

CCA-1506

YU ISSN 0011-1643

UDC 541

Original Scientific Paper

## The Equivalent Bond Orbital Model Revisited: I. Orbitals, Orbital Energies and PE Spectra of Saturated Hydrocarbons

Evi Honegger, Zhong-zhi Yang\*, and Edgar Heilbronner

Physikalisch-Chemisches Institut, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

Received December 6, 1983

The EBO model, originally proposed by Lennard-Jones and Hall, many years ago, is reexamined using localized orbitals (LMO) stemming from SCF *ab initio* calculations. It is found that only a limited set of matrix elements is needed to build a *Fock* matrix  $F_{\lambda}$  (in localized basis) the diagonalization of which yields orbital energies of sufficient precision for use in the assignment of photoelectron spectra within *Koopmans* approximation. The model so obtained can be easily parametrized with respect to a given calibration set, if the relative size of the off-diagonal elements suggested by the *ab initio* calculation is conserved. It is argued that such EBO models, which are essentially of Hückel-type, are necessary for the qualitative or semi-quantitative rationalization of experimental and theoretical data (from more sophisticated calculations). Some of the more important limitations of LMO-based EBO models are discussed.

### I. INTRODUCTION

The extension of Hückel type treatments to sigma systems has a long and well known history. These treatments are independent electron models using an orthonormal basis and interaction matrix elements restricted to nearest neighbours only. Presumably the most attractive approximation of this kind, proposed many years ago by Hall and Lennard-Jones<sup>1</sup> is the equivalent bond orbital model which has been used, with variations, mainly to rationalize »one electron properties«, such as the ionization energies of organic molecules. The reader is referred to work by Hall<sup>2</sup>, Lorquet<sup>3</sup>, Brailsford and Ford<sup>4</sup>, Herndon<sup>5</sup>, Murrell and Schmidt<sup>6</sup>, and by Gimarc<sup>7</sup>, as well as the references given therein.

In this and the following contributions we endeavour to construct once more such a Hückel-type molecular orbital treatment as an aid for the assignment of photoelectron (PE) spectra of organic (C, H, N, O) compounds, to be used within the usual correlation techniques<sup>8</sup>, assuming the applicability of *Koopmans*' theorem<sup>9</sup>. In this endeavour we follow the ideas developed by the authors quoted above, albeit with an important difference.

In previous attempts, all of the necessary matrix elements have been calibrated by comparison with a set of experimental data, *e. g.* the ionization

\* Permanent address: Theoretical Chemistry Institute, Jilin University, Chang Chun, Jilin, People's Republic of China.

energies derived from PE spectra, under the implicit assumption that the values of these energies and the corresponding radical cation states of the ionization products are accurately known. However, evidence accumulated in the meantime has revealed that this information was not and is not always known with the necessary accuracy that had been assumed. On the other hand it has been observed that *ab initio* models using a STO basis yield rather reliable predictions even if a minimal basis is used, *e. g.* for hydrocarbons. This is particularly true for the relative spacings of the PE bands, even if their absolute position is shifted with respect to the observed values. Thus one might expect that a judicious mixture of experimental and theoretical data, the latter relating to localized orbitals stemming from *ab initio* calculations is liable to yield in a rather straightforward manner a much improved model treatment, which can be used with some confidence for the interpretation and rationalization of PE spectra by performing what is in essence a HMO type calculation.

For the present we limit ourselves to saturated hydrocarbons only. This will allow us to discuss in some detail the procedure leading to such models and to review, by comparison, the previous attempts.

## II. THE CALIBRATION SET

In analogy to the work mentioned above, we shall need a calibration set of hydrocarbon PE spectra to develop our model. We limit this set to the saturated hydrocarbons ( $C_nH_m$ ) methane (1), ethane (2), propane (3), butane (4), isobutane (5) and cyclohexane (6), although the He(I) and He(II) PE spectra of many others are known. The reason for this restriction is that the PE spectra of the higher alkanes  $C_nH_{2n+2}$  ( $n > 4$ ) and cycloalkanes  $C_nH_{2n}$  ( $n > 6$ ) consist of a considerable number of strongly overlapping bands from which no significant information about their individual positions can be deduced by deconvolution. (The smaller cycloalkanes with  $n = 3$  or 4 will be discussed separately because of the special features involved). In fact even for the limited calibration set mentioned above the exact values of the band positions, *i. e.* the ionization energies  $I_j^m$  corresponding to the positions of the band maxima, are affected with rather wide limits of error.

The pioneering work in this particular field of saturated hydrocarbon PE spectroscopy is due to Price and his coworkers<sup>10-12</sup> who were the first to measure and interpret the He(II) spectra of hydrocarbons. They noted that these spectra present two clearly separated regions, the first terminating around 15 eV to 18 eV and the second extending from this value to  $\sim 30$  eV. The former series of bands is due to the ejection of an electron from outer valence orbitals dominated by the 2*p* atomic orbitals of the carbon atoms and by the hydrogen 1*s* orbitals, the second series of bands is similarly associated with inner valence orbitals dominated by the carbon 2*s* atomic orbitals. Therefore it seemed appropriate to name the two spectral regions the 2*p*- and the 2*s*-region, respectively<sup>10,11</sup>. By analogy we call the corresponding set of orbitals the 2*p*- and 2*s*-manifold.

Table I summarizes the available information about our calibration set. To let the reader develop a feeling for the limits of error which must neces-

TABLE I  
 Band Positions  $I_i^m$  of the He(I) and He(II) PE Spectra of Methane, Ethane, Propane, Butane, Isobutane and Cyclohexane.  
 All Values are in eV. (Apart from the References Given, the Reader is also Referred to References 13, 17, 19, and 20.)

Methane			Ethane								
Bd. Orb.	14	Ref.	Bd. Orb.	14	16	12	15				
① $1t_2$	$\left\{ \begin{array}{l} 13.6 \\ 14.4 \\ (15.0) \end{array} \right\}$	$\left\{ \begin{array}{l} 13.6 \\ 14.4 \\ 15.0 \end{array} \right\}$	① $1e_g$	$\left\{ \begin{array}{l} 11.99 \\ 12.70 \\ 13.5 \end{array} \right\}$	$\left\{ \begin{array}{l} 12.0 \\ 12.7 \\ 15.0 \\ 15.8 \end{array} \right\}$	$\left\{ \begin{array}{l} 12.0 \\ 12.7 \\ 15.0 \\ 15.8 \end{array} \right\}$	$\left\{ \begin{array}{l} 12.69 \\ 12.69 \\ 15.35 \end{array} \right\}$				
								② $3a_{1g}$	$\left\{ \begin{array}{l} 15.15 \\ 15.9 \end{array} \right\}$	$\left\{ \begin{array}{l} 15.0 \\ 15.8 \end{array} \right\}$	$\left\{ \begin{array}{l} 15.0 \\ 15.8 \end{array} \right\}$
								③ $1e_u$			
② $2a_1$	22.9	22.91	④ $2a_{2u}$	20.1	20.4	20.42	20.42				
			⑤ $2a_{1g}$		23.9	23.9	23.91				

Propane			n-Butane														
Bd. Orb.	Ref.			Bd. Orb.	Ref.												
	14	16	6		14	16	12	15	18								
① 2b <sub>1</sub>	11.51	11.5	11.5	① 7a <sub>g</sub>	11.09	11.2											
② 6a <sub>1</sub>	12.14	12.1	12.1	② 2b <sub>g</sub>	11.66	11.7											
③ 4b <sub>2</sub>	(12.6)	12.6	12.7	③ 2a <sub>u</sub>	(12.3)	12.5	12.1										
④ 1a <sub>2</sub>	13.53	13.5	13.5	④ 6a <sub>g</sub>	12.74	12.5											
⑤ 3b <sub>2</sub>	(14.2)	14.1	14.1	⑤ 6b <sub>u</sub>	(13.2)	13.8											
⑥ 5a <sub>1</sub>	15.33	15.2	15.3	⑥ 5b <sub>u</sub>	(14.2)	14.2											
⑦ 1b <sub>1</sub>	15.85	16.0	16.0	⑦ 1b <sub>g</sub>	14.59	15.0											
				⑧ 5a <sub>g</sub>	(15.0)	15.6	15.0										
				⑨ 1a <sub>u</sub>	15.99	16.1											
				⑩ 4b <sub>u</sub>			18.8	19.11									
⑧ 4a <sub>1</sub>		19.5 <sup>a</sup>	19.15	⑪ 4a <sub>g</sub>			20.7	20.81									
⑨ 2b <sub>2</sub>		22.1 <sup>a</sup>	22.1	⑫ 3b <sub>u</sub>			23.0	23.00									
⑩ 3a <sub>1</sub>		24.7 <sup>a</sup>	24.5	⑬ 3a <sub>g</sub>			24.7	24.73									

<sup>a</sup> Reference 18.

