Electronic Structure of Saturated Hydrocarbons in the Semi-Empirical Equivalent Orbital Method

2. "Through Space Interactions" from the Data for Diamond and Neopentane

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The problem of obtaining the matrix elements of Hartree-Fock Hamiltonians for alkanes using the EO method is considered. It has been shown that the data on the electronic structure of diamond together with t_1/e splitting in the neopentane photoelectron spectrum are helpful to produce such EO method parameter scale which involves even "through space" interactions. In terms of the EO method the photoelectron spectra of propane, butane, isobutane, and neopentane are interpreted. The valence band structure of polyethylene in analytical form is obtained.

1. Introduction

It has been shown in a previous paper (Part I) [1] that the experimental data on the electron structure of methane, ethane, and diamond permit us to determine the matrix elements of the nearest neighbour bond interactions. It was pointed out that the t_1/e splitting in neopentane photoelectron spectrum depends exclusively on "through space" [7] interactions, which we did not take into account in Part 1. It was shown that the data on the well known electronic structure of diamond are very useful for the calculation of the spectra of alkanes; in this paper we shall obtain the parameters of "through space" interactions β_k, k, β_w, w, β_m. β_p, p (Fig. 1) from diamond (because there is no reliable symmetry assignment available for the photoelectron spectra of large hydrocarbons except the spectrum of neopentane). We shall use the t_1/e splitting in neopentane too.

2. The Dispersion Law for Diamond

Let us calculate the dispersion curves for the symmetry directions $\Delta = [100]$ and $\Lambda = [111]$ of the first Brillouin zone using the equivalent orbital method. We shall take into account all the mentioned interactions and use the symmetry properties [2].

Let us divide formally all the atoms of the diamond lattice into two classes {A} and {B} so that each atom of class {B} is surrounded by atoms of class {A} and each atom of class {A} is surrounded by atoms of class {B}. We shall associate
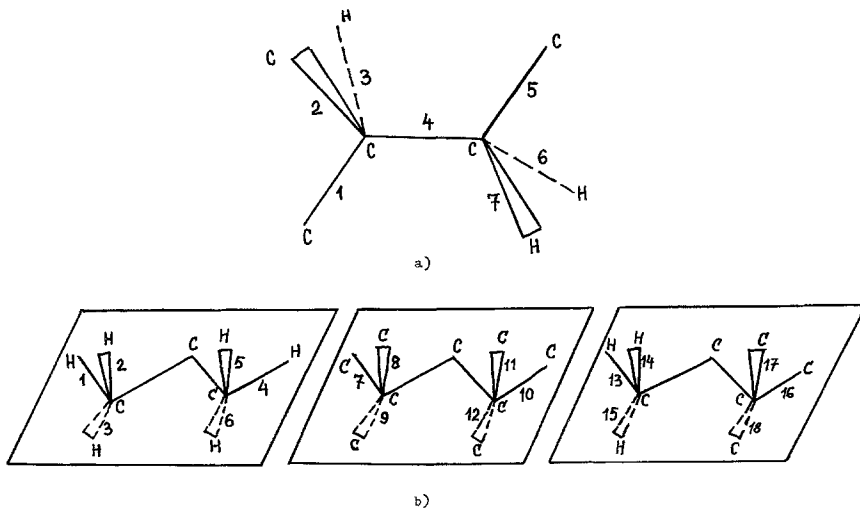
Fig. 1a and b. The matrix elements of the various interactions. (a) The nearest neighbour and the second neighbour interactions: $a = \langle 6|\mathscr{F}|6\rangle$, $b = \langle 6|\mathscr{F}|7\rangle$, $c = \langle 4|\mathscr{F}|4\rangle$, $d = \langle 7|\mathscr{F}|4\rangle$, $f = \langle 7|\mathscr{F}|3\rangle$, $g = \langle 6|\mathscr{F}|3\rangle$, $r = \langle 2|\mathscr{F}|6\rangle$, $s = \langle 2|\mathscr{F}|7\rangle$, $\beta_A = \langle 1|\mathscr{F}|2\rangle$, $\beta_t = \langle 1|\mathscr{F}|5\rangle$, $\beta_g = \langle 2|\mathscr{F}|5\rangle$. (b) Through space interactions: $w = \langle 1|\mathscr{F}|4\rangle$, $p = \langle 2|\mathscr{F}|5\rangle$, $k = \langle 2|\mathscr{F}|6\rangle$, $m = \langle 2|\mathscr{F}|4\rangle$, $\beta_w = \langle 7|\mathscr{F}|10\rangle$, $\beta_p = \langle 8|\mathscr{F}|11\rangle$, $\beta_k = \langle 8|\mathscr{F}|12\rangle$, $\beta_m = \langle 8|\mathscr{F}|10\rangle$, $\delta_w = \langle 13|\mathscr{F}|16\rangle$, $\delta_p = \langle 14|\mathscr{F}|17\rangle$, $\delta_k = \langle 14|\mathscr{F}|18\rangle$, $\delta_m = \langle 14|\mathscr{F}|16\rangle$

