225. A Simple Equivalent Bond Orbital Model for the Rationalization of the C_{2s}-Photoelectron Spectra of the Higher *n*-Alkanes, in Particular of Polyethylene

by **Edgar Heilbronner**

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

(25.VII.77)

Summary

The higher homologues of *n*-alkanes $H(CH_2)_NH$ with $N > \sim 13$ yield photoelectron spectra in which the C_{2s}-bands merge to form a double humped, unresolved C_{2s}-band system in the interval of $I = 15$ to 25 eV [1]. It is shown that with the help of an equivalent bond orbital model one can derive a closed formula, which gives the individual C_{2s}-band positions $I_j^m = -\varepsilon_j$ in function of N and j with sufficient accuracy, assuming the validity of *Koopmans'* approximation. The calculated I_j^m values ($j = 1$ to N) folded with an appropriate shape function for the individual C_{2s}-bands reproduce the observed *Franck-Condon* envelope of the C_{2s}-band system within narrow limits of error. However, a comparison of the observed total width of the C_{2s}-band system with the computed one, indicate that for large *n*-alkanes ($N \geqslant \sim 13$), the simplification which consists of taking into account only the interaction matrix elements between vicinal bond orbitals [2], is no longer a satisfactory one.

1. Introduction. - The He(II) photoelectron spectra of the *n*-alkanes $H(CH_2)_NH$ were first recorded and discussed by *Potts, Price & Streets* [3] ($N = 1$ to 5) and recently by *Pireaux et al.* [1] ($N = 1$ to 9, 13, 36). (The latter publication should be consulted for a complete set of references on alkane He(I) and He(II) spectra.) It was shown that the series of N peaks ascribed to the ejection of a photoelectron from a dominantly 2s-type orbital converges with increasing N to a two-peaked band system, as shown in *Figure 1* for $N = 9$, 13 and 36. As *Pireaux et al.* have shown, the convergence to a band of finite width and the intensity distribution within the band system are well reproduced by an *ab initio* SCF model.

In this communication we wish to discuss the electronic factors which lead to the formation of a C_{2s}-band (for $N \rightarrow \infty$) in somewhat more detail, using a simple equivalent orbital model [4], which is suggested by the results of semi-empirical or *ab initio* SCF calculations [2].

If the $m = 3N + 1$ canonical valence shell orbitals φ_r ($r = 1,2,\ldots m$) of an alkane C_NH_{2N+2}, obtained from a semi-empirical or *ab initio* SCF calculation, are

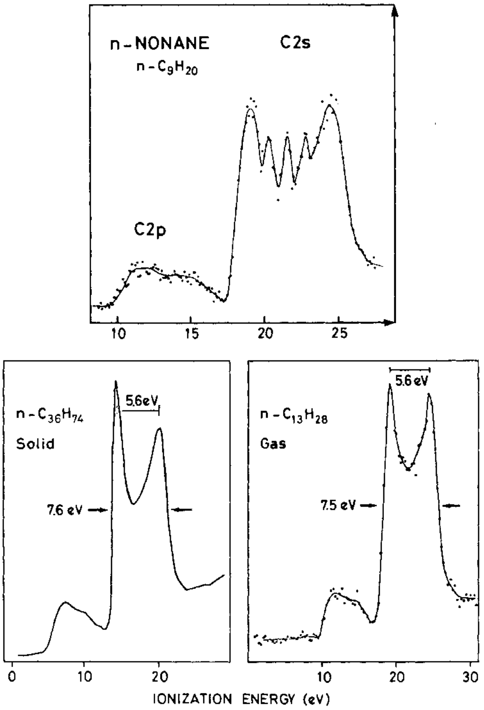


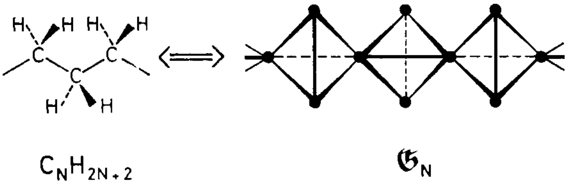
Fig. 1. *Photoelectron spectra of the normal alkanes* $H(CH_2)_NH$ *with* $N=9$, *13 and 36 recorded by* Pireaux et al. *[1].* The spectra have been redrawn from the original figures given in [1]