Isobutane				Cyclohexane			
Bd. Orb.	Ref.			Bd. Orb.	Ref.		
	14	12	6		14	12	18
① 6a <sub>1</sub>	11.13		11.4	① 4e <sub>g</sub>	10.32		10.3
② 5e	11.7 (12.1)		12.1	② 4a <sub>1g</sub>	10.93		10.9
③ 1a <sub>2</sub>	12.85		12.8	③ 4e <sub>u</sub>	11.38		11.4
④ 4e	13.52		13.4	④ 1a <sub>1u</sub>	11.9		11.9
	13.91			⑤ 3e <sub>u</sub>	12.94		12.2
⑤ 3e	14.86		14.9	⑥ 3e <sub>g</sub>	12.94		12.9
	15.3			⑦ 3a <sub>2u</sub>	14.62		14.6
⑥ 5a <sub>1</sub>	15.95		16.0	⑧ 3a <sub>1g</sub>	14.62		15.0
					16.16		16.2
⑦ 4a <sub>1</sub>	18.37			⑨ 2b <sub>1u</sub>		18.06	
⑧ 2e	21.9			⑩ 2e <sub>2g</sub>		19.49	
⑨ 3a <sub>1</sub>	24.8			⑪ 2e <sub>1u</sub>		23.1	
				⑫ 2a <sub>1g</sub>		25.7	

sarily affect the proposed band positions  $I_j^m$  we have digitized the available PE spectra and collected their computer plots on a common scale in Figures 1 to 3.

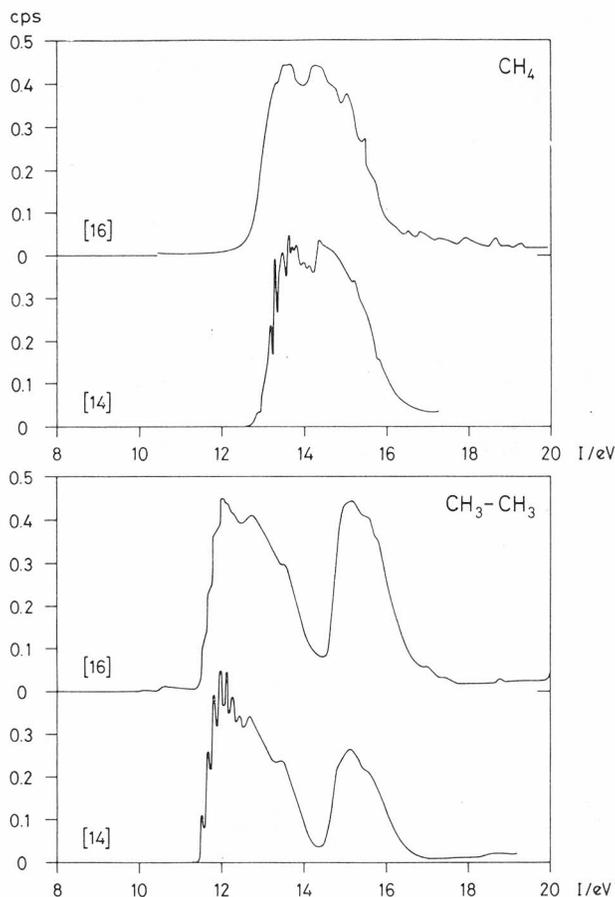


Figure 1. Computer plots of digitized PE spectra of methane and ethane. Original data from refs. 14 and 16.

### Comments

The numbering  $(j)$  of the individual bands in Table I assumes one band per state  $\tilde{X}, \tilde{A}, \tilde{B}, \dots$  of the radical cation. Thus a single  $(j)$  is assigned to doubly ( $e$ ) or triply ( $t$ ) degenerate energy levels although the corresponding band is usually split into recognizable subbands by the *Jahn-Teller* effect. For simplicity a given radical cation state  $\tilde{X}, \tilde{A}, \tilde{B}, \dots$  is characterized by the vacated molecular orbital  $\varphi_j^{-1}$ , i. e. the orbital which determines the dominant *Koopmans* configuration.

$$\begin{aligned}
 {}^2\bar{\Phi}_j &= \left\| \dots \varphi_{j-1} \overline{\varphi_{j-1}} \varphi_j \overline{\varphi_{j+1}} \varphi_{j+1} \overline{\dots} \right\| \\
 {}^2\bar{\Phi}_j &= \left\| \dots \varphi_{j-1} \overline{\varphi_{j-1}} \overline{\varphi_j} \varphi_{j+1} \overline{\varphi_{j+1}} \dots \right\|
 \end{aligned}
 \tag{1}$$

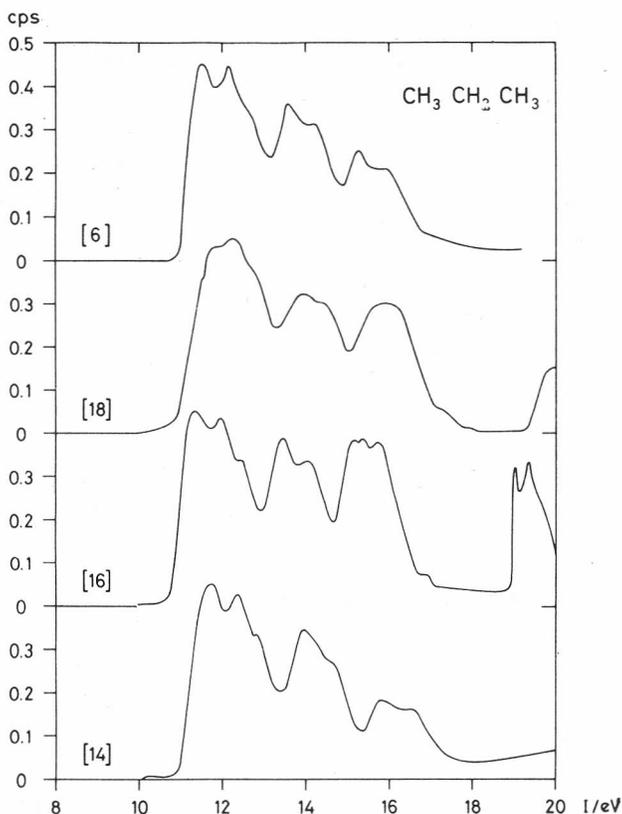


Figure 2. Computer plots of digitized PE spectra of propane. Original data from refs. 6, 14, 16, and 18.

*Methane (1).* — Due to the high  $T_d$  symmetry of this molecule the state sequence of its radical cation  $\text{CH}_3^+$  ( $1^+$ ) is uniquely determined. However, the  $1t_2^{-1}$  band is split by the *Jahn-Teller* effect<sup>21</sup> into a band system with two (three?) recognizable maxima, extending over a range of  $\sim 2.5$  eV. The values quoted in Table I refer to these maxima. The centroid of the band system is assumed to lie close to  $\sim 14.4$  eV. For lack of better information, this is the value we have used for calibration purposes.

*Ethane (2).* — In its preferred staggered conformation this molecule has  $D_{3d}$  symmetry. Notwithstanding the fact that the four highest occupied orbitals (cf. 22) and thus the four *Koopmans* configurations which dominate the states  $\tilde{X}$ ,  $\tilde{A}$ ,  $\tilde{B}$ ,  $\tilde{C}$  of  $\text{CH}_3\text{CH}_3^+$  ( $2^+$ ) belong to different irreducible representations of  $D_{3d}$ , the sequence of the first two bands ( $1e_g^{-1}$ ,  $3a_{1g}^{-1}$ ) is not well established for reasons that have been discussed by Richartz *et al.*<sup>23</sup>. In view of this uncertainty and because of the small split one can assume for all practical purposes that these two states are (almost) accidentally degenerate with a common value of 12.7 eV. We note in passing that the calculations by Kimura *et al.*<sup>14</sup> are

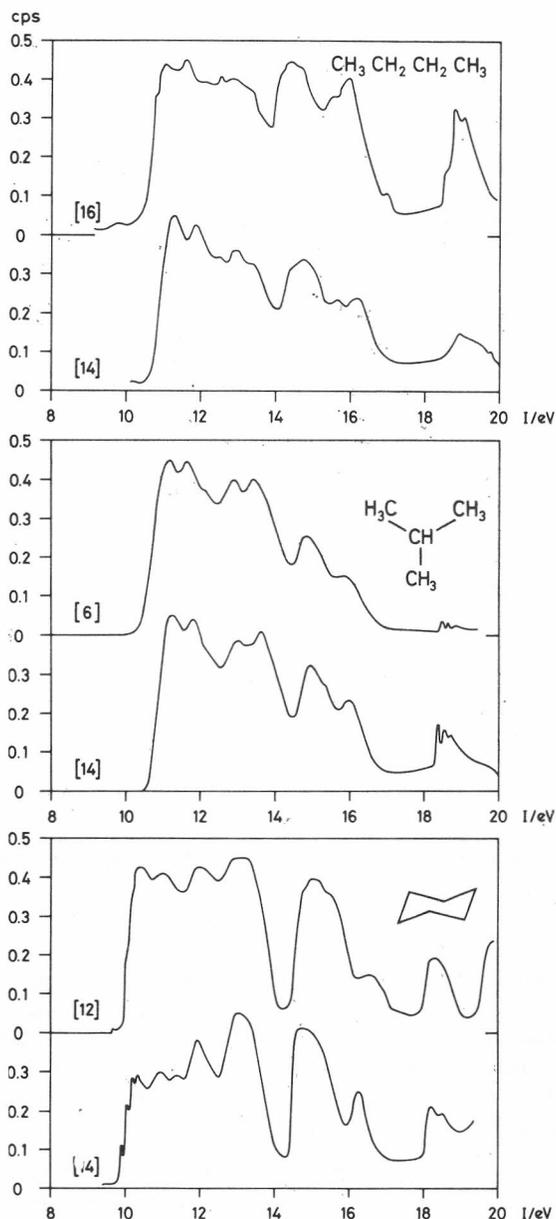
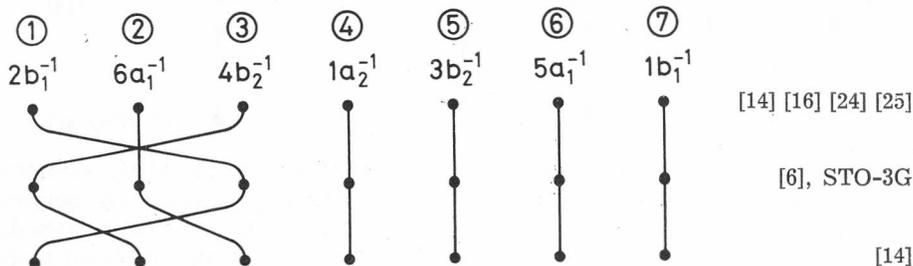