each bond A—B with the atom B which takes part in the bonding. So we establish a one-to-one correspondence between the atoms B and the bonds >B<. These bonds form four classes of the parallel and equally directed bonds. Let us take for each bond the corresponding EO's φ_j. Then for each class of the EO's we obtain the Bloch function:

$$\psi_j(k|r) = \frac{1}{\sqrt{N}} \sum_R e^{ikR} \varphi_j(r - R); \quad j = 1,...,4. \tag{2.1}$$

The group of the wave vector $G(k)$ for the Δ direction is C_{4v}. The group of the wave vector $G(k)$ for the Λ direction is C_{3v}. Therefore, the symmetrized Bloch functions are:

$$\Delta = [100] \text{ direction}; \ G(k) = C_{4v}$$

$$\Psi_1 = \frac{1}{\sqrt{2}} \{\psi_1 + \psi_4\} \quad \text{representation } \Delta_1$$

$$\Psi_2 = \frac{1}{\sqrt{2}} \{\psi_2 + \psi_3\} \quad \text{representation } \Delta_1 \tag{2.2}$$

$$\Psi_3 = \frac{1}{\sqrt{2}} \{\psi_1 - \psi_4\} \quad \text{representation } \Delta_5$$

$$\Psi_4 = \frac{1}{\sqrt{2}} \{\psi_2 - \psi_3\} \quad \text{representation } \Delta_5 ,$$

$$\Lambda = [111] \quad \text{direction} ; \; G(k) = C_{3v}$$

$$\Psi_1 = \psi_1 \quad \text{representation } \Lambda_1$$

$$\Psi_2 = \frac{1}{\sqrt{3}} \{\psi_2 + \psi_3 + \psi_4\} \quad \text{representation } \Lambda_1 \tag{2.3}$$

$$\Psi_3 = \frac{1}{\sqrt{2}} \{\psi_3 - \psi_4\} \quad \text{representation } \Lambda_3$$

$$\Psi_4 = \frac{1}{\sqrt{6}} \{2\psi_2 - \psi_3 - \psi_4\} \quad \text{representation } \Lambda_3 .$$

The dispersion curves in both directions are the solutions of the secular equation:

$$\begin{vmatrix} \mathcal{H}_{11} - \varepsilon(k) & \mathcal{H}_{12} \\ \mathcal{H}_{21} & \mathcal{H}_{22} - \varepsilon(k) \end{vmatrix} = 0 \tag{2.4}$$

and any of the following equations

$$\mathcal{H}_{33} - \varepsilon(k) = 0 ; \quad \mathcal{H}_{44} - \varepsilon(k) = 0 \tag{2.5}$$

where $\mathcal{H}_{ij} = \langle \Psi_i | \mathcal{F} | \Psi_j \rangle$, and $\mathcal{F}$ is the Hartree-Fock operator. Now, the matrix elements in the symmetrized Bloch function basis are:

Δ-direction

$$\mathcal{H}_{11} = \frac{1}{2} \{H_{11} + H_{14} + H_{41} + H_{44}\}$$

$$\mathcal{H}_{12} = \frac{1}{2} \{H_{12} + H_{42} + H_{13} + H_{43}\} \tag{2.6}$$

$$\mathcal{H}_{22} = \frac{1}{2} \{H_{22} + H_{23} + H_{32} + H_{33}\}$$

$$\mathcal{H}_{33} = \frac{1}{2} \{H_{11} + H_{44} - H_{14} - H_{41}\} ,$$

Λ-direction

$$\mathcal{H}_{11} = H_{11}$$

$$\mathcal{H}_{12} = \frac{1}{\sqrt{3}} \{H_{12} + H_{13} + H_{14}\} \tag{2.7}$$

$$\mathcal{H}_{22} = \frac{1}{3} \{H_{22} + H_{33} + H_{44} + H_{23} + H_{24} + H_{32} + H_{34} + H_{42} + H_{43}\}$$

$$\mathcal{H}_{33} = \frac{1}{2} \{H_{33} + H_{44} - H_{34} - H_{43}\} ,$$

where $H_{ij} = \langle \psi_i | \mathcal{F} | \psi_j \rangle$.

