Application of the Equivalent Bond Orbital Model. - Applying the simplifications (8) and (9) to a given hydrocarbon defines a matrix $\mathbf{H}_\lambda$ of the form

$$\mathbf{H}_\lambda = A\mathbf{E} + B\mathbf{T} \tag{10}$$

where **E** is the unit matrix and **T** the topological bond matrix $\mathbf{T} = (T_{\mu\nu})$, with elements $T_{\mu\nu} = 1$ if μ and ν are bonded, and $T_{\mu\nu} = 0$ otherwise. The arguments given in section 2 lead us to expect that diagonalization of $\mathbf{H}_\lambda$, where A and B are on appropriate average of the values listed in *Table 2*, will yield orbital energies ε_j which are at least acceptable first order approximations to the $\varepsilon_j^{STO\text{-}3G}$ values one would obtain from $\mathbf{F}_\lambda$. However, it is obvious that (10) is nothing but the well worked equivalent orbital model as proposed thirty years ago!

Introducing the substitution $\varepsilon_j = A + Bx_j$, the problem is reduced to solving the secular determinant $|\mathbf{T} - x\mathbf{E}| = 0$, *i.e.* calculating the characteristic values x_j of the graph $\mathfrak{G}$ corresponding to the given hydrocarbon [25]. This graph is obtained as follows: 1) To each localized equivalent orbital λ_μ is assigned a vertex μ of $\mathfrak{G}$. 2) If two localized equivalent orbitals λ_μ, λ_ν are vicinal, the vertices μ, ν of $\mathfrak{G}$ are joined by an edge $\mu\nu$. This is shown for ethane, ethylene and acetylene in the following diagram, where (a) is the formula of the molecule, (b) the equivalent formula in terms of localized orbitals λ_μ, (c) the corresponding graph $\mathfrak{G}$:



It is amusing to note that a three-dimensional representation (d) of the graphs $\mathfrak{G}$ corresponds to the classical *van't Hoff* model of these hydrocarbons *i.e.* two tetrahedra joined by a common vertex for ethane, two tetrahedra joined by a common edge for ethylene and two tetrahedra joined by a common face for acetylene. In fact, using this analogy is the simplest way of setting up the graph $\mathfrak{G}$ for more complicated hydrocarbons.

Note that all these graphs $\mathfrak{G}$ are strongly non-alternant and that their characteristic values x_j must occur in the interval $-6 \leqslant x_j \leqslant 6$, because the highest order of a vertex (*i.e.* the number of edges terminating at a given vertex) is 6, *e.g.* the central vertex in the graph (c) of ethane (see (10)).

It is now an easy task to set up the incidence matrix **T** corresponding to the graph $\mathfrak{G}$ of a hydrocarbon C_NH_M and to diagonalize it. The lowest N roots x_j ($j = 1, 2, \ldots$) should then correlate linearly with the N C_{2s}-ionization energies I_j^m if *Koopmans'* approximation is implied:

$$I_j^m = -A - Bx_j; \qquad j = 1, 2, \ldots N \tag{12}$$

The parameters A and B are those defined in (8), but it is of course of advantage to adjust them by a least squares technique.

We shall now show, that in the case of the alkanes and cycloalkanes the above model is indeed much better than one might have expected in view of its extreme simplicity.

In *Table 3* are listed the characteristic values x_j for the lowest N orbitals of the hydrocarbons C_NH_{2N+2} (alkanes) and C_NH_N (cyclo-alkanes) together with the observed ionization energies I_j^m taken from their C_{2s}-photoelectron spectra [17].