Figure 3. Computer plots of digitized PE spectra of butane, isobutane and cyclohexane. Original data from refs. 6, 12, 14, and 16.

quoted as having been performed for  $D_{3h}$  symmetry (eclipsed conformation), but the labels given by these authors belong neither to  $D_{3h}$ , nor  $D_{3d}$ .

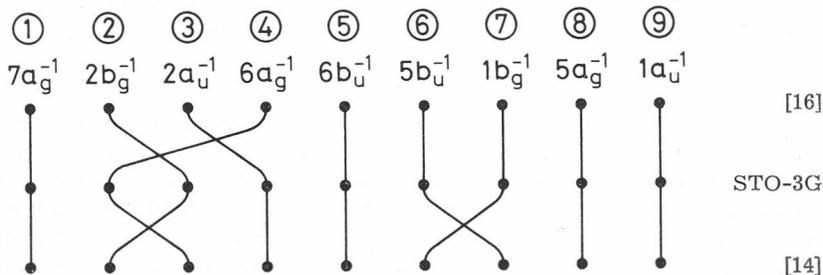
*Propane (3).* — The coordinate system of this molecule, which belongs to the  $C_{2v}$  group, has been oriented with the  $x$  axis perpendicular to the plane

containing the three carbon atoms and to the  $C_2(z)$  axis. All partial conformations are assumed staggered. The band assignments proposed by the different authors compare as follows ( $2p$  manifold only):



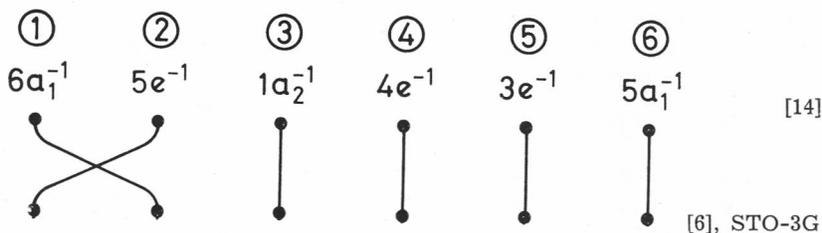
Kimura *et al.*<sup>14</sup> proposed two assignments: the first one (top line) stems from a SCF [6-31G], the second (bottom line) from a CI [6-31G] calculation. If taken at face value and not giving preference to any of the theoretical treatments used, this would mean that the assignment of the first three states is uncertain within a range  $\sim 1.2$  eV.

*Butane* (4). — The preferred conformation of butane is antiplanar with all local conformations staggered, *i. e.* symmetry  $C_{2h}$ . Note that the assignment presented by Kimura *et al.*<sup>14</sup> is only with reference to an assumed  $C_s$  symmetry. However, from the orbital diagrams given in Ref. 14 one can deduce the assignment under  $C_{2h}$  (bottom line below). Depending on the theoretical procedure used for the interpretation of the PE spectrum of butane the assignments vary as follows ( $2p$  manifold only):



The assignment given by Bieri and Åsbrink<sup>16</sup> is quoted as being based on a STO-3G calculation. However, we are not able to reproduce the values given, which differ more from ours than could be expected for a change of geometry within reasonable limits. The experimental values quoted by us in Ref. 18 for  $I_j^m$  of butane with  $j = 5, 6, 7$  and  $8$  are misprinted and have to be shifted by 1.00 eV, as indicated in Table I.

*Isobutane* (5). — For this molecule of  $C_{3v}$  symmetry Murrell and Schmidt<sup>6</sup> have given both the PE spectrum and corresponding ionization energies. However, the latter do not seem to correspond to the band maxima of the spectrum presented by these authors. For consistency we have therefore reevaluated the  $I_j^m$  values which are given in Table I (see also Ref. 18). The different assignments given for this PE spectrum ( $2p$  manifold only) compare as follows:



*Cyclohexane* (6). — If all the bond angles of this molecule of  $D_{3d}$  symmetry were tetrahedral ( $109^\circ 27'$ ), then all local conformations would be perfectly staggered. However, the CCC bond angles are slightly larger than tetrahedral ( $111.5^\circ$ )<sup>26</sup> and as a consequence the molecule is flatter than the idealized model, with local conformations deviating somewhat from pure gauche towards a syn periplanar one. In the following we have neglected these deviations from ideal geometry in our calculations. Our tentative assignment (cf. Table I) differs from that given by Kimura *et al.*<sup>14</sup> in the interchange of  $3e_g^{-1}$  and  $3a_{2u}^{-1}$  (bands ⑥, ⑦). It should be noted that the latter authors assign the same ionization energies within 0.01 eV to the pair  $1a_{1u}^{-1}$ ,  $3e_u^{-1}$  (12.94 eV) and  $3e_g^{-1}$ ,  $3a_{2u}^{-1}$  (14.62 eV), which is very unlikely.

### III. THE CONSTRUCTION AND ANALYSIS OF LOCALIZED MOLECULAR ORBITALS

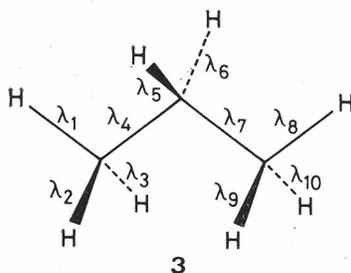
The construction of localized molecular orbitals  $\lambda_\mu$  (LMO) from *ab initio* SCF canonical orbitals  $\varphi_j$  (CMO) is carried out as discussed in previous contributions<sup>27-30</sup>. For convenience and because of its widespread applications we use the STO-3G procedure<sup>31</sup> with minimal basis set as a chemically unbiased model. It has been shown previously that this model is a rather good one for the qualitative and quantitative interpretation of the PE spectra of aliphatic and alicyclic hydrocarbons<sup>27,28</sup>.

All calculations have been carried out assuming standard bond lengths ( $R_{CC} = 154$  pm;  $R_{CH} = 109$  pm)<sup>31</sup> and idealized tetrahedral angles ( $109^\circ 27'$ ) throughout, rather than experimental ones. The reason is that we want to apply our procedure to molecules, the exact structural parameters of which are unknown. Thus the error introduced by assuming standard bond lengths and tetrahedral angles are an integral part of our model and the corresponding residual variance must necessarily be assessed by using the same approximation for our calibration set.

Of the  $3n + m/2$  CMOs  $\varphi_j$  of a hydrocarbon  $C_nH_m$ ,  $N = 2n + m/2$  are doubly occupied in its singlet ground state  $\tilde{X}$ . These CMOs are collected in a row vector  $\boldsymbol{\varphi} = (\varphi_1 \dots \varphi_j \dots \varphi_N)$  which is then subjected to an orthogonal transformation  $\mathbf{L} = (L_{ij})$ , ( $i, j = 1, 2, \dots, N$ ), yielding a set of  $N$  localized orbitals  $\boldsymbol{\lambda} = (\lambda_1 \dots \lambda_j \dots \lambda_N)$  according to  $\boldsymbol{\lambda} = \boldsymbol{\varphi} \mathbf{L}$ . The transformation matrix  $\mathbf{L}$  is chosen according to the localization criterion proposed by Foster and Boys<sup>32</sup>, *i.e.* by maximizing the sum of squares of the distances between the orbital gravity centres. The Fock matrix  $\mathbf{F}_\lambda$  corresponding to the LMO set  $\boldsymbol{\lambda}$  is obtained from the CMO energies  $\varepsilon_j$  relating to the CMOs  $\varphi_j$  by the orthogonal transformation

$$\mathbf{F}_\lambda = \mathbf{L}^T \cdot \text{diag}(\varepsilon_1 \dots \varepsilon_j \dots \varepsilon_N) \mathbf{L} \quad (2)$$