In this paper we are going to obtain the matrix elements $\beta_g, \beta_t, \beta_A$, and $\beta_p, \beta_k, \beta_w, \beta_m$ from the electronic structure of diamond, therefore we have to take into

account all these interactions in the formulae for H_{ij}. Hence, (Fig. 2)

$$H_{11} = \alpha + 2\beta_t\{\cos(q_x + q_y) + \cos(q_x + q_z) + \cos(q_y + q_z)\}$$
$$+ 2\beta_p\{\cos(q_x - q_y) + \cos(q_x - q_z) + \cos(q_y - q_z)\};$$

$$H_{22} = \alpha + 2\beta_t\{\cos(q_x + q_y) + \cos(q_z - q_y) + \cos(q_z - q_x)\}$$
$$+ 2\beta_p\{\cos(q_x - q_y) + \cos(q_z + q_y) + \cos(q_z + q_x)\};$$

$$H_{33} = \alpha + 2\beta_t\{\cos(q_z - q_y) + \cos(q_x - q_y) + \cos(q_x + q_z)\}$$
$$+ 2\beta_p\{\cos(q_y + q_z) + \cos(q_x + q_y) + \cos(q_x - q_z)\};$$

$$H_{44} = \alpha + 2\beta_t\{\cos(q_x - q_y) + \cos(q_z + q_y) + \cos(q_x - q_z)\}$$
$$+ 2\beta_p\{\cos(q_x + q_y) + \cos(q_z - q_y) + \cos(q_x + q_z)\};$$

$$H_{12} = \beta_A\{1 + e^{i(q_x + q_y)}\} + 2\beta_g\cos q_z\{e^{iq_x} + e^{iq_y}\} + \beta_w e^{-i(q_x + q_y)} + 2\beta_k\cos(q_x - q_y)$$
$$+ 2\beta_m\cos q_z\{e^{-iq_x} + e^{-iq_y}\} + \beta_w e^{i(2q_x + 2q_y)} + \beta_k\{e^{i2q_x} + e^{i2q_y}\};$$

$$H_{13} = \beta_A\{1 + e^{i(q_x + q_z)}\} + 2\beta_g\cos q_y\{e^{iq_x} + e^{iq_z}\} + \beta_w e^{-i(q_x + q_z)} + 2\beta_k\cos(q_x - q_z)$$
$$+ 2\beta_m\cos q_y\{e^{-iq_x} + e^{-iq_z}\} + \beta_m e^{i(2q_x + 2q_z)} + \beta_k\{e^{i2q_x} + e^{i2q_z}\}; \qquad (2.8)$$

$$H_{14} = \beta_A\{1 + e^{i(q_y + q_z)}\} + 2\beta_g\cos q_x\{e^{iq_y} + e^{iq_z}\} + \beta_w e^{-i(q_y + q_z)} + 2\beta_k\cos(q_y - q_z)$$
$$+ 2\beta_m\cos q_x\{e^{-iq_y} + e^{-iq_z}\} + \beta_w e^{i(2q_y + 2q_z)} + \beta_k\{e^{i2q_y} + e^{i2q_z}\};$$

$$H_{23} = \beta_A\{1 + e^{i(q_z - q_y)}\} + 2\beta_g\cos q_x\{e^{iq_z} + e^{-iq_y}\} + \beta_w e^{i(q_y - q_z)} + 2\beta_k\cos(q_y + q_z)$$
$$+ 2\beta_m\cos q_x\{e^{-iq_z} + e^{iq_y}\} + \beta_w e^{i(2q_z - 2q_y)} + \beta_k\{e^{i2q_z} + e^{-i2q_y}\};$$