For the linear or branched (C_NH_{2N+2}) and cyclic (C_NH_{2N}) hydrocarbons listed in *Table 3*, the *Figures 1* and *2* show the correlation of the computed characteristic values x_j with the observed ionization energies I_j^m of the bands in the C_{2s}-system. Using all the points except the one for the highest ionization energy of cyclopropane ($x_j = 4.372$; $I_j^m = 26.5$ eV) and weighing each point according to the degeneracy of the orbital, the linear regression functions obtained by the usual least-squares adjustment are:

$$\begin{aligned} C_NH_{2N+2}\colon\ & I_j^m = [(16.10 \pm 0.08) + (2.11 \pm 0.03)\, x_j]\ \text{eV} \\ & r = 0.9980; \quad \phi = 27 \\ C_NH_{2N}\colon\ & I_j^m = [(15.67 \pm 0.09) + (2.19 \pm 0.03)\, x_j]\ \text{eV} \\ & r = 0.9970; \quad \phi = 27 \end{aligned} \tag{13}$$

Pooling all the data (except the $1a_1'$-ionization energy of cyclopropane) in a single regression yields:

$$\begin{aligned} & I_j^m = [(15.83 \pm 0.07) + (2.17 \pm 0.03)\, x_j]\ \text{eV} \\ & r = 0.9961; \quad \phi = 56 \end{aligned} \tag{14}$$

In (13) and (14), r is the correlation coefficient and ϕ the number of degrees of freedom on which the standard deviations of the slope and the intercept at $x_j = 0$ depend.

As is obvious from *Figure 2*, the point for the $1a_1'$-ionization energy of cyclopropane deviates from the regression (13), and thus from the pooled regression (14) by 1.1 eV, which is more than five times the standard deviation $s(I_j^m) = 0.21$ eV for the scatter of the points about the line (14). The obvious reason is, that the self-energies and the interaction matrix elements for the localized CC-bond orbitals in cyclopropane differ significantly from those of the other hydrocarbons, as is evident from the entries in *Table 2*. Therefore we were justified to eliminate this point from the least-squares treatment leading to (13) (C_NH_{2N}) and (14).

Table 3. *Characteristic values x_j and ionization energies I_j^m of the C_{2s}-type molecular orbitals of saturated hydrocarbons* (all ionization energies in eV). The symmetry labels for the orbitals of the cycloalkanes C_NH_{2N} refer to a symmetry group D_{nh} (with $n = N$), *i.e.* to the symmetry of the graph $\mathfrak{G}$ underlying the calculation of the characteristic values

Hydrocarbon	Orbital	x_j	I_j^m
CH_4	$1a_1$	3.000	22.9
C_2H_6	$1a_{1g}$	3.646	23.9
	$1a_{2u}$	2.000	20.4
C_3H_8	$1a_1$	3.925	24.7
	$1b_2$	2.791	22.1
	$2a_1$	1.552	19.5
n-C_4H_{10}	$1a_g$	4.071	24.7
	$1b_u$	3.262	23.0
	$2a_g$	2.219	20.7
	$2b_u$	1.340	18.8
i-C_4H_{10}	$1a_1$	4.133	24.8
	$1e$	2.791	21.9
	$2a_1$	1.140	18.4
n-C_5H_{12}	$1a_1$	4.155	24.8
	$1b_2$	3.555	23.7
	$2a_1$	2.717	21.7
	$2b_2$	1.859	19.9
	$3a_1$	1.228	18.7
i-C_5H_{12}	1a'	4.220	24.9
	2a'	3.368	23.3
	1a"	2.791	22.0
	3a'	2.068	20.4
	4a'	1.030	18.3
neo-C_5H_{12}	$1a_1$	4.303	25.1
	$1t_2$	2.791	21.9
	$2a_1$	0.697	17.8
cyclo-C_3H_6	$1a_1'$	4.372	26.5
	$1e'$	1.732	19.5
cyclo-C_4H_8	$1a_{1g}$	4.372	25.5
	$1e_u$	2.562	21.0
	$1b_{1g}$	1.000	18.2
cyclo-C_5H_{10}	$1a_1'$	4.372	-
	$1e_1'$	3.105	22.2
	$1e_2'$	1.265	18.3
cyclo-C_6H_{12}	$1a_{1g}$	4.372	25.7
	$1e_{1u}$	3.449	23.1
	$1e_{2g}$	1.732	19.5
	$1b_{1u}$	1.000	18.1
cyclo-C_7H_{14}	$1a_1'$	4.372	-
	$1e_1'$	3.675	23.7
	$1e_2'$	2.183	20.6
	$1e_3'$	1.135	18.1
cyclo-C_8H_{16}	$1a_{1g}$	4.372	-
	$1e_{1u}$	3.828	23.9
	$1e_{2g}$	2.562	21.4
	$1e_{3u}$	1.414	18.8
	$1b_{1g}$	1.000	17.7