If this procedure is carried out for a variety of hydrocarbons, it is found that the diagonal and off-diagonal matrix elements  $F_{\lambda, ij} = \langle \lambda_i | \mathcal{F} | \lambda_j \rangle$  of  $F_{\lambda}$ , where  $\mathcal{F}$  is the Fock operator of the particular system, exhibit almost perfect transferability for pairs of LMOs  $\lambda_i, \lambda_j$  of same type in different hydrocarbons  $C_nH_m$ , but in identical configurational and conformational environments. As a numerical example we present in Table II the  $F_{\lambda}$  matrix of propane in its lowest energy conformation (all  $F_{\lambda, ij}$  in eV; labels as shown below):



From this result and the analogous results for the other members 1 to 6 of the calibration set we can draw a number of conclusions (cf. also ref. 27):

(a) *Self-Energies  $A_j$ .* — The self energies  $A_j^\circ \equiv F_{\lambda, jj}$  of the individual localized orbitals  $\lambda_j$ , *i. e.* the diagonal terms, yield with minute differences,  $A_{CC}^\circ = -17.50$  eV and  $A_{CH}^\circ = -16.95$  eV (*i. e.* the mean taken over the calibration set). The difference  $A_{CC}^\circ - A_{CH}^\circ \approx 0.5$  eV albeit significant, is small enough, so that for some purposes both values can be assumed to be equal,  $A = A_{CC} = A_{CH}$ , in a first crude approximation, *e. g.* for the rationalization of the 2s band system of He(II) PE spectra of saturated hydrocarbons<sup>27,28</sup> (see below). As a matter of fact, the almost equality of  $A_{CC}^\circ$  and  $A_{CH}^\circ$  is the main reason why the CMOs  $\varphi_j$  extend rather uniformly over a given saturated hydrocarbon, independent of their orbital energy  $\epsilon_j$ . It follows that the positive charge of the radical cation  $C_nH_m^+$  in a given *Koopmans* configuration  ${}^2\Phi_j$  (cf. (1)) is also rather smooth and uniform, with the consequence to be discussed below.

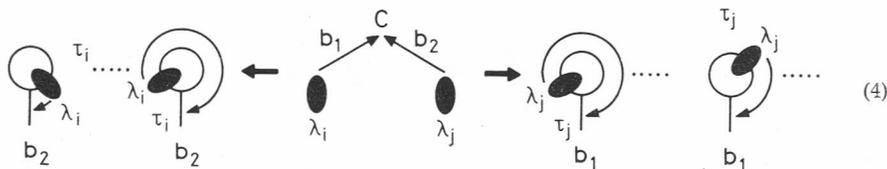
(b) *Geminal Cross Terms  $B_{ij}$ .* — All cross-terms  $B_{ij}^\circ \equiv F_{\lambda, ij}$  between geminal LMOs  $\lambda_i, \lambda_j$ , issuing from a common carbon centre are the same within small limits of error, independent of the nature of the two LMOs  $\lambda_i, \lambda_j$ . Therefore  $B_{CC, CC} = B_{CC, CH} = B_{CH, CH} = -2.89$  eV =  $B$  is a perfectly acceptable approximation, as long as all bond angles are the same, *i. e.* tetrahedral ( $109^\circ 27'$ ). As will be discussed later,  $|B|$  increases with decreasing bond angle.

(c) *Vicinal Cross Terms  $\Gamma_{ij}$ .* — The matrix elements  $\Gamma_{ij}^\circ \equiv F_{\lambda, ij}$  between two vicinal LMOs  $\lambda_i, \lambda_j$  which bracket a given CC-bond joining  $\lambda_i$  to  $\lambda_j$  depend on the local conformation of the two LMOs  $\lambda_i, \lambda_j$  characterized by the local twist angle  $\tau_{ij}$ . For a *syn*-planar conformation with  $\tau_{ij} = 0^\circ$  by definition, the cross-term  $\Gamma_{ij}^\circ$  is negative, for an antiplanar conformation with  $\tau_{ij} = 180^\circ$  positive. Subjecting a series of STO-3G model calculations with the twist angle  $\tau_{ij}$  spanning the interval  $0^\circ \leq \tau_{ij} \leq 180^\circ$  to the localization transformation, one finds that  $\Gamma_{ij}^\circ = \Gamma(\tau_{ij})$  follows a simple cosine function  $\Gamma_{ij}^\circ \approx \Gamma^\circ \cos \tau_{ij}$  without a statistically significant constant term. Within the required limits of

<sup>1</sup> An upper index  $^\circ$  indicates that the matrix element is carried over unchanged from the *ab initio* calculation in localized basis. All other elements (without upper index  $^\circ$ ) are calibrated or adjusted, as stated in the text.

error one finds that the factor  $I^\circ$  of the above formula is again independent of the nature of the LMOs  $\lambda_i$ ,  $\lambda_j$  and has a value of  $I^\circ = -1.00$  eV. Thus in analogy to the geminal cross-term  $B_{ij}$ , we have for a given value of  $\tau_{ij} \equiv \tau$  that  $I_{CC,CC}(\tau) = I_{CC,CH}(\tau) = I_{CH,CH}(\tau) = I(\tau)$ .

(d) *1,4-Interaction Terms  $\Delta_{ij}$ .* — These interaction terms refer to two LMOs  $\lambda_i$ ,  $\lambda_j$  separated by two linking bonds  $b_1$ ,  $b_2$ , e. g. the two  $\lambda_{CH}$  LMOs of the two methyl groups in propane (3). Obviously  $\Delta_{ij}^\circ$  must depend on two twist angles  $\tau_i$ ,  $\tau_j$  which we define as follows: The twist angles  $\tau_i$ ,  $\tau_j$  are taken with respect to the plane defined by the linking bonds  $b_1$ ,  $b_2$ , the positive twist direction corresponding to the vector pointing towards the atom C common to  $b_1$  and  $b_2$ , as shown in the following Newman projection.



Thus the syn planar conformation of  $\lambda_i$  with  $b_2$  or of  $\lambda_j$  with  $b_1$  corresponds to  $\tau_i = \tau_j = 0$ . Reversal of the vectors associated with the bonds  $b_1$  and/or  $b_2$  results in a change of sign of  $\tau_i$  and/or  $\tau_j$ .

STO-3G calculations for propane with the terminal methyl groups in different conformations yield the following dependence of  $\Delta_{CH,CH}^\circ(\tau_i, \tau_j)$  for the LMOs  $\lambda_i = \lambda_{CH}$ ,  $\lambda_j = \lambda_{CH}$  of the two methyl groups respectively: For convenience all values have been rounded to two decimals only.

$$\Delta_{CH,CH}^\circ(\tau_i, \tau_j)/\text{eV}$$

$\tau_i \backslash \tau_j$	$0^\circ$	$60^\circ$	$120^\circ$	$180^\circ$	$240^\circ$	$300^\circ$	$360^\circ$
$0^\circ$	-0.84	-0.33	0.21	0.33	0.21	-0.33	-0.84
$60^\circ$	-0.33	0.02	0.15	0.13	0.01	-0.29	-0.33
$120^\circ$	0.21	0.15	-0.08	-0.18	-0.13	0.01	0.21
$180^\circ$	0.33	0.13	-0.18	-0.29	-0.18	0.13	0.33
$240^\circ$	0.21	0.01	-0.13	-0.18	-0.08	0.15	0.21
$300^\circ$	-0.33	-0.29	0.01	0.13	0.15	0.02	-0.33
$360^\circ$	-0.84	-0.33	0.21	0.33	0.21	-0.33	-0.84

As can be seen, the dependence of  $\Delta_{CH,CH}$  on  $\tau_i$ ,  $\tau_j$  is rather complicated and it is therefore more convenient to express this dependence in form of an equivalent Fourier series

$$\Delta_{CH,CH}^\circ(\tau_i, \tau_j) = \sum_{\mu=0}^3 \sum_{\nu=0}^3 a_{\mu\nu} \cos(\mu\tau_i) \cos(\nu\tau_j) + \sum_{\mu=1}^2 \sum_{\nu=1}^2 b_{\mu\nu} \sin(\mu\tau_i) \sin(\nu\tau_j) \quad (6)$$

with  $a_{\mu\nu} = a_{\nu\mu}$  and  $b_{\mu\nu} = b_{\nu\mu}$  assuming the following values, calculated from the original data underlying (5).

$a_{\mu\nu}$	0	1	2	3
0	-0.0401	-0.0554	-0.0263	(-0.0032)
1		-0.4327	-0.0742	(-0.0077)
2			-0.0226	(-0.0032)
3				(-0.0005)

$b_{\mu\nu}$	1	2
1	0.1050	0.0447
2		(0.0120)

(7)

For practical purposes the terms of (6) corresponding to the values of (7) in parenthesis can be neglected. This is especially true if the same formula (6) is used for the  $\Delta_{CH,CC}$  and  $\Delta_{CC,CC}$  terms, which is appropriate only if the two LMOs concerned belong to an open chain or to a ring with 7 or more CC-bonds.

(e) *Higher Interaction Terms.* — If two LMOs  $\lambda_i, \lambda_j$  are separated by three or more bonds, the corresponding interaction term  $F_{\lambda_i, \lambda_j}$  becomes in general so small that it can safely be neglected. In principle such small terms could be taken care of *via* perturbation treatments, but the resulting improvement is not significant.

#### IV. EQUIVALENT BOND ORBITAL MODELS

We are now in a position to develop improved equivalent bond orbital models in two slightly different ways:

(a) An EBO model which mimics STO-3G calculations with respect to orbital energies.