$$H_{24} = \beta_A\{1 + e^{i(q_z - q_x)}\} + 2\beta_g\cos q_y\{e^{-iq_x} + e^{iq_z}\} + \beta_w e^{i(q_x - q_z)} + 2\beta_k\cos(q_z + q_x)$$
$$+ 2\beta_m\cos q_y\{e^{-iq_z} + e^{iq_x}\} + \beta_w e^{i(2q_z - 2q_x)} + \beta_k\{e^{i2q_z} + e^{-i2q_x}\};$$

$$H_{34} = \beta_A\{1 + e^{i(q_y - q_x)}\} + 2\beta_g\cos q_z\{e^{-iq_x} + e^{iq_y}\} + \beta_w e^{i(q_x - q_y)} + 2\beta_k\cos(q_x + q_y)$$
$$+ 2\beta_m\cos q_z\{e^{iq_x} + e^{-iq_y}\} + \beta_w e^{i(2q_y - 2q_x)} + \beta_k\{e^{i2q_y} + e^{-i2q_x}\}.$$

For symmetry directions $\Delta = [100]$ and $\Lambda = [111]$ the matrix elements H_{ij} can be simplified. We have for $\Delta = [100]$ $q_y = q_z = 0$, $q_x = q$ and for $\Lambda = [111]$ $q_x = q_y = q_z = q$. Now, we obtain for dispersion curves the following equations

$$\Delta = [100] \text{ direction}$$

$$\varepsilon_{1,2}(q) = \mathscr{H}_{11} \pm |\mathscr{H}_{12}| \qquad (2.9)$$

where

$$\mathscr{H}_{11} = \mathscr{H}_{22} = \alpha + 2\{\beta_A + \beta_t + \beta_p + \beta_w + 2\beta_k\} + 4\{\beta_t + \beta_g + \beta_p + \beta_m\}\cos q$$
$$\mathscr{H}_{12} = 2\{\beta_A + 2\beta_g + 2\beta_m + \beta_k + (\beta_A + 2\beta_g)e^{iq} + (\beta_w + 2\beta_m)e^{-iq} + 2\beta_k\cos q \qquad (2.9)$$
$$+ (\beta_w + \beta_k)e^{i2q}\}$$

and

$$\varepsilon_{3,4}(q) = \alpha - 2\{\beta_A - \beta_t + \beta_w + 2\beta_k - \beta_p\}$$
$$- 4\{\beta_g - \beta_t + \beta_m - \beta_p\}\cos q \qquad (2.10)$$

$$\Lambda = [111] \text{ direction}$$

$$\varepsilon_{1,2}(q) = \tfrac{1}{2}\{\mathscr{H}_{11} + \mathscr{H}_{22}\} \pm \{\tfrac{1}{4}(\mathscr{H}_{11} - \mathscr{H}_{22})^2 + \mathscr{H}_{12}\mathscr{H}_{21}\}^{\frac{1}{2}} \qquad (2.11)$$
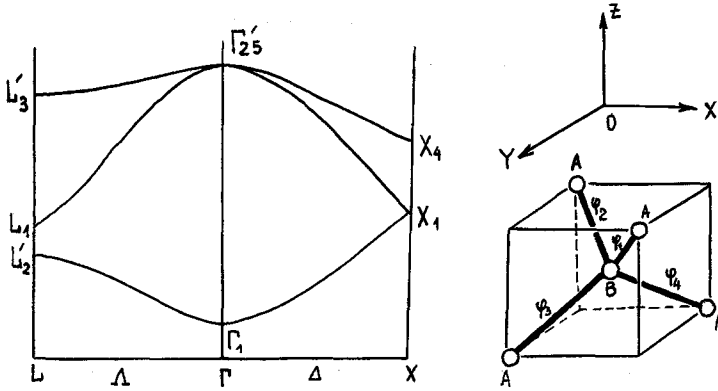
Fig. 2. Band structure of the diamond valence band and the orientation of the bonds in diamond

where

$$\mathcal{H}_{11} = \alpha + 6\beta_p + 6\beta_t \cos 2q$$

$$\mathcal{H}_{22} = \alpha + 2\beta_p + 4\{\beta_A + \beta_g + \beta_t + \beta_w + \beta_m\} + 2\{\beta_t + 2\beta_g + 2\beta_p + 2\beta_m + 4\beta_k\} \cos 2q$$