transformed into n localized orbitals λ_r by a localization procedure of the *Edmiston-Ruedenberg* [5] or the *Foster-Boys* [6] type, one makes the following observation: The diagonal elements $F_{\lambda,rr} \equiv A(\lambda_r)$ of the *Hartree-Fock* matrix **F** of the localized basis have practically the same value for localized CC- and CH-orbitals, *i.e.* $A(\lambda_{CC}) \approx A(\lambda_{CH})$, within small limits of error. Furthermore, the cross-terms $F_{\lambda,rs} \equiv B(\lambda_r, \lambda_s)$ between the localized orbitals λ_r, λ_s of two vicinal bonds are again almost independent of the type of λ_r and λ_s, *i.e.* $B(\lambda_{CC}, \lambda_{CC}) \approx B(\lambda_{CC}, \lambda_{CH}) \approx B(\lambda_{CH}, \lambda_{CH})$. Finally the long range interaction matrix elements $F_{\lambda,rs}$ ($r=s$, r and s *not* vicinal), *e.g.* $\Gamma(\lambda_r, \lambda_s)$, $\Delta(\lambda_r, \lambda_s)$, ..., for two localized orbitals separated by one, two or more bonds, although by no means negligible, are much smaller than $B(\lambda_r, \lambda_s)$. This suggests that for many simple applications the following approximation should prove satisfactory [2]:

$$\begin{aligned} &A(\lambda_{CC}) = A(\lambda_{CH}) = A \\ &B(\lambda_{CC}, \lambda_{CC}) = B(\lambda_{CC}, \lambda_{CH}) = B(\lambda_{CH}, \lambda_{CH}) = B \qquad (1) \\ &\Gamma(\lambda_r, \lambda_s) = \Delta(\lambda_r, \lambda_s) = \cdots = 0 \end{aligned}$$

This is of course nothing but the well known equivalent orbital approximation of *Hall & Lennard-Jones* [4] which has been shown to be a reasonably good model for the rationalization of photoelectron spectroscopic data, in particular of hydrocarbons [2].

If one is prepared to accept the simplifying assumptions (1) then the model reduces to a HMO-type treatment. Setting $-X = (A-E)/B$, all that has to be done is to calculate the spectrum X_j, $j = 1, 2, \cdots n$ of a graph $\mathfrak{G}$ in which the n vertices represent the n localized orbitals λ_r and the edges the cross terms between them [2]. A three-dimensional representation of $\mathfrak{G}$ for an *n*-alkane looks like its classical *van't Hoff* model, consisting of a series of tetrahedra joint at their vertices:



We wish to show that this simple model accounts remarkably well for the observed C_{2s}-band structure in the photoelectron spectra of the higher *n*-alkanes, in particular of polyethylene $-(CH_2)_\infty-$.

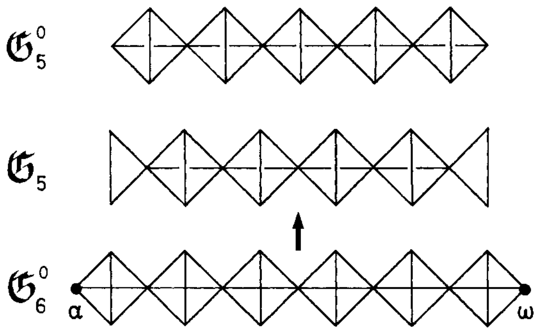
2. Model Calculation. - Assuming *Koopmans'* approximation, the N ionization energies $I_{2s,j}$ of the C_{2s}-band system of an *n*-alkane $H(CH_2)_NH$ are obtained from the N largest characteristic values X_j^o $(j = 1, 2, \cdots N)$ of the graph $\mathfrak{G}_N^o$, *i.e.* from the eigenvalues of the corresponding incidence matrix, according to

$$I_{2s,j} = -E_j = A + X_j^o B \qquad (3)$$

It has been shown previously [2] that (3) yields an almost perfect description of the C_{2s}-band sequence after empirical calibration of A and B, using the data for the lower members of the alkanes C_NH_{2N+2}, cf. upper regression (13) of ref. [2]:

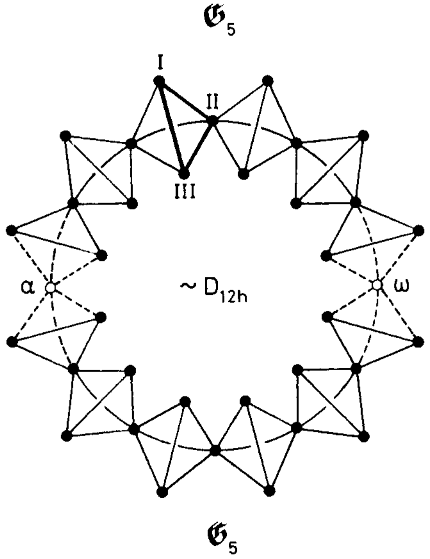
$$A = -16.10\ \text{eV};\ B = -2.11\ \text{eV} \qquad (4)$$

Unfortunately the exact values X_j^o of $\mathfrak{G}_N^o$ needed in (3) can not be given in closed form as a function of N and j, but have to be calculated from the incidence matrix of $\mathfrak{G}_N^o$ by standard diagonalization procedures, *e.g.* for *n*-pentane $H(CH_2)_5H$ from the incidence matrix corresponding to $\mathfrak{G}_5^o$:



(5)

In contrast, the characteristic values X_j of the graph $\mathfrak{G}_N$ obtained from $\mathfrak{G}^{\circ}_{N+1}$ by removing the two terminal vertices α and ω and the edges leading to them (see example (5) for $N=5$) can be derived easily by a procedure described some time ago [7]. It consists in joining two graphs $\mathfrak{G}_N$ across two additional vertices α and ω, to obtain a highly symmetrical compound graph with $6N+6$ vertices belonging to the topological symmetry $D_{(2N+2)h}$, as shown in the following diagram for $N=5$.



(6)

In the resultant graph the unit I, II, III is repeated $2N+2$ times (*i.e.* 12 times in the graph shown in (6)) and it is therefore very easy to compute directly the three characteristic values $X_{I,j}$, $X_{II,j}$, $X_{III,j}$ belonging to each of the $N+2$ irreducible representations $\Gamma^{(j)}$ of the subgroup C_{2N+2} of $D_{(2N+2)h}$. Of these characteristic values $X_{R,j}$ ($R=I, II, III$; $j=0, 1, 2 \cdots N+1$), those belonging to the N degenerate irreducible representations $\Gamma^{(j)}$ with index $j=1,2,\cdots N$, are also the required (non-degenerate) characteristic values of the reduced graph $\mathfrak{G}_N$. If we order the X_{Rj} values in such a way that $X_{I,j}>X_{II,j}>X_{III,j}$ then the N characteristic values $X_{I,j}$ are those which correspond according to (3) to the N C_{2s}-ionisation energies $I_{2s,j}$, under the implicit assumption that the graph $\mathfrak{G}_N$ represents a fair approximation of $\mathfrak{G}^{\circ}_N$. Obviously this will be true if N is large.

According to the rules given previously [7] the characteristic values $X_{R,j}$ are obtained by solving the following determinant for $j=1,2,\cdots N$, using the abbreviation $\varkappa=\exp(2\pi i/(2N+2))$:

$$\left\| \begin{matrix} -X_{R,j} & 1+\varkappa^{-j} & 1 \\ 1+\varkappa^{j} & -X_{R,j}+2\cos\left(\frac{2\pi j}{2N+2}\right) & 1+\varkappa^{j} \\ 1 & 1+\varkappa^{-j} & -X_{R,j} \end{matrix} \right\| = 0 \qquad (7)$$

If we are interested only in the largest root $X_{I,j}$, which we shall abbreviate X_j for convenience, we have from (7)

$$X_{I,j} \equiv X_j = \frac{1}{2} + C + \left(C^2 + 3C + \frac{17}{4}\right)^{1/2} \qquad (8)$$

$$C = \cos(2\pi j/(2N+2))$$

As can be seen from the following comparison, the approximate values X_j derived from formula (8) are sufficiently accurate for all practical purposes if $N \geqslant 9$:

j	From $\mathfrak{G}_9^o$ X_j^o	From $\mathfrak{G}_9$ (8) X_j	Difference ΔX_j
1	4.29	4.28	0.01
2	4.05	4.02	0.03
3	3.67	3.61	0.06
4	3.19	3.11	0.08
5	2.66	2.56	0.10
6	2.13	2.04	0.09
7	1.66	1.60	0.06
8	1.30	1.27	0.03
9	1.08	1.07	0.01