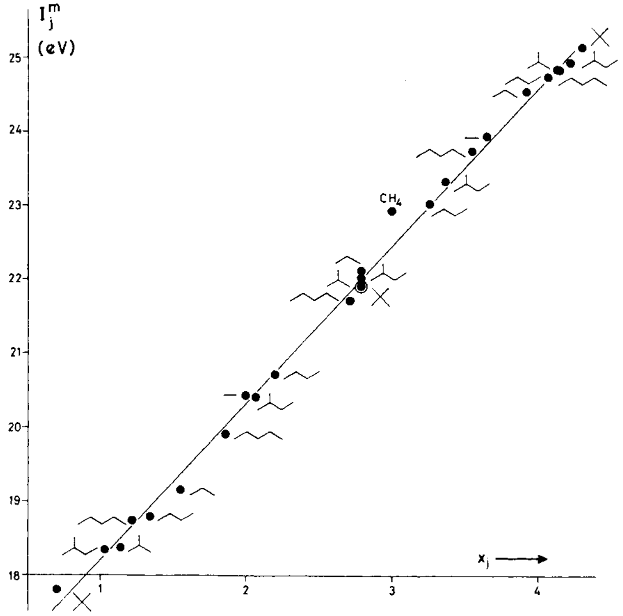


Fig. 1. *Linear regression (13) of observed C_{2s}-ionization energies I_j^m on the characteristic values x_j for linear and branched hydrocarbons C_NH_{2N+2}*

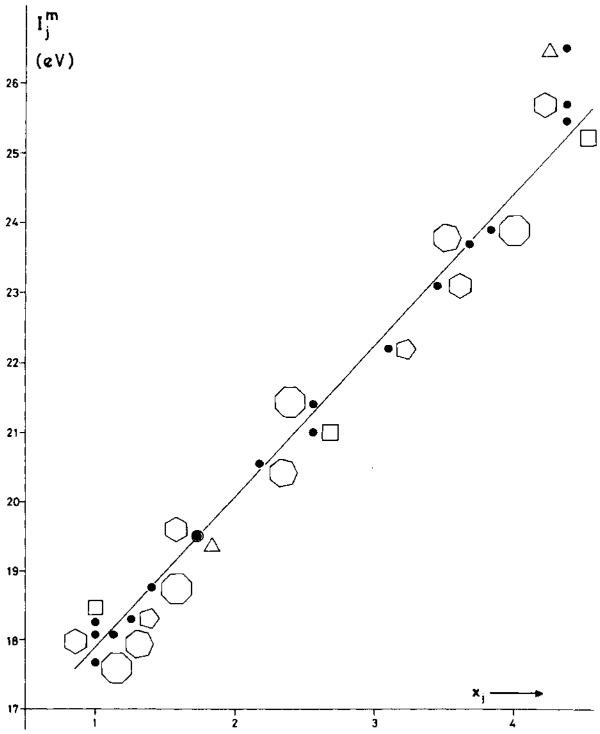


Fig. 2. *Linear regression (13) of observed C_{2s}-ionization energies I_j^m on the characteristic values x_j for cycloalkanes C_NH_{2N}*