(b) An EBO model calibrated to yield predictions of ionization energies of saturated hydrocarbons, assuming the validity of *Koopmans'* theorem.

To achieve goal (a), all that has to be done is to take over the matrix elements  $F_{\lambda_i, \lambda_j} \equiv A_j, B_{ij}, I_{ij}, \dots$  derived above and to construct the matrix  $\mathbf{F}_\lambda$  for the hydrocarbon of interest. Diagonalization of  $\mathbf{F}_\lambda$  yields the desired result. However, as we shall see, it is sufficient to restrict the off-diagonal elements to the  $B_{ij}, I_{ij}$  and  $\Delta_{ij}$  only, the other elements yielding contributions too small to be relevant for all practical purposes.

In the second case (b) we introduce two types of ad hoc adjustments to obtain optimum agreement between observed and calculated ionization energies, namely a shift  $\delta A$  of the diagonal elements and a scaling factor  $f$  for the off-diagonal elements. The procedure is described in detail below.

We shall classify our models depending on the type of matrix elements used, as follows:

$AB$ -model: includes only  $A_j$  and  $B_{ij}$

$AI$ -model: includes  $A_j, B_{ij}$  and  $I_{ij}$

$AI\Delta$ -model: includes  $A_j, B_{ij}, I_{ij}$  and  $\Delta_{ij}$ .

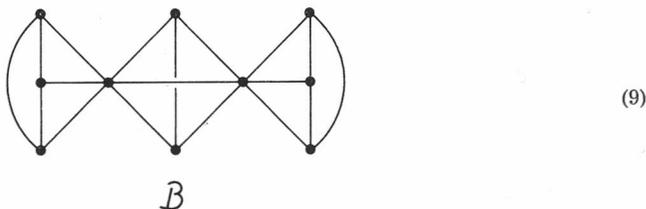
An upper index »<sup>o</sup>« indicates that all matrix elements are those obtained directly from the STO-3G procedure without alteration (case (a)), otherwise they are calibrated on the basis of the ionization energies of a calibration set.

### The AB-model

This model has been extensively discussed in previous communications 27 to 30. In the  $AB^\circ$  version one would use  $A^\circ_{CC} = -17.50$  eV,  $A^\circ_{CH} = -16.95$  eV,  $B^\circ_{CC,CC} = B^\circ_{CC,CH} = B^\circ_{CH,CH} = -2.89$  eV. However, if this drastic reduction in the type of matrix elements is introduced, the differentiation between  $A^\circ_{CC}$  and  $A^\circ_{CH}$  becomes rather irrelevant. Thus the only adequate approximation for such a model is to assume equal  $A$  for all bonds and equal  $B$  for all geminal interactions, so that the model is defined by the set of LMOs and the following matrix elements:

$$\begin{array}{l}
 \text{AB-model} \\
 A_{CC} = A_{CH} = A \\
 B_{CC,CC} = B_{CC,CH} = B_{CH,CH} = B
 \end{array}
 \quad (8)$$

Under these circumstances the EBO model degenerates to a standard HMO treatment based on the line graph  $\mathcal{B}$  of the structure graph  $\mathcal{G}$ <sup>33</sup> of the hydrocarbon; e. g. for propane (cf. ref. 27):



If  $\mathbf{B}$  is the adjacency matrix of the graph  $\mathcal{B}$ , then the spectrum of  $\mathbf{B}$ , i. e. the eigenvalues  $x_j$  obtained by solving

$$\|\mathbf{B} - x\mathbf{1}\| = 0 \quad (10)$$

yields the orbital energies

$$\varepsilon_j = A + x_j B \quad (11)$$

of the AB-model. The model is attractive because formula (11) allows a simple calibration of  $A$  and  $B$  via  $\varepsilon_j = -I_j^m$  on the basis of observed ionization energies  $I_j^m$ . As has been shown<sup>27,28</sup> this yields rather good correlations for the  $2s$ -manifold of hydrocarbons with  $A = -15.8$  eV and  $B = -2.2$  eV. On the other hand, the model is more or less useless for the  $2p$ -manifold because of the high accidental degeneracy of the eigenvalue  $x_j = -1$  and the fact that the model is completely insensitive towards conformational changes of the molecules.

### The $AI$ -model

This is the simplest EBO model which takes care of local conformations and thus lifts the degeneracies within the  $2p$ -manifold inherent in the AB-model. To mimic STO-3G results, the following set of parameters is used:

*AI<sup>o</sup>-model*

$$A^{\circ}_{CC} = -17.50 \text{ eV}$$

$$A^{\circ}_{CH} = -16.95 \text{ eV}$$

$$B^{\circ}_{CC,CC} = B^{\circ}_{CC,CH} = B^{\circ}_{CH,CH} = -2.89 \text{ eV}$$

$$I^{\circ}_{CC,CC} = I^{\circ}_{CC,CH} = I^{\circ}_{CH,CH} = I^{\circ}_{i,j} = I^{\circ} \cos \tau_{ij}$$

$$I^{\circ} = -1.00 \text{ eV}$$

(12)

*The AA-model*

This is the most complete STO-3G orbital energy simulator which should be used in practice. The inclusion of even higher interaction matrix elements becomes rather cumbersome and is not worthwhile for practical applications. The set of parameters to be used is that of the *AI<sup>o</sup>*-model (12) plus the  $\Delta^{\circ}_{ij}$  elements calculated according to formulae (6) and (7) for given twist angles  $\tau_i, \tau_j$ . Within the limits of error required, some of the terms in the Fourier expansion (6) can be dropped, especially if we accept the simplification that the same expression for  $\Delta^{\circ}_{ij}$  should be valid whatever the two LMOs  $\lambda_i, \lambda_j$  involved are, *i. e.*,  $\lambda_i, \lambda_j =$  both  $\lambda_{CC}$  or  $\lambda_{CH}$ , or a combination of the two.

*AA<sup>o</sup>-model*

$$A^{\circ}_{CC} = -17.50 \text{ eV}$$

$$A^{\circ}_{CH} = -16.95 \text{ eV}$$

$$B^{\circ}_{CC,CC} = B^{\circ}_{CC,CH} = B^{\circ}_{CH,CH} = -2.89$$

$$I^{\circ}_{CC,CC} = I^{\circ}_{CC,CH} = I^{\circ}_{CH,CH} = I^{\circ}_{i,j} = I^{\circ} \cos \tau_{ij}$$

$$I^{\circ} = -1.00 \text{ eV}$$

$$\Delta^{\circ}_{CC,CC} = \Delta^{\circ}_{CC,CH} = \Delta^{\circ}_{CH,CH} = \Delta^{\circ}_{ij}(\tau_i, \tau_j)$$

$$\Delta^{\circ}_{ij}(\tau_i, \tau_j) \text{ according to (6), (7).}$$

(13)

*Comments*

1) The above analysis has made use of the standard STO-3G model<sup>31</sup>, *i. e.* the one most popular and widely used model when this work was initiated some years ago (cf. ref. 27). However, any other *ab initio* treatment would have done as well, provided that it yields the same quality of agreement between computed and observed ionization energies of saturated hydrocarbons. Because

of the calibration to be performed in the next chapter the choice of a particular type of *ab initio* model is less important than it may seem at first sight. The main reason is that the relative dependence of the off-diagonal terms of  $\mathbf{F}_\lambda$  on conformation is about the same in all treatments.

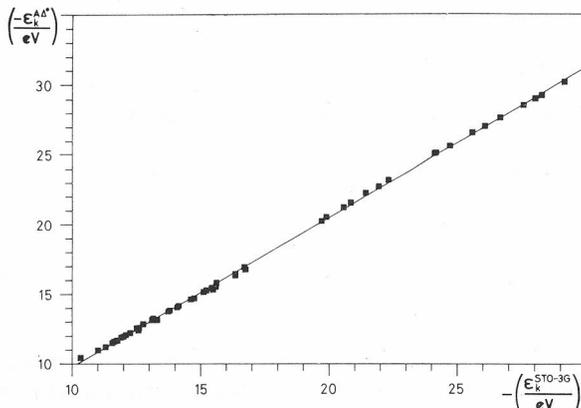


Figure 4. Linear regression of  $-\varepsilon_k^{AA^\circ}$  on  $-\varepsilon_k^{\text{STO-3G}}$ , cf. formula (14).

2) The  $AA^\circ$ -model (13) is an excellent STO-3G simulator, as far as the orbital energies  $\varepsilon_k$  of simple (open chain) saturated hydrocarbons are concerned. This is shown by the linear regression of Figure 4 in which the  $\varepsilon_k^{AA^\circ}$  are plotted vs. the STO-3G values  $\varepsilon_k^{\text{STO-3G}}$  for our calibration set (Table I). The regression line is

$$\left(\frac{-\varepsilon_k^{AA^\circ}}{\text{eV}}\right) = (-0.954 \pm 0.061) + (1.073 \pm 0.030) \left(\frac{-\varepsilon_k^{\text{STO-3G}}}{\text{eV}}\right) \quad (14)$$

with a standard deviation of  $s(\varepsilon^{\text{STO-3G}}) = 0.134$  eV and a regression coefficient of  $r = 0.9998$ . How do the other models compare to the  $AA^\circ$  one? To answer this question we give in Table III a numerical example. The orbital energies of propane (**3**) are calculated on five levels of approximation: (a) by carrying out the complete standard STO-3G treatment (which lead to the  $\mathbf{F}_\lambda$  matrix of Table II), (b) by diagonalizing the  $\mathbf{F}_\lambda$  matrix of the  $AA^\circ$ -model, *i. e.* containing only the matrix elements (13), (c) by making use of the  $AI^\circ$ -model *i. e.* containing only the matrix elements (12), (d) by diagonalizing a  $\mathbf{F}_\lambda$  matrix containing the rounded diagonal terms  $A = (A_{\text{CC}}^\circ + A_{\text{CH}}^\circ)/2 = 17.2$  eV and only the rounded geminal interaction terms  $B = -2.9$  eV. The comparison speaks for itself and needs no comment.