(9)

It has been shown by *Pauncz* [8] that the corrections ΔX_j (last column of (9)) can be calculated by a first-order perturbation method. However this seems hardly worthwhile in the present case, in view of the errors with which the experimental $I_{2s,j}$-values are affected and because we are mainly interested in the case $N \rightarrow \infty$, for which the ΔX_j become zero.

For $N \rightarrow \infty$, *i.e.* for a stretched polyethylene molecule $H(CH_2)_\infty H$, the limiting values derived from (8) are $X_1 = (3+\sqrt{33})/2 = 4.372$ and $X_\infty = 1.000$. The corresponding density of states in the intervall $1.000 \leqslant X_j \leqslant 4.372$ is shown graphically in *Figure 2.* Note that the state-density distribution is not symmetrical, the density of states near X_1 being higher than near X_∞.

To derive the expected C_{2s}-band contour one has to fold the calculated spectrum $\{X_j\}$ with the shape-function for an individual component. This function could be either a *Gaussian* G(X) or a *Lorentzian* L(X)

$$G(X) = (1/\sigma\sqrt{2\pi}) \exp(-(X-X_j)^2/2\sigma^2)$$

$$L(X) = (\tau/\pi)/((X-X_j)^2 + \tau^2) \qquad (10)$$

where τ is half the full width at half heights ($FWHH = 2\tau$), with $\tau \approx 1.2\sigma$. Both G(X) and L(X) are normalized to unity.

From the well resolved spectra of methane, ethane and propane given in the paper by *Pireaux et al.* [1] one deduces FWHH = 1.3 to 1.8 eV. Using the value of B given in (4) we have $\tau = 0.3$ to 0.4 units of X or $\sigma = 0.2_5$ to 0.3_5 units of X.

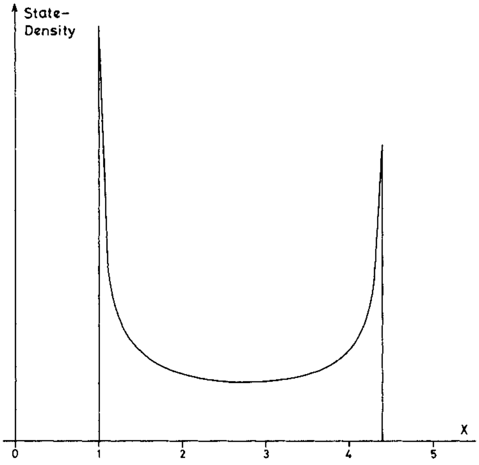


Fig. 2. *Density of states for the intervall* $X_\infty = 1.00 \leqslant X \leqslant X_1 = 4.372$ *of an equivalent bond orbital model of polyethylene* $H(CH_2)_\infty H$ (see formula (8) with $N = \infty$, $1 \leqslant j \leqslant \infty$)

The results of such a calculation for $N = 9$ (see (9)) and $N = \infty$ are presented in *Figure 3*. In both cases two *Gaussians* G(X) with slightly different width ($\sigma = 0.20$ or 0.25 units of X) and a *Lorentzian* L(X) with $\tau = 0.30$ have been used. Note that $\tau = 0.30$ yields the same FWHH for L(X) as $\sigma = 0.25$ for G(X). Comparison with the experimental findings shown in *Figure 1* reveals that our simple model yields as good an agreement with observation as can be reasonably be expected. For *n*-nonane the use of G(X) with $\sigma = 0.20$ gives definitely the best prediction. This