$$\mathcal{H}_{12} = \sqrt{3}\{\beta_A + 2\beta_k + 4\beta_g \cos q e^{iq} + (\beta_A + 2\beta_k)e^{i2q} + \beta_w(e^{-i2q} + e^{i4q}) + 4\beta_m \cos q e^{-iq}\}$$

and

$$
\begin{aligned}
\varepsilon_{3,4}(q) = \alpha &- 2\{\beta_A + \beta_g - 2\beta_t + \beta_w + \beta_m - \beta_p\} \\
&- 2\{\beta_g - \beta_t + 2\beta_k + \beta_m - 2\beta_p\} \cos 2q \ .
\end{aligned}
\tag{2.12}
$$

The valence band of diamond is plotted in Fig. 2. With the numerical data of Herman [3], we have (in eV):

The total bandwith of the valence band $E_v = \varepsilon(\Gamma'_{25}) - \varepsilon(\Gamma_1)$

$$E_v = -8\beta_A - 16\beta_g - 8\beta_w - 16\beta_k - 16\beta_m = 21 \ . \tag{2.13}$$

The bandwith of the p-subband $\Delta E_p = \varepsilon(\Gamma'_{25}) - \varepsilon(X_4)$

$$\Delta E_p = -8\beta_g + 8\beta_t + 8\beta_p - 8\beta_m = 5.5 \ . \tag{2.14}$$

The bandwidth of the upper sp-subband $\Delta E_1 = \varepsilon(\Gamma'_{25}) - \varepsilon(X_1)$

$$\Delta E_1 = -4\beta_A + 8\beta_t + 8\beta_p - 4\beta_w - 8\beta_k = 12 \tag{2.15}$$

The difference of the levels $\delta E_p = \varepsilon(\Gamma'_{25}) - \varepsilon(L'_3)$

$$\delta E_p = -4\beta_g + 4\beta_t - 8\beta_k - 4\beta_m + 8\beta_p = 2 \ . \tag{2.16}$$

The difference of the levels $\Delta E_{L_1} = \varepsilon(\Gamma'_{25}) - \varepsilon(L_1)$

$$\Delta E_{L_1} = -2\beta_A - 4\beta_g + 12\beta_t - 2\beta_w - 4\beta_k - 4\beta_m = 12.5 \ . \tag{2.17}$$

The difference of the levels $\Delta E_{L'_2} = \varepsilon(\Gamma'_{25}) - \varepsilon(L'_2)$

$$\Delta E_{L'_2} = -6\beta_A - 4\beta_g + 4\beta_t + 8\beta_p - 6\beta_w + 4\beta_k - 4\beta_m = 15 \ . \tag{2.18}$$

3. Calculation of Parameters

It should be noted that Eq. (2.18) follows from Eqs. (2.13)–(2.17). The solution of the Eqs. (2.13)–(2.17) is

$$\left.\begin{array}{rl}\beta_t = & 0.60 \\ \beta_p = & -0.17 \\ \beta_k = & 0.02 \\ \beta_g + \beta_m = & -0.25 \\ \beta_A + \beta_w = & -2.17 \, . \end{array}\right\} \tag{2.19}$$

Let us use the LCAO form of the EO's φ_{C-C} and φ_{C-H} for obtaining the matrix element of (C–H)–(C–H) interaction p from the (C – C)–(C–C) interaction β_p (Fig. 1).

$$\left.\begin{array}{l} \varphi_{A-B} = \dfrac{1}{\sqrt{2}} \{\chi_A + \chi_B\} \\[2mm] \varphi_{A-H} = \dfrac{1}{\sqrt{1+\lambda^2}} \{\lambda\chi_A + \chi_H\} \end{array}\right\} \tag{2.20}$$

where χ_H is the hydrogen $1s$-orbital and χ_A is the carbon sp^3-orbital.