4. Discussion of the Results. - 1) Obviously the most remarkable feature of the linear regressions (13), (14) the first two of which are shown graphically in *Figures 1* and *2*, is the closeness of fit, which is best appreciated by looking at the variances $V(I_j^m)$ about the regressions: (13) C_NH_{2N+2}: $V(I_j^m)=0.021$ eV^2; C_NH_{2N}: $V(I_j^m)=0.036$ eV^2; (14) $V(I_j^m)=0.044$ eV^2. The latter one should be compared to the variance about the regression if the $\varepsilon_j^{\text{STO-3G}}$ values are used as independent variables. Based on the data listed in *Table 1* we find in this case $V(I_j^m)=0.088$ eV^2, which is significantly larger, even on a 99 percent security level, than the above value obtained for regression (14). Thus we are confronted with the rather unexpected result, that our naive equivalent orbital model yields a closer fit than the STO-3G results although both contain two least-squares adjusted parameters. This may well be due to the particular choice of the sample used for calibration and is presumably not generally true. However, from a pragmatic point of view there is, for the moment, nothing to choose between an STO-3G or a simple equivalent orbital model, as long as we stick to hydrocarbons of the kind used for their calibration.

If (14) is used for predictive purposes, the lower and upper 90 percent confidence limits deviate from the value computed according to (14), by approximately 0.3_5 eV.

2) The parameters A and B of (12) and (14), *i.e.* the mean self-energies $A=-15.8$ eV and mean vicinal cross-terms $B=-2.2$ eV defined in (8) should be compared to those derived by *Brailsford & Ford* [9] and by *Murrell & Schmidt* [10] who calibrated their equivalent orbital model using only the C_{2p}-band of propane, *n*-butane, *n*-pentane and *n*-hexane, or of methane, ethane, propane, iso-butane and neo-pentane respectively. They obtained:

	[9]	[10]	this work
A_{CC}	−16,3 eV	−16,4 eV	−15,8 eV
A_{CH}	−15,9 eV	−15,6 eV	
$B_{CC,CC}$	− 1,3 eV	−	−2,2 eV
$B_{CC,CH}$	− 1,9 eV	− 2,3 eV	
$B_{CH,CH}$	− 2,4 eV	− 2,2 eV	

(15)

In this context it should be mentioned that the above authors included some of the $\Gamma_{\mu\nu}$-terms in their calibration, which we have neglected (see (9)). Taking this difference into account, the overall agreement is rather satisfactory, especially if one considers that the parametrizations described in refs. [9] and [10] have been carried out within an ionization energy range well separated from that used in the present investigation. This strongly suggests that our model could be easily adjusted to include the C_{2p}-band system of hydrocarbons, through the use of first-order perturbation techniques. The inclusion of such perturbation is necessary because our graphs $\mathfrak{G}$ for saturated hydrocarbons yield a highly degenerate characteristic value $x=+1$, corresponding to a set of equally degenerate molecular orbitals of the C_{2p}-manifold with orbital energies $\varepsilon=A-B$. Obviously this accidental degeneracy must be lifted if we wish to use our model for a rationalization of the C_{2p}-band system.

3) Although the regressions shown in *Figures 1* and *2* indicate that our equivalent bond orbital model is rather successful if used for an analysis of the C_{2s}-band structure of hydrocarbons, they do not fully reveal the surprising quality of this naive approach. In *Figure 3* we present, one above the other, the correlation diagrams obtained separately for the experimental ionization energies I_j^m and for the characteristic values x_j of the examples given in *Table 3*. It is remarkable that even fine details in relative shifts of the ionization energies I_j^m are faithfully matched by shifts of the corresponding characteristic values x_j, which are of course purely topological in origin. For example, attention is drawn to the upward drift of the orbital energies associated with the central band of the C_{2s}-band system of the odd *n*-alkanes, the characteristic trend of the energies of the lowest and highest C_{2s}-orbital of the branched alkanes, or the agreement of the two correlation diagrams obtained for the cycloalkanes which are practically superimposable.