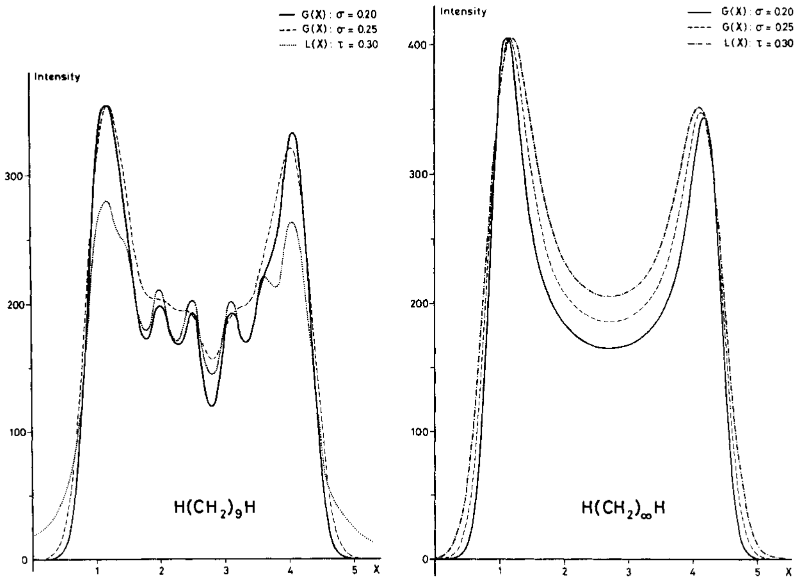
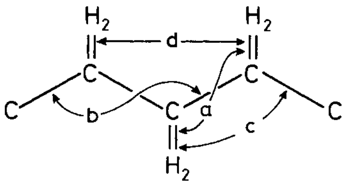


Fig. 3. *Calculated contours of the* C_{2s} *band systems of nonane* $H(CH_2)_9H$ *and of polyethylene* $H(CH_2)_\infty H$, *using the equivalent bond orbital model and an empirical line shape function (10).* The intensities are in arbitrary units. The *Gaussian* G(X) (FWHH $= 2\sigma$) and *Lorentzian* L(X) (FWHH $= 2\tau$) are defined in formulae (10). The values quoted for σ and τ are in units of X.

σ-value corresponds to a FWHH of an individual band of only 1.0 eV, *i.e.* a significantly smaller value than the one deduced from the spectra of the lower *n*-alkanes obtained by *Pireaux et al.* [1]. As suggested by *Gelius* [10], a tentative rationalization of this observation would be that vibrational broadening of the individual bands diminishes as the size of the system increases, because increasing delocalization of the positive hole would entail smaller reorganization and thus smaller displacements of the interatomic distances on relaxation.

3. Discussion. - If the value $B = -2.11$ eV given in (4) is used, then we predict from the distance between the two prominent maxima of the envelopes shown in *Figure 3,* a separation of 5,9 to 6.4 eV and of 6.1 to 6.5 eV for *n*-nonane and "polyethylene" respectively, the exact value of the calculated peak to peak gap depending somewhat on the FWHH assumed for the shape functions G(X) or L(X) (see (10)) of the individual components. In fact the difference X_1-X_∞ of the limiting values for $N \to \infty$ derived from (8) (see *Fig. 2*) is 3.372 units of X, which corresponds to a gap of 7.11 eV. Comparison with *Figure 1* shows that these calculated values are larger than the observed ones, *i.e.* 5.3 eV for *n*-nonane and 5.6 eV for the C_{36}-hydrocarbon. On the other hand the difference between the first and fifth peak in the C_{2s}-band system of *n*-pentane is 6.30 eV according to the results of *Pireaux et al.* [1], *i.e.* wider than the gap observed for *n*-nonane, *n*-$H(CH_2)_{13}H$ or *n*-$H(CH_2)_{36}H$, but in good agreement with the theoretical result obtained from the diagonalization of the incidence matrix corresponding to the graph $\mathfrak{G}_5^0$ shown in (5) which yields $-2.927\ B = 6.18$ eV. It is noteworthy that the smaller gap for the higher *n*-alkanes is due mainly to a shift of the band onset towards higher ionization energies (first peak of the *n*-pentane C_{2s}-bands at 18.7 eV, first maximum in the C_{2s}-band of $H(CH_2)_{13}H$ at ~ 20.0 eV). This contrasts with the prediction from our model, which places the first peak of *n*-pentane at $-(A + 1.228\ B) = 18.7$ eV (*i.e.* identical to the experimental value), but the first maximum in the polyethylene band system at $-(A + (1.1 \text{ to } 1.2)B) = 18.4$ to 18.6 eV (*i.e.* about 1.5 eV lower than observed).