Now it should be noted that the matrix elements of the third neighbour bond interactions [so called "through space" interactions (Fig. 1)] include interactions between atoms which are separated by two, three, and four bonds. Below we
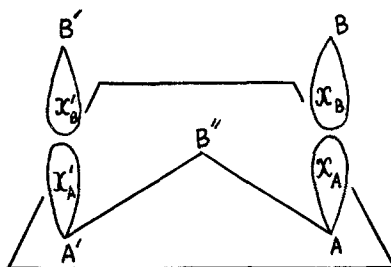

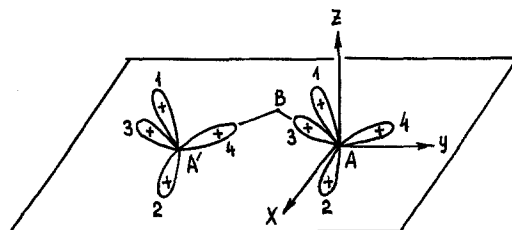Fig. 3. AOs interaction in β_p configuration

Fig. 4. The hybrid orbital orientation

use the following approximation. We take into account the AO's interactions of the atoms separated over two bonds only. Then we have (Fig. 3)

$$\beta_p = \langle \chi_A | \mathscr{F} | \chi_A' \rangle . \tag{2.21}$$

Using the LCAO form of χ_A and χ_A' hybrid orbitals (Fig. 4)

$$\left.\begin{aligned}
\chi_A^1 &= \frac{1}{2} s^A + \frac{1}{2} p_x^A + \frac{1}{\sqrt{2}} p_z^A \\[6pt]
\chi_A^2 &= \frac{1}{2} s^A + \frac{1}{2} p_x^A - \frac{1}{\sqrt{2}} p_z^A \\[6pt]
\chi_A^3 &= \frac{1}{2} s^A - \frac{1}{2} p_x^A - \frac{1}{\sqrt{2}} p_y^A \\[6pt]
\chi_A^4 &= \frac{1}{2} s^A - \frac{1}{2} p_x^A + \frac{1}{\sqrt{2}} p_y^A
\end{aligned}\right\} \tag{2.22}$$

we obtain

$$\beta_p = \frac{1}{4} \{\beta_{ss}' + 3\beta_\pi'\} . \tag{2.23}$$

Here

$$\beta_{ss}' = \langle s^A | \mathscr{F} | s^{A'} \rangle ; \qquad \beta_\pi' = \langle p_z | \mathscr{F} | p_z^{A'} \rangle .$$

By analogy, we can write

$$\beta_k = \frac{1}{8} \{\beta_{ss}' - \beta_\pi'\} \tag{2.24}$$

and

$$\beta_{ss}' = -0.04 \text{ eV}, \qquad \beta_\pi' = -0.21 \text{ eV} .$$

It should be noted that the H-atoms in p-configuration (Fig. 1) are located at the same distance from each other as the carbon atoms (though from a formal viewpoint the H-atoms are separated over four bonds).
Therefore we write

$$p = \frac{\lambda^2}{4(1+\lambda^2)} \{\beta_{ss}' + 3\beta_\pi'\} + \frac{\langle 1s^H | \mathscr{F} | 1s^{H'} \rangle}{1+\lambda^2} . \tag{2.25}$$

It is however obvious that the interaction between these H-atoms is weaker than that between the C atoms located at the same distance, because the distance (2.54 Å) exceeds considerably the sum of Van-der-Waals radii for the H-atoms (2.34 Å), but the distance 2.54 Å is less than the sum of the carbon Van-der-Waals radii. Therefore the second term in Eq. (2.25) will be neglected and we obtain $p \approx -0.1$ eV.

Let us now estimate the β_g and β_m interactions. In our approximation we can write

$$\beta_m = \frac{1}{8} \beta_{ss}' - \frac{1}{4\sqrt{2}} \beta_{sp}' - \frac{1}{8} \beta_\pi' .$$

Using numerical estimations for β'_{ss} and β'_{π} we have $\beta_m = 0.03 - \dfrac{1}{4\sqrt{2}}\beta'_{sp} > 0.03$ eV.

It is not possible now to obtain an exact estimation for the value β'_{sp} but one can believe that the value β'_{sp} is approximately β'_{ss} or β'_{π}. Then we have $\beta_m \simeq 0.1$ eV and $\beta_g \simeq -0.35$ eV.