Consequently one is led to the conclusion, that for reasons unknown, the approximation (8) is justified, at least for simple alkanes, and that this equivalent orbital model allows the computation of much better expectation values for C_{2s}-ionization energies than one might have expected. That there are limitations to its applicability is shown by the results derived for cyclopropane (see *Figure 2*), but their origin is well understood in this particular case.

4) If the regression (14) is used in conjunction with the characteristic values x_j derived from the graph 𝔊, then the ionization energies I_j^m (calc.) collected in *Table 4*

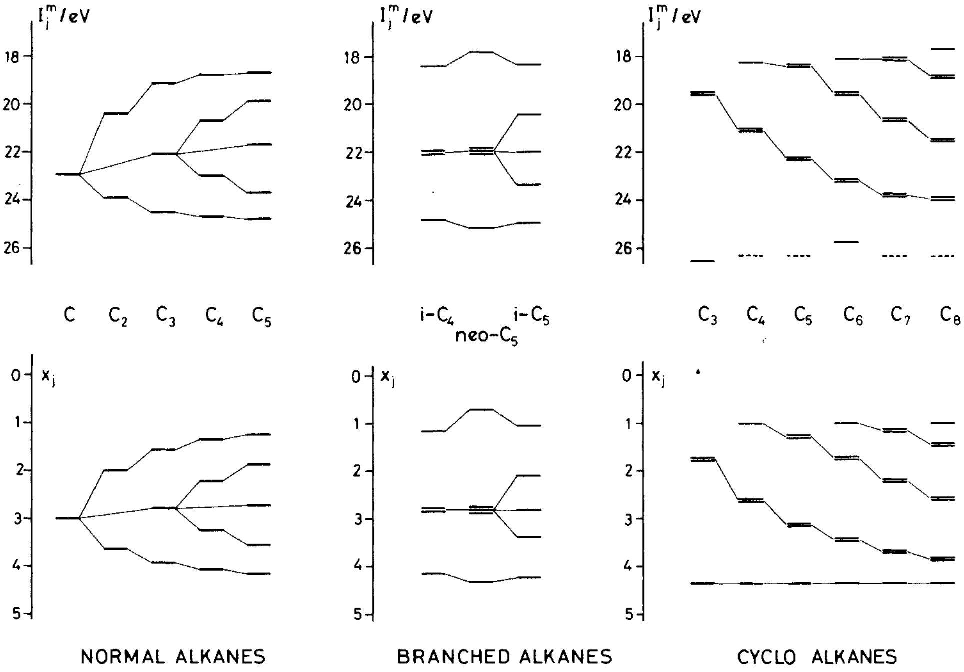
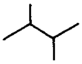
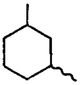
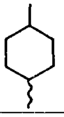
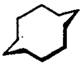
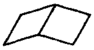
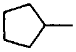
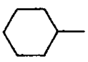
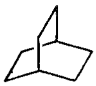
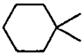
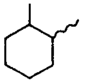
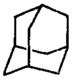


Fig. 3. *Comparison of the experimental correlation diagrams of the C_{2s}-ionization energies I_j^m with the corresponding correlation diagrams of the characteristic values x_j*

are computed for a series of sixteen saturated hydrocarbons not included in the calibration of our equivalent orbital model. The reason for not having taken them into consideration is that the experimental data I_j^m (exper.) [17] are not as good as for the original sample presented in *Table 3*. The comparison of matched pairs I_j^m (exper.) *vs.* I_j^m (calc.) does not contradict and in fact supports the above statements

Table 4. *Comparison of observed C_{2s}-ionization energies I_j^m of hydrocarbons with those calculated, using the characteristic values x_j of the corresponding graph 𝔊 and the regression function (14)* (all values in eV). It should be mentioned that some of the experimental data given for the larger systems are uncertain, *cf.* [17]