One could argue that such differences are not too serious, in view of the crudeness of the model and because of the extrapolation to high values of N, which are well beyond the parametrization range (N = 1 to 6), of the parameters A and B given in (4). Nevertheless this discrepancy suggests that it might be rather instructive to investigate what the effect of the neglected matrix elements $F_{\lambda,rs}$ of the *Hartree-Fock* matrix **F** of the localized basis would be. Inspection of the results obtained for the lower *n*-alkanes [2,9] reveals that only four additional cross terms are of some importance, namely the terms $\Gamma(\lambda_r, \lambda_s)$ between two localized bond orbitals separated by one bond and the term $\Delta(\lambda_r, \lambda_s)$ where λ_r and λ_s are 1,3-positioned CH-orbitals. With reference to the following diagram the additional interaction terms are [9]:



(11)

a) The interaction term $\Gamma\,(\mathrm{CH_2, CH_2})$ between two consecutive in-phase methylene group orbitals $\lambda_{\mathrm{CH_2,j}} = (\lambda_{\mathrm{I,j}} + \lambda_{\mathrm{III,j}})/\sqrt{2}$ (indices I and III with reference to the graph given in (6)): $\Gamma\,(\mathrm{CH_2, CH_2}) = \langle \lambda_{\mathrm{CH_2,j}} | \mathscr{F} | \lambda_{\mathrm{CH_2,j\pm 1}} \rangle$.

b) The interaction term $\Gamma\,(\mathrm{CC, CC})$ between a given bond orbital $\lambda_{\mathrm{II,j}}$ and the one but next: $\Gamma\,(\mathrm{CC, CC}) = \langle \lambda_{\mathrm{II,j}} | \mathscr{F} | \lambda_{\mathrm{II,j\pm 2}} \rangle$.

c) The interaction term between $\lambda_{\mathrm{CH_2,j}}$ and the localized carbon-carbon bond orbital, one bond removed from $\lambda_{\mathrm{CH_2,j}}$: $\Gamma\,(\mathrm{CH_2, CC}) = \langle \lambda_{\mathrm{CH_2,j}} | \mathscr{F} | \lambda_{\mathrm{II,j+1}} \rangle = \langle \lambda_{\mathrm{CH_2,j}} | \mathscr{F} | \lambda_{\mathrm{II,j\text{-}2}} \rangle$.

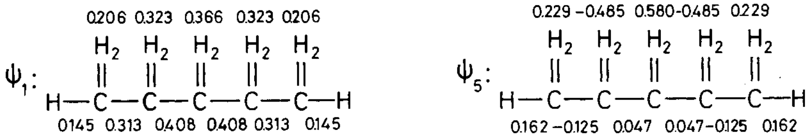
d) The interaction term between two methylene orbitals $\lambda_{\mathrm{CH_2}}$ separated by two CC-bonds: $\Delta\,(\mathrm{CH_2, CH_2}) = \langle \lambda_{\mathrm{CH_2,j}} | \mathscr{F} | \lambda_{\mathrm{CH_2,j\pm 2}} \rangle$.

From the numerical result of the application of localization procedures to semiempirical or *ab initio* SCF models of hydrocarbons [2,9] one finds (rounded to ±0.05), *e.g.* from the STO-3G model:

$$\begin{aligned} &\text{a) } \Gamma\,(\mathrm{CH_2, CH_2}) && \approx -0.2\,\mathrm{B} \\ &\text{b) } \Gamma\,(\mathrm{CC, CC}) && \approx -0.4_5 \\ &\text{c) } \Gamma\,(\mathrm{CH_2, CC}) && \approx 0.3_5\,\mathrm{B} \\ &\text{d) } \Delta\,(\mathrm{CH_2, CH_2}) && \approx 0.1_5\,\mathrm{B} \end{aligned} \tag{12}$$

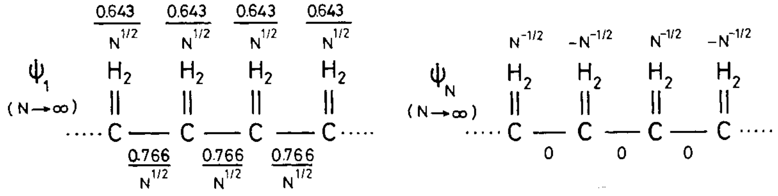
It is assumed that all local conformations of the CCCC-moieties of the polymethylene chain are of the staggered antiplanar type. Note also that for finite N we have in excellent agreement $\Gamma\,(\mathrm{CC, CC}) = \Gamma\,(\mathrm{CC, CH_{terminal}})$, where $\mathrm{CH_{terminal}}$ is the terminal CH bond lying in the plane of the carbon skeleton.