In order to calculate the other parameters we use the t_1/e splitting in neopentane. (This splitting depends on "through space" interactions only.) Really,

$$\varepsilon_e - \varepsilon_{t_1} = 4m - 2k - 2w. \tag{2.26}$$

Using the above mentioned approximation for "through space" interactions, we have

$$\beta_w = \frac{1 + \lambda^2}{2} w^{1}, \tag{2.27}$$

$$\beta_k = \frac{1 + \lambda^2}{2} k, \tag{2.28}$$

$$\beta_m = \frac{1 + \lambda^2}{2} m. \tag{2.29}$$

Using the C–H bond dipole moment 0.4 D we have $\lambda = 0.924$. According to the photoelectron spectroscopy data [4]

$$\varepsilon_e - \varepsilon_{t_1} = 1.35 \text{ eV}.$$

Then from the Eqs. (2.26)–(2.29) we obtain

$$4\beta_m - 2\beta_k - 2\beta_w = 1.47 \text{ eV}$$

and $\beta_w = -0.55$ eV. Now from Eq. (2.19) we derive $\beta_A = -1.62$ and from (2.27 –(2.29) $m = 0.09$, $w = -0.51$, and $k = 0.02$ eV.

4. Methane and Ethane

It is obvious that all the parameters for the (C–H)–(C–H) interactions are to be obtained from the methane and ethane photoelectron spectra, because just these parameters determine the photoelectron spectra of these molecules (Part 1). It was pointed out in Part 1, that because of the large (0.8 eV) Jahn-Teller splitting it is not reasonable to use the ionisation potential of the highest occupied level of methane. Therefore, for the a_1 level of the methane spectrum we have (Part 1):

$$a + 3b = -23 \text{ eV}.$$

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[1] Actually, $\beta_w = \dfrac{1 + 2\lambda s_{C-H} + \lambda^2}{2 + 2s_{C-C}} W$, but the overlap integrals $s_{C-C} \approx s_{C-H} \approx 0.6$ and we obtain the same numerical estimations.

For ethane we can write the following equations

$$a - b + f - g = -12.0$$
$$a - b - f + g = -15.2$$
$$a + 2b - f - 2g = -20.4$$

and

$$\begin{vmatrix} c - \varepsilon & \sqrt{6}\,d \\ \sqrt{6}\,d & a + 2b + f + 2g - \varepsilon \end{vmatrix} = 0$$

$$\varepsilon_1 = -13.1; \quad \varepsilon_2 = -24.2.$$

Direct application of these equations together with the a_1 level of the methane spectrum yields $a = -15.95$, $b = -2.35$, $f = 0.98$, $g = -0.62$ eV and

$$c = \varepsilon_1 + \varepsilon_2 - \{a + 2b + f + 2g\} = -16.39 \text{ eV}$$

$$d = -2.09 \text{ eV}.$$

For the (C–H)–(C–C) interaction parameters we have (Part 1):

$$r = \frac{1}{2}\left\{ f\, \frac{\sqrt{1+\lambda^2}}{\lambda\sqrt{2}} + \beta_t \frac{\sqrt{2}\,\lambda}{\sqrt{1+\lambda^2}} \right\} = 0.80$$

$$s = \frac{1}{2}\left\{ g\, \frac{\sqrt{1+\lambda^2}}{\lambda\sqrt{2}} + \beta_g \frac{\sqrt{2}\,\lambda}{\sqrt{1+\lambda^2}} \right\} = -0.49$$

$$\delta_w = \frac{1}{2}\left\{ w\, \frac{\sqrt{1+\lambda^2}}{\lambda\sqrt{2}} + \beta_w \frac{\sqrt{2}\,\lambda}{\sqrt{1+\lambda^2}} \right\} = -0.53$$

$$\delta_p = \frac{1}{2}\left\{ p\, \frac{\sqrt{1+\lambda^2}}{\lambda\sqrt{2}} + \beta_p \frac{\sqrt{2}\,\lambda}{\sqrt{1+\lambda^2}} \right\} = -0.14$$

$$\delta_k = \frac{1}{2}\left\{ k\, \frac{\sqrt{1+\lambda^2}}{\lambda\sqrt{2}} + \beta_k \frac{\sqrt{2}\,\lambda}{\sqrt{1+\lambda^2}} \right\} = 0.02$$

$$\delta_m = \frac{1}{2}\left\{ m\, \frac{\sqrt{1+\lambda^2}}{\lambda\sqrt{2}} + \beta_m \frac{\sqrt{2}\,\lambda}{\sqrt{1+\lambda^2}} \right\} = 0.1.$$

We have summarized the results of the above consideration in Table 1.