Hydrocarbon	I_j^m(exp.)	I_j^m(calc.)	Hydrocarbon	I_j^m(exp.)	I_j^m(calc.)
2,3-dimethylbutane 	---- 23.5 21.9 21.9 19.8 17.9	25.2 23.5 21.9 21.9 19.7 17.6	1,3-dimethylcyclohexane 	cis trans ---- ---- ---- ---- 23.5 23.5 21.5 21.7 21.3 21.5 19.3 19.4 18.6 18.8 18.1 17.5	 25.6 24.1 23.6 21.7 21.6 19.3 18.6 17.5
n-hexane 	---- ---- 22.4 20.7 19.3 18.7	25.0 24.0 22.5 20.9 19.4 18.4	1,4-dimethylcyclohexane 	cis trans ---- ---- ---- ---- 23.0 22.8 22.3 22.3 20.9 20.7 19.7 19.7 18.7 18.7 17.5 18.2	 25.6 24.2 23.3 22.3 21.1 19.6 18.5 17.5
n-heptane 	---- 24.3 23.0 21.5 20.1 19.1 18.6	25.0 24.2 23.1 21.6 20.2 19.0 18.3	cyclodecane 	---- 24.3 24.3 22.5 22.2 20.2 20.2 19.0 18.8 ----	25.3 24.5 24.5 22.6 22.6 20.3 20.3 18.6 18.6 18.0
n-octane 	---- 23.7 23.3 22.2 20.7 19.7 18.9 18.6	25.1 24.5 23.5 22.3 21.0 19.8 18.8 18.2	bicyclo[2.2.0]hexane 	---- 23.4 21.5 19.9 19.3 16.6	26.0 23.3 21.9 20.3 19.6 17.0
methylcyclopentane 	---- 23.2 22.3 20.9 18.3 18.3	25.5 23.3 22.6 21.2 18.6 17.9	norbornane 	---- ---- 22.7 22.0 19.4 18.2 17.6	25.9 23.3 23.0 22.3 19.6 17.8 17.7
methylcyclohexane 	---- 23.8 23.2 21.3 19.5 18.8 18.0	25.5 23.8 23.3 21.7 19.6 19.1 17.7	bicyclo[2.2.2]octane 	---- (23.1) 23.1 23.1 19.5 19.5 19.0 ----	25.8 23.6 23.3 23.3 19.6 19.6 18.6 17.3
1,1-dimethylcyclohexane 	---- 24.0 23.0 21.5 21.5 19.4 18.6 17.1	25.6 24.1 23.3 21.9 21.6 19.6 18.8 17.0	quadricyclane 	---- 23.5 23.5 20.3 18.0 17.6 16.9	26.9 23.7 22.7 20.8 18.1 17.9 17.2
1,2-dimethylcyclohexane 	cis trans ---- ---- ---- ---- 23.5 23.7 21.9 21.9 21.0 21.0 19.2 19.0 18.9 19.0 17.3 18.1	 25.6 23.9 23.7 22.2 21.1 19.2 19.0 17.3	adamantane 	---- 23.6 21.0 18.8 17.1	26.1 23.9 x 3 21.4 x 2 18.5 x 3 17.0

concerning the predictive qualities of the model. However, one should realize that such comparisons of two ordered arrays, *i.e.* I_j^m (exper.) and I_j^m (calc.) within each molecule, leads by necessity to high correlations and therefore the agreement might not be as significant as it seems to be.

This work is part 108 of project No. 2.518-0.76 of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.* Part 107, see [17]. We acknowledge financial support from *Ciba-Geigy SA, Sandoz SA* and *F. Hoffmann-La Roche & Co. SA*, Basel.

REFERENCES

[1] *J. E. Lennard-Jones,* Proc. Roy. Soc. *A198,* 1, 14 (1949); *G. G. Hall & J. E. Lennard-Jones,* Proc. Roy. Soc. *A202,* 155 (1950), *A205,* 357 (1951); *G. G. Hall,* Proc. Roy. Soc. *A202,* 166 (1950); *J. E. Lennard-Jones & G. G. Hall,* Trans. Farad. Soc. *48,* 581 (1952).