We consider two cases, namely that of *n*-pentane N = 5, a medium size alkane within the parametrization range, and that of an infinite polymethylene chain, N = ∞. In both cases we concentrate on the lowest (ψ_1) and highest (ψ_N) molecular orbital of the $\mathrm{C_{2s}}$-manifold. Solving the eigenvalue problem defined by the graph $\mathfrak{G}_5^0$ (see top of (5)) we obtain for the coefficients of the basis orbitals $\lambda_{\mathrm{CC,j}}$ the terminal $\lambda_{\mathrm{CH,terminal}}$ and the methylene orbitals $\lambda_{\mathrm{CH_2,j}}$ in the linear combinations ψ_1 and ψ_5 the following values:



(13)

In the case of an (infinite) polymethylene chain (N → ∞) the coefficients of $\lambda_{\mathrm{CH_2}}$ and of λ_{CC} in the lowest occupied orbital ψ_1, are $\mathrm{c_{1,CH_2}} = 4/\mathrm{N}\,(33+\sqrt{33}))^{1/2}$ and $\mathrm{c_{1,CH_2}} = (1+\sqrt{33})\,\mathrm{c_{1,CH_2}}/(4\sqrt{2})$, those in ψ_N are $\mathrm{c_{N,CH_2}} = \pm \mathrm{N}^{-1/2}$ and $\mathrm{c_{N,CC}} = 0$, for all bonds:



(14)

Using first order perturbation theory we now evaluate from (13) and (14) the individual shifts of the orbital energies due to the contributions of the long-range interactions (12):

$$
\begin{array}{c}
n\text{-Pentane } (H(CH_2)_5H) \\[4pt]
\begin{array}{rlrl@{\qquad}rlrl}
 & \psi_5 & & & & \psi_1 & & \\
-1.569 & \Gamma(CH_2,CH_2) & = & 0.31\,B & 0.740 & \Gamma(CH_2,CH_2) & = & -0.15\,B \\
0.007 & \Gamma(CC,CC) & = & 0.00\,B & 0.749 & \Gamma(CC,CC) & = & -0.34\,B \\
-0.652 & \Gamma(CH_2,CC) & = & -0.22\,B & 1.511 & \Gamma(CH_2,CC) & = & 0.53\,B \\
1.001 & \Delta(CH_2,CH_2) & = & \underline{0.15\,B} & 0.510 & \Delta(CH_2,CH_2) & = & \underline{0.08\,B} \\
 & \text{Sum} & & 0.24\,B & & \text{Sum} & & 0.12\,B
\end{array} \\[8pt]
\text{Polyethylene } (H(CH_2)_\infty H) \\[4pt]
\begin{array}{rlrl@{\qquad}rlrl}
 & \psi_\infty & & & & \psi_1 & & \\
-2.000 & \Gamma(CH_2,CH_2) & = & 0.40\,B & 0.826 & \Gamma(CH_2,CH_2) & = & -0.16\,B \\
0.000 & \Gamma(CC,CC) & = & 0.00\,B & 1.174 & \Gamma(CC,CC) & = & -0.53\,B \\
0.000 & \Gamma(CH_2,CC) & = & 0.00\,B & 0.985 & \Gamma(CH_2,CC) & = & 0.35\,B \\
2.000 & \Delta(CH_2,CH_2) & = & \underline{0.30\,B} & 0.826 & \Delta(CH_2,CH_2) & = & \underline{0.12\,B} \\
 & \text{Sum} & & 0.70\,B & & \text{Sum} & & -0.22\,B
\end{array}
\end{array}
\qquad (15)
$$