3) It must be emphasized that the models presented in this publication apply only to unstrained saturated hydrocarbons *i. e.* in which all bond angles are close to the tetrahedral one ( $109.5^\circ$ ). It is known that the geminal interaction term  $B_{ij}$  between two LMOs  $\lambda_i, \lambda_j$  depends on the bond angle  $\vartheta_{ij}$ : The smaller  $\vartheta_{ij}$ , the larger the absolute value  $|B_{ij}|$ .<sup>27,29,30</sup> Consequently the incorporation of small rings *e. g.* cyclopropane and/or cyclobutane rings will necessitate an adjustment of the pertinent matrix elements of  $\mathbf{F}_\lambda$  as will be shown later.<sup>34</sup>

4) STO-3G calculations on cyclohexane (**6**) have shown that the  $A_{\text{CC,CC}}^\circ$  matrix elements (between 1,4-positioned LMOs  $\lambda_{\text{CC}}$ ) are systematically smaller

The Fock Matrix  $F_\lambda$  of Propane in Localized Basis  $\lambda$ . All Values in eV. The Numbering of the LMOs  $\lambda_j$  Corresponds to that Given in (3)

	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\lambda_{CC}$	$\lambda_4$	$\lambda_5$	$\lambda_{CH}$	$\lambda_6$	$\lambda_{CC}$	$\lambda_8$	$\lambda_{CH}$	$\lambda_9$	$\lambda_{CH}$	$\lambda_{10}$
$\lambda_1$	-16.91	-2.88	-2.88	-2.89	-2.89	-0.54	-0.54	-0.54	0.95	-0.29	0.13	0.13	0.13	0.13
$\lambda_{CH}$	$\lambda_2$	-16.94	-2.89	-2.89	-2.89	-0.54	0.98	0.98	-0.52	0.13	-0.29	0.02	-0.29	0.02
$\lambda_3$	-2.88	-2.89	-16.94	-2.89	-2.89	0.98	-0.54	-0.54	-0.52	0.13	0.02	-0.29	0.02	-0.29
$\lambda_{CC}$	$\lambda_4$	-2.89	-2.89	-17.50	-17.50	-2.89	-2.89	-2.89	-2.90	0.95	-0.52	-0.52	-0.52	-0.52
$\lambda_5$	-0.54	-0.54	-0.54	-2.89	-2.89	-16.97	-2.90	-2.90	-2.89	-0.54	-0.54	0.98	-0.54	0.98
$\lambda_{CH}$	$\lambda_6$	0.98	0.98	-2.89	-2.89	-2.90	-16.97	-16.97	-2.89	-0.54	0.98	-0.54	0.98	-0.54
$\lambda_{CC}$	$\lambda_7$	0.95	-0.52	-0.52	-2.90	-2.89	-2.89	-2.89	-17.50	-2.89	-2.89	-2.89	-2.89	-2.89
$\lambda_8$	-0.29	0.13	0.13	0.95	0.95	-0.54	-0.54	-0.54	-2.89	-16.91	-2.88	-2.88	-2.88	-2.88
$\lambda_{CH}$	$\lambda_9$	0.13	-0.29	-0.29	-0.52	0.98	0.98	0.98	-2.89	-2.88	-16.94	-2.89	-2.89	-2.89
$\lambda_{10}$	0.13	0.02	-0.29	-0.52	-0.52	0.98	-0.54	-0.54	-2.89	-2.88	-2.89	-2.89	-2.89	-16.94

TABLE III

Comparison of Computed Orbital Energies of Propane using a) the Standard STO-3G Treatment, b) the  $A\Delta^0$ -Model, c) the  $AI^0$ -Model, d) the  $AB^0$ -Model and e) the »AB« Model (with Rounded and Averaged A- and B-Values as Indicated in the Text. Note that this is not the AB-Model Defined in (8)). All Values in eV

Orb.	STO-3G	$A\Delta^0$	$AI^0$	$AB^0$	»AB«
$4b_2$	11.642	11.61	11.70	12.23	12.09
$6a_1$	12.005	11.97	11.80	12.97	12.94
$2b_1$	12.067	12.09	11.94	14.06	14.30
$1a_2$	13.739	13.75	14.06	14.06	14.30
$3b_2$	14.152	14.17	14.56	14.06	14.30
$5a_1$	15.438	15.46	15.17	14.06	14.30
$1b_1$	16.359	16.34	16.18	14.06	14.50
$4a_1$	21.442	21.56	21.50	21.54	21.78
$2b_2$	24.969	25.06	25.14	25.12	25.09
$3a_1$	28.679	28.58	28.55	28.54	28.40

(by a factor of approximately 1/2) than those derived from the formulae (6) (7). Although this could easily be taken care of, experience has shown that the error introduced by using the same  $\Delta_{ij}$  values as for open-chain systems can be neglected. If necessary, the corresponding corrections can be easily introduced by first-order perturbation calculations using the linear combinations of the LMOs.

#### V. CALIBRATION OF THE $AI^0$ AND $A\Delta^0$ -MODELS

As the calibration procedure is the same for both models, we shall explain it with reference to the more complete one, *i. e.* the  $A\Delta^0$ -model. Figure 5 shows a plot of experimental ionization energies  $I_j^m$  vs. the negative orbital energies

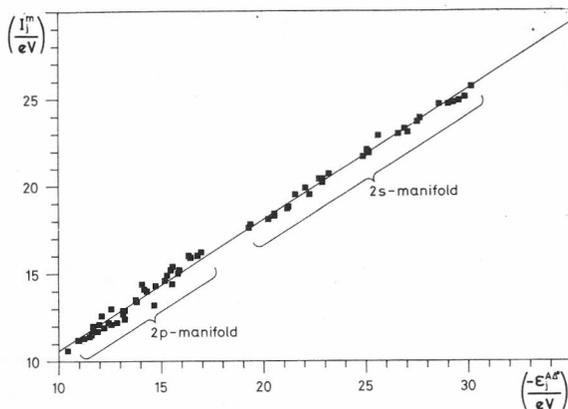


Figure 5. Linear regression of observed ionization energies  $I_j^m$  on  $-\epsilon_j^{A\Delta^0}$ , cf. formula (15).

derived from the  $A\Delta^\circ$ -model defined in (13). The points refer to the calibration set (Table I) and to the ionization energies of the 2s-manifolds of pentane, isopentane, neopentane and 2,2-dimethylbutane<sup>18</sup>. (Although the He(I $\alpha$ ) PE spectra of the 2p-manifold of the first three of the latter hydrocarbons are known<sup>14</sup> it is impossible to deconvolute these band systems). The regression line is given by

$$\left(\frac{I_j^m}{\text{eV}}\right) = (3.100 \pm 0.122) + (0.750 \pm 0.006) \left(\frac{-\varepsilon_k^{A\Delta^\circ}}{\text{eV}}\right) \quad (15)$$

with standard error  $s(I_j^m) = 0.320$  eV and correlation coefficient 0.998.

We are now in a position to calibrate our  $A\Delta^\circ$ -model to yield the parametrized  $A\Delta$ -model. This is achieved by adding to the diagonal terms  $A_j$  an increment  $\delta A$  and by multiplying the off-diagonal elements  $B_{ij}$ ,  $I_{ij}$ ,  $\Delta_{ij}$  with a common factor  $f$ . Because of the orthogonality of the  $N$  LMOs in the basis  $\lambda = (\lambda_1 \dots \lambda_j \dots \lambda_N)$ , the orbital energy  $\varepsilon_k^{A\Delta^\circ}$  belonging to the molecular orbital  $\varphi_k = \lambda \mathbf{c}_k$  of a hydrocarbon  $C_nH_m$  is given by

$$\varepsilon_k^{A\Delta^\circ} = \mathbf{c}_k^T \mathbf{F}_\lambda \mathbf{c}_k = \frac{N_{\text{CC}}}{N} A^\circ_{\text{CC}} + \frac{N_{\text{CH}}}{N} A^\circ_{\text{CH}} + B^\circ_k + I^\circ_k + \Delta^\circ_k \quad (16)$$

where  $N_{\text{CC}} = 3n - \frac{m}{2}$  and  $N_{\text{CH}} = m$  are the number of  $\lambda_{\text{CC}}$  and  $\lambda_{\text{CH}}$  LMOs respectively ( $N = N_{\text{CC}} + N_{\text{CH}} = 3n + \frac{m}{2}$ ), and where the  $B^\circ_k$ ,  $I^\circ_k$  and  $\Delta^\circ_k$  are defined as

$$\begin{aligned} B^\circ_k &= \sum_i \sum_j c_{ik} c_{jk} B^\circ_{ij} \\ I^\circ_k &= \sum_i \sum_j c_{ik} c_{jk} I^\circ_{ij} \\ \Delta^\circ_k &= \sum_i \sum_j c_{ik} c_{jk} \Delta^\circ_{ij} \end{aligned} \quad (17)$$