[2] *R. Daudel,*'Structure Electronique des Molécules', Gauthier-Villar, Paris 1962; p. 123 to 130.

[3] *G. Klopman,* Tetrahedron *19,* Suppl. 2, 111 (1963).

[4] *G. G. Hall,* Proc. Roy. Soc. *A205,* 541 (1951); Trans. Farad. Soc. *49,* 113 (1953).

[5] *M. I. Al-Joboury & D. W. Turner,* J. chem. Soc. *1963,* 5141; *F. I. Vilessov, B. C. Kurbatov & A. N. Terenin,* Dokl. Akad. Nauk SSSR *138,* 1329 (1962).

[6] *D. W. Turner, C. Baker, A. D. Baker & C. R. Brundle,* 'Molecular Photoelectron Spectroscopy', Wiley-Interscience, London 1970.

[7] *A. W. Potts, H. J. Lempka, D. G. Streets & W. C. Price,* Phil. Trans. *A268,* 59 (1970); *A. W. Potts, T. A. Williams & W. C. Price,* Farad. Disc. *54,* 103 (1972); and references given therein.

[8] *C. Sandorfy,* in 'Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet', Reidel Publishing Co., Dordrecht 1974; *A. Richartz, R. J. Buenker, P. J. Bruna & S. P. Peyerimhoff,* Mol. Physics *33,* 1345 (1977).

[9] *D. F. Brailsford & B. Ford,* Mol. Physics *18,* 621 (1970).

[10] *J. N. Murrell & W. Schmidt,* Trans. Farad. Soc. *68,* 1709 (1972).

[11] *W. C. Herndon,* Chem. Physics Letters *10,* 460 (1971).

[12] *B. M. Gimarc,* J. Amer. chem. Soc. *95,* 1417 (1972).

[13] *F. Pauzat, J. Ridard & Ph. Millié,* Mol. Physics *24,* 1039 (1972).

[14] *W. Schmidt & B. T. Wilkins,* Angew. Chem. *84,* 168 (1972); *W. Schmidt,* Tetrahedron *29,* 2129 (1973).

[15] *J. A. R. Samson,* Techniques in Vacuum Ultraviolet Spectroscopy, John Wiley & Sons, London 1967; *F. Burger & J. P. Maier,* J. Electron Spectrosc. *5,* 783 (1974).

[16] *A. W. Potts & D. G. Streets,* J. chem. Soc. Faraday II, *1974,* 875; *D. G. Streets & A. W. Potts,* ibid. *1974,* 1505.

[17] *G. Bieri, F. Burger, E. Heilbronner & J. P. Maier,* Helv. *60,* 2213 (1977).

[18] *J. J. Pireaux, S. Svensson, E. Basilier, P. A. Malmqvist, U. Gelius, R. Caudano & K. Siegbahn,* Phys. Rev. A*14,* 2133 (1976).

[19] *W. J. Hehre, R. F. Stewart & J. A. Pople,* J. chem. Physics *51,* 2657 (1969); *W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton & J. A. Pople,* Program No. 236, QCPE, Bloomington, Indiana.

[20] *J. A. Pople & D. L. Beveridge,* 'Approximate Molecular Orbital Theory', McGraw-Hill Book Company, New York 1970.

[21] *P. Rosmus,* private communication.

[22] *J. M. Foster & S. F. Boys,* Rev. mod. Physics *32,* 300 (1969).

[23] *O. Chalvet, R. Daudel, S. Diner & J. P. Malrieu,* 'Localization and Delocalization in Quantum Chemistry', D. Reidel Publishing Company, Dordrecht 1975; and references given therein.

[24] *J. D. Dill, A. Schmelzer & E. Heilbronner,* to be published.

[25] *D. H. Rouvray,* 'The Topological Matrix in Quantum Chemistry', in: *A. T. Balaban,* 'Chemical Applications of Graph Theory', Academic Press, London-New York-San Francisco 1976.