If the changes in orbital energies due to the Γ- and Δ-terms listed in (12) are divided by B and added to $X_1^o = 4.155$ and $X_5^o = 1.228$ of *n*-pentane or $X_1^o = 4.372$ and $X_\infty^o = 1.000$ of polyethylene respectively, then the following characteristic values result:

$$
\begin{array}{ll}
n\text{-Pentane; } H(CH_2)_5H: & \text{Polyethylene; } H(CH_2)_\infty H: \\
X_1' = X_1^o + 0.12 = 4.28 & X_1' = X_1^o - 0.22 = 4.15 \\
X_5' = X^o + 0.24 = 1.47 & X_\infty' = X_\infty^o + 0.60 = 1.60
\end{array}
\qquad (16)
$$

From this it is obvious that the difference $\Delta X^o = |X_5^o - X_1^o| = 2.93$ obtained for *n*-pentane by diagonalizing the incidence matrix of the graph $\mathfrak{G}_5^o$ changes slightly to $\Delta X' = |X_5' - X_1'| = 2.81$ if the Γ- and Δ-terms (12) are taken into consideration, whereas the difference $\Delta X^o = |X_\infty^o - X_1^o| = 3.37$ of polyethylene decreases significantly to $\Delta X' = |X_\infty' - X_1'| = 2.55$. This means that if the corrected values had been used for a calibration of B, we would have obtained from the experimentally observed positions of the first and fifth maximum of the C_{2s}-band system of pentane (18.70 eV and 25.0 eV respectively) a value of $B' = -2.24$ eV, instead of the value $B = -2.12$ eV given in (4). If the new value B′ is used in conjunction with $\Delta X' = 2.55$ for polyethylene a band width of 5.7 eV is predicted, which is in perfect agreement with the observed difference between the two maxima in the C_{2s}-band of $H(CH_2)_{13}H$ and $H(CH_2)_{36}H$ and therefore only slightly to small as an estimate of the observed band width.

Thus the above perturbation treatment shows that a more detailed, semiquantitative discussion has to take higher order terms into account, relative to the strongly simplified HMO-type treatment based on the graphs $\mathfrak{G}_N^o$. In particular, if the model is calibrated using the lower alkanes C_NH_{2N+2} with $N=6$ only, the effect of the higher cross terms gets absorbed in the parameters A and B. If these are used for alkanes with $N>6$ the influence on Γ, Δ and higher terms should be taken into consideration.

I thank Dr *U. Gelius* for his helpful comments and Prof. *K. Siegbahn* for having provided a copy of the paper quoted in [1] prior to publication.

This work is part 109 of project No. 2.518-76 of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* (Part 108 see ref. [2]). Support by *Ciba-Geigy SA, F. Hoffmann-La Roche* et Cie. SA and *Sandoz* SA is gratefully acknowledged.

REFERENCES

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

[2] *G. Bieri, J. W. Dill, E. Heilbronner & A. Schmelzer,* Helv. *60,* 2234 (1977).

[3] *W. C. Price, A. W. Potts & D. G. Streets,* in 'Electron Spectroscopy', Edit. D. A. Shirley, North Holland, Amsterdam 1972, p. 187; *A. W. Potts, T. A. Williams & W. C. Price,* Farad. Disc. chem. Soc. *54,* 104 (1972); *A. W. Potts & D. G. Streets,* J. chem. Soc. Faraday II *70,* 875 (1974); *D. G. Streets & A. W. Potts,* ibid. *70,* 1505 (1974).

[4] *J. E. Lennard-Jones,* Proc. Roy. Soc. *A198,* 1, 14 (1949); *G. G. Hall & J. E. Lennard-Jones,* ibid. *A 202,* 155 (1950), *A 205,* 357 (1951); *G. G. Hall,* ibid. *A 202,* 166 (1950).

[5] *C. Edmiston & K. Ruedenberg,* Rev. mod. Physics *35,* 457 (1963), J. chem. Physics *43,* S97 (1965); *W. England, L. S. Salmon & K. Ruedenberg,* Fortschr. chem. Forsch. *23,* 31 (1971).

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

[7] *E. Heilbronner,* Helv. *37,* 921 (1954).

[8] *R. Pauncz,* Acta physica Acad. Sci. Hungaricae, *6,* 15 (1956).

[9] *G. Bieri, E. Heilbronner & A. Schmelzer,* unpublished results.

[10] *U. Gelius,* private communication.