Accordingly, regression (15) is of the form

$$I_k^m = a + b(-\varepsilon_k^{A\Delta^\circ}) = a + b \left( \frac{N_{\text{CC}}}{N} A^\circ_{\text{CC}} + \frac{N_{\text{CH}}}{N} A^\circ_{\text{CH}} + B^\circ_k + I^\circ_k + \Delta^\circ_k \right) \quad (18)$$

We now shift  $A^\circ_{\text{CC}}$  and  $A^\circ_{\text{CH}}$  by  $\delta A$  and we multiply  $B^\circ_k$ ,  $I^\circ_k$ ,  $\Delta^\circ_k$  by a factor  $f$  in such a way that

$$I_k^m = -\varepsilon_k^{A\Delta} = \frac{N_{\text{CC}}}{N} (A^\circ_{\text{CC}} + \delta) + \frac{N_{\text{CH}}}{N} (A^\circ_{\text{CH}} + \delta) + f (B^\circ_k + I^\circ_k + \Delta^\circ_k) \quad (19)$$

Thus the calibrated  $AI^-$ - or  $AA^-$ -model is now defined as follows.

$AI^-$ - or  $AA^-$ -Model for  $C_nH_m$

- 1) Calculate  $\mathbf{F}_\lambda^0$  according to the  $AA^0$ -model defined in (13)
- 2) Multiply all off-diagonal terms  $F_{\lambda,ij}$  by  $f$ , and, (21)
- 3) add to all diagonal terms  $F_{\lambda,ii}$  the value  $\delta A$  computed according to (20).
- 4) Diagonalize  $\mathbf{F}_\lambda$  so obtained.

Note that according to (20)  $\delta A$  depends on the composition of the hydrocarbon  $C_nH_m$  although not very critically. On the other hand,  $f$  is the same for all hydrocarbons.

As an example we apply the procedure (21) to the  $AA^0$ -model, which yielded regression (15) for the calibration set. According to (20) we obtain

$$\delta A = -3.100 \text{ eV} - \frac{0.250}{N} (N_{CC}A_{CC} + N_{CH}A_{CH}) \quad (22)$$

$$f = 0.750$$

with  $N_{CC} = 3n - m/2$ ,  $N_{CH} = m$  and  $N = N_{CC} + N_{CH} = 3n + m/2$  for a hydrocarbon  $C_nH_m$ . In Figure 6 is shown the regression of the experimental ionization energies  $I_j^m$  on  $-\varepsilon_j^{AA}$ . The regression line is

$$\left( \frac{I_j^m}{\text{eV}} \right) = (0.036 \pm 0.15) + (0.997 \pm 0.008) \left( \frac{-\varepsilon_j^{AA}}{\text{eV}} \right) \quad (23)$$

which does not differ significantly from  $I_j^m = -\varepsilon_j^{AA}$ . For obvious reasons  $s(I_j^m) = 0.33 \text{ eV}$  and  $r = 0.998$  are practically the same as for the regression (15).

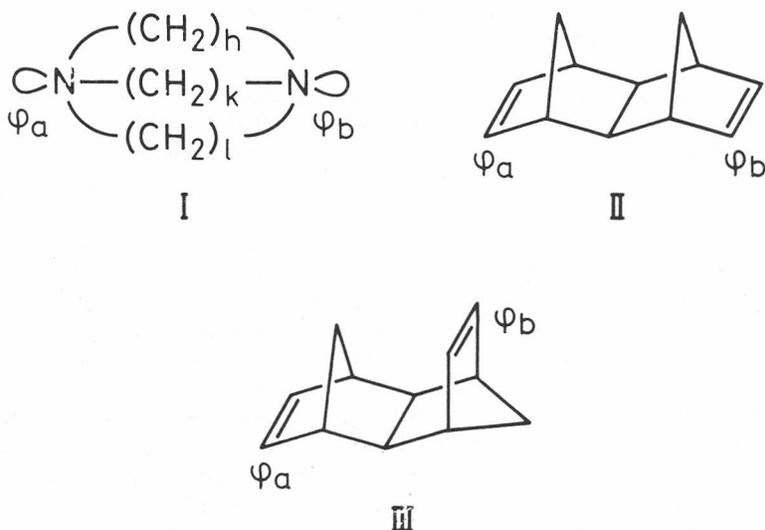
## VI. DISCUSSION

The extension of the above formalism to molecules which contain *e.g.*  $\pi$ -systems and/or lone pairs is rather obvious, and we shall come back to these in connection with a discussion of particular problems<sup>34</sup>. However, before we do so it is necessary to answer an important question. In view of the fact that efficient *ab initio* or semiempirical treatments are available in programmed form, the theoretically inclined chemist may well ask why he should bother about such equivalent bond orbital models, considered obsolete by the purists. The answer is obvious, at least for those who are mainly experimentalists.

To systematize and rationalize ones experimental and also ones theoretical results derived from sophisticated treatments, it is necessary to have at ones disposal an adequate language *i.e.* a formalism in which these results can be expressed and can be easily handled qualitatively. It is stating the obvious that the simple *Hückel* model has filled this gap, at least since the original work of *Woodward* and *Hoffmann*, and that it has developed into such a language in which a considerable percentage of all published work is nowadays described.

One of the reasons is that this model makes use of a set of orthogonal basis functions, which is probably the most important innovation introduced by *Hückel* into theoretical chemistry. This *Hückel* language has to rely on the availability of very simple methods for generating orbitals. Whereas the standard *Hückel* treatment, taught nowadays at the high-school level, yields the necessary  $\pi$ -orbital diagrams, most chemists are not familiar with correspondingly simple schemes for obtaining  $\sigma$ -orbital diagrams. This is where the EBO model, using orthogonal localized bond orbitals comes into its own, yielding the symmetry and nodal properties of molecular  $\sigma$ -orbitals in an equally straightforward manner.

Concerning the usefulness of such orbitals we shall give but one example, albeit an important one. The long-range interaction between functional groups is still a topic of active research<sup>35</sup>. A particularly fruitful line of attack has been initiated by Hoffmann<sup>36</sup> who introduced the concepts of »through space« and »through bond« interaction between pairs of semi-localized orbitals  $\varphi_a$ ,  $\varphi_b$ . The relay orbitals providing »through bond« interaction are more often than not the  $\sigma$ -orbitals of alkyl moieties linking  $\varphi_a$  and  $\varphi_b$ . Examples being currently discussed are the interactions of nitrogen lone pairs in diazabicyclo[*h.k.l*]alkanes (I)<sup>37</sup> or of the non-conjugated double bond  $\pi$ -orbitals in dienes such as II or III.<sup>38</sup> In all these cases it is obviously of practical importance to gain a



heuristically useful insight how changes in the conformation and/or the configuration of the alkyl moieties influence the relay properties of the  $\sigma$ -orbitals. Needless to say that the EBO-model is particularly appropriate in this respect. In other words, the models reviewed and redefined in this contribution should not be viewed as an alternative to more sophisticated treatments, but rather as a convenient and reliable method for providing the necessary basis for a qualitative or semiquantitative discussion in the framework of the usual orbital language.

It is only fair to draw attention to the shortcomings of the EBO model, although these must be rather obvious. First of all the models, as described,

are unreliable for very compact, polycyclic systems because of the neglect of the numerous, albeit small, long-range interaction terms, which can add up to rather sizeable orbital energy shifts in the  $2p$ -manifold. On the other hand, the  $2s$ -manifold is much less sensitive towards such interactions. Secondly, examination of the regressions presented in Figures 5 (regression (15)) and 6

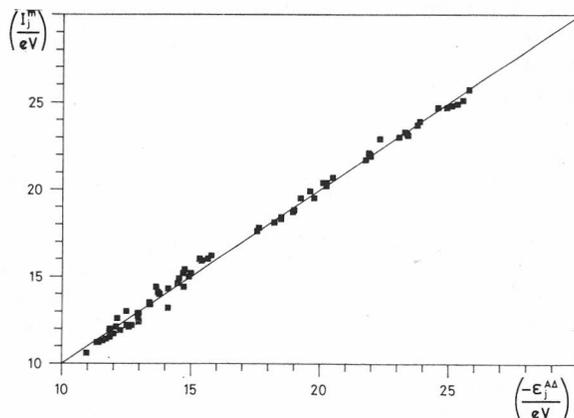


Figure 6. Linear regression of observed ionization energies  $I_j^m$  on  $-\epsilon_j^{AA}$  (i. e. after calibration according to (21)), cf. formula (23).

(regression (23)) shows that the points of the  $2p$ -manifold, taken by themselves, would lead to a steeper slope of 0.854 (instead of 0.750 in (15)) of the regression line. Thus the predicted band positions  $I_j^m$  at the low energy side of the spectrum tend to be on the high side, if regression (15) or the reparametrization (23) which is based on the former, is used.

A third difficulty concerns the size of the  $\Delta_{ij}^{\circ}$  (or higher) interaction terms, which are probably too small relative to  $B_{ij}^{\circ}$  and  $I_{ij}^{\circ}$  if taken from an *ab initio* calculation using gaussian functions. Although this does not seem to yield appreciable differences between observed and calculated values in the cases considered above, experience has shown that long-range »through space« interactions are sometimes under-estimated. A typical example is the »through space« interaction between the  $\pi$ -orbital in position 3,4 and the methyl-group of 2-methylbutadiene, which will be discussed in a subsequent contribution<sup>39</sup>.

Finally it must be mentioned that our EBO model for saturated hydrocarbon  $\sigma$ -orbitals shares a major complication with all other models. Due to the high density of states within the  $2p$ -manifold, the orbital sequence must necessarily be uncertain for close lying molecular orbitals. Indeed, numerical experiments have shown that a large number of random crossings occur if different semi-empirical and *ab initio* results are matched against each other. However, this may well be irrelevant, because the closeness of so many states within a small energy interval is inductive to extensive vibronic mixing (quite apart from the effect of the interaction between *Koopmans* and *non-Koopmans* configurations yielding these states).

*Acknowledgements.* — This work is part No. 156 of project 2.017—0.81 of the Schweizerischer Nationalfonds zur Förderung der Wissenschaften. (Part 155 cf. 40). Support by Ciba-Geigy SA, Sandoz SA, and F. Hoffmann-La Roche & Co. SA, Basel, is gratefully acknowledged.

## REFERENCES

1. G. G. Hall, *Proc. R. Soc. London, Ser. A* **205** (1951) 541; J. Lennard-Jones and G. G. Hall, *Trans. Faraday Soc.* **48** (1952) 581; and references therein.
2. G. G. Hall, *Trans. Faraday Soc.* **50** (1954) 319.
3. J. C. Lorquet, *Mol. Phys.* **9** (1965) 101.
4. D. F. Brailsford and B. Ford, *Mol. Phys.* **18** (1970) 621.
5. W. C. Herndon, *Chem. Phys. Lett.* **10** (1971) 460.
6. J. N. Murrell and W. Schmidt, *J. Chem. Soc. Faraday Trans. 2* **68** (1972) 1709.
7. B. M. Gimarc, *J. Amer. Chem. Soc.* **95** (1973) 1417.
8. E. Heilbronner and J. P. Maier, *Some Aspects of Organic Photoelectron Spectroscopy*, in: *Electron Spectroscopy, Theory, Techniques and Applications*, Vol. 1, C. R. Brundle and A. D. Baker (Eds.), Academic Press, London 1977.
9. T. Koopmans, *Physica* **1** (1934) 104.
10. A. W. Potts, D. G. Streets, and W. C. Price, *Inst. Physics Conference on Photoionization Phenomena and Photoelectron Spectroscopy* (Oxford 1970), p. 22; W. C. Price, A. W. Potts, and D. G. Streets in *Electron Spectroscopy*, D. A. Shirley, (Ed.), North Holland Publishing Comp., Amsterdam 1972, p. 187.
11. A. W. Potts and W. C. Price, *Proc. R. Soc. London, Ser. A* **326** (1972) 165.
12. A. W. Potts and D. G. Streets, *J. Chem. Soc. Faraday Trans. 2* **70** (1974) 875.
13. *Molecular Photoelectron Spectroscopy*, D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, Wiley-Interscience, London 1970.
14. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, Japanese Scientific Societies Press, Tokyo 1981.
15. J. J. Pireaux, S. Svensson, E. Basilier, P.-Å. Malmqvist, U. Gelius, R. Caudano, and K. Siegbahn, *Phys. Rev. A* **14** (1976) 2133.
16. G. Bieri and L. Åsbrink, *J. Electron Spectrosc. Relat. Phenom.* **20** (1980) 149.
17. H. M. Rosenstock, D. Sims, S. S. Schroyer, and W. J. Webb, *Ion Energetics, Part I 1971-1973*, Ion Energetics Data Center, National Measurement Laboratory, National Bureau of Standards, Washington D. C., 1980.
18. G. Bieri, F. Burger, E. Heilbronner, and J. P. Maier, *Helv. Chim. Acta* **60** (1977) 2213.
19. S. Iwata and K. Kimura, Keio University Hiyoshi, Yokohama and Institute for Molecular Science, Okazaki, Japan, 1980.
20. B. Narayan, *Mol. Phys.* **23** (1972) 281.
21. R. N. Dixon, *Mol. Phys.* **20** (1971) 113.
22. R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys.* **8** (1975) 56.
23. A. Richartz, R. J. Buenker, and S. D. Peyerimhoff, *Chem. Phys.* **28** (1978) 305; A. Richartz, R. J. Buenker, P. J. Bruna, and S. D. Peyerimhoff, *Mol. Phys.* **33** (1977) 1345.
24. A. Richartz, R. J. Buenker, and S. D. Peyerimhoff, *Chem. Phys.* **31** (1978) 187.
25. W. Müller, Ch. Nager, and P. Rosmus, *Chem. Phys.* **51** (1980) 43.
26. M. Davis and O. Hassel, *Acta Chem. Scand.* **17** (1963) 1181; H. R. Buys and H. J. Geise, *Tetrahedron Lett.* (1970) 2991.
27. G. Bieri, J. D. Dill, E. Heilbronner, and A. Schmelzer, *Helv. Chim. Acta* **60** (1977) 2234.
28. E. Heilbronner, *Helv. Chim. Acta* **60** (1977) 2248.
29. P. Bischof, Ph. E. Eaton, R. Gleiter, E. Heilbronner, T. B. Jones, H. Musso, A. Schmelzer, and R. Stober, *Helv. Chim. Acta* **61** (1978) 547.
30. E. Heilbronner, T. B. Jones, A. Krebs, G. Maier, K.-D. Malsch, J. Pocklington, and A. Schmelzer, *J. Amer. Chem. Soc.* **102** (1980) 564.
31. W. J. Ehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51** (1969) 2657; W. J. Ehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, QCPE, Bloomington, Indiana; *Approximate Molecular Orbital Theory*, J. A. Pople and D. L. Beveridge, McGraw Hill Book Company, New York, 1970.

32. J. M. Foster and S. F. Boys, *Rev. Mod. Phys.* **32** (1969) 300.
33. W. Klyne and V. Prelog, *Experientia* **16** (1960) 521; J. D. Dunitz, Conformations of Medium Rings, in: *Perspectives in Structural Chemistry*, Vol. II, J. D. Dunitz and J. A. Ibers (Eds.), J. Wiley Sons, New York, 1968.
34. E. Honegger and E. Heilbronner, in preparation.
35. R. Gleiter, *Angew. Chem.* **86** (1974) 770; R. Gleiter and L. Paquette, *Acc. Chem. Res.* **16** (1983) 328; H.-D. Martin and B. Meyer, *Angew. Chem.* **95** (1983) 281.
36. R. Hoffmann, *Acc. Chem. Res.* **4** (1971) 1.
37. R. W. Alder, *Acc. Chem. Res.* **16** (1983) 321.
38. M. N. Paddon-Row, H. K. Patney, R. S. Brown, and K. N. Houk, *J. Amer. Chem. Soc.* **103** (1981) 5575; M. N. Paddon-Row, *Acc. Chem. Res.* **15** (1982) 245.
39. E. Honegger, Z.-z. Yang, E. Heilbronner, W. v. E. Doering, W. R. Dolbier, and J. Schmidhauser, *Helv. Chim. Acta* **67** (1984) 640.
40. E. Heilbronner, J. Wirz, and R. L. Soulen, *Helv. Chim. Acta*, **67** (1984) 47.

### SAŽETAK

#### Preispitivanje modela ekvivalentnih veznih orbitala: I. Orbitale, orbitalne energije i PE spektri zasićenih ugljikovodika

*Evi Honegger, Zhong-zhi Yang i Edgar Heilbronner*

Preispitan je model ekvivalentnih veznih orbitala (EBO) korištenjem lokaliziranih molekulskih orbitala (LMO) dobivenih *ab initio* računima. Ustanovljeno je, da je potreban vrlo malen broj matičnih elemenata za izgradnju Fockove matrice, ako se kao baza koriste lokalizirane orbitale. Dijagonalizacijom tako dobivene Fockove matrice dolazimo do orbitalnih energija dovoljno visoke točnosti da u okviru Koopmanove aproksimacije budu vrlo korisne u asignaciji fotoelektronskih spektara. Nadalje, takav model može se vrlo lako parametrizirati korištenjem prikladnog kalibracijskog skupa molekula. Pri tome treba jedino paziti da omjeri nedijagonalnih elemenata Fockove matrice dobiveni *ab initio* računom ostanu sačuvani. Dobiveni EBO model ustvari je Hückelova tipa. On se odlikuje ne samo krajnjom jednostavnošću nego je i vrlo dobar za kvalitativnu ili polukvantitativnu interpretaciju eksperimentalnih podataka odnosno vrlo točnih teorijskih računa. Razmotrene su također i granice EBO modela.