Table 1. The matrix elements of the Hartree-Fock operator in the EO basis. The nearest neighbour, the second neighbour, and the through space interactions

a	b	c	d	f	g	r	s	
−15.95	−2.35	−16.39	−2.09	0.98	−0.62	0.80	−0.49	
β_t	β_g	β_A	m	β_m	k	β_k	p	β_p
0.60	−0.35	−1.62	0.09	0.1	0.02	0.02	−0.1	−0.17
δ_w	δ_m	w	β_w	δ_k	δ_p			
−0.53	0.1	−0.51	−0.55	0.02	−0.14			

Table 2. Comparison of the theoretical and experimental IPs of several saturated hydrocarbons

C_3H_8				$CH(CH_3)_3$		
Experiment [4, 5]	Present data	Brailsford and Ford [5]	ab initio [4]	Experiment [4]	Present data	ab initio [4]
11.4^c	$11.41\,b_2$	$11.24\,b_2$	$11.83\,b_1$	11.2^c	$11.17\,a_1$	$11.58\,e$
12.1^c	$11.9\ \ a_1$	$12.08\,a_1$	$12.37\,a_1$	11.6^c	$11.74\,e$	$12.26\,a_1$
12.6^a	$12.09\,b_1$	$12.40\,b_1$	$12.69\,b_2$	12.8	$12.81\,a_2$	$13.71\,a_2$
13.65	$13.48\,a_2$	$13.44\,a_2$	$14.32\,a_2$	13.4	$13.59\,e$	$14.37\,e$
14.2	$14.13\,b_1$	$14.25\,b_1$	$14.67\,b_1$	14.9	$15.13\,e$	$15.8\ \ e$
15.3	$15.2\ \ a_1$	$15.19\,a_1$	$15.99\,a_1$	16.0	$15.91\,a_1$	$17.03\,a_1$
15.8	$15.87\,b_2$	$15.79\,b_2$	$17.01\,b_2$	18.5	$18.47\,a_1$	$20.52\,a_1$
19.4	$19.37\,a_1$	$19.33\,a_1$	$21.38\,a_1$	—	$22.24\,e$	$24.65\,e$
22.2	$22.22\,b_1$	$21.97\,b_1$	$24.49\,b_1$	—	$24.91\,a_1$	$28.18\,a_1$
24.3	$24.65\,a_1$	$24.32\,a_1$	$27.55\,a_1$			

[a] This value seems to be unreliable, because it corresponds to a shoulder.

[b] These values are taken from the experimental data.

[c] The present ordering of the two highest occupied levels in propane and isobutane disagrees with *ab initio* data [4]. But Murrell and Schmidt assignment of the highest occupied levels of alkanes is not quite trustworthy, because even for the photoelectron spectrum of ethane their assignment disagrees with the experimental one.
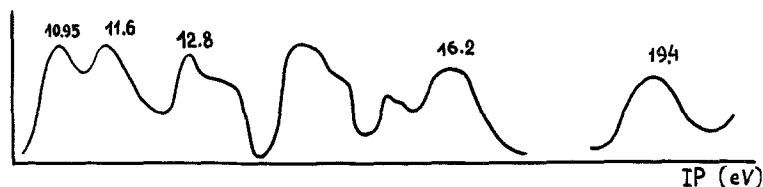

Fig. 5. The photoelectron spectrum of butane [5]

5. Calculation of Vertical IP's of Saturated Hydrocarbons

Using the parameters of Table 1 we have calculated the photoelectron spectra of propane, isobutane, neopentane, and butane. The results are shown in Table 2 together with the experimental data for C_3H_8, isobutane, and $C(CH_3)_4$ [4, 5]. *Ab initio* data [4], and the results of Brailsford and Ford [5] are also given[2]. It is obvious that the theoretical data agree with the experiment. For propane the disagreement between the theoretical and experimental data is not higher than 0.1–0.2 eV (except for the broad band about 24.3 eV and the unresolved level about 12.6 eV). For isobutane it is only for three levels that the disagreement between the theoretical and experimental data is more than 0.1 eV. An analogous agreement we have for neopentane too. For butane the comparison with the

[2] Comparing the present data with those of Brailsford and Ford one has to take into account that the Brailsford-Ford parameter scale was obtained from the propane and butane spectra and gives the incorrect band structure of diamond [1].

$C(CH_3)_4$				C_4H_{10}	
Experiment [4]	Present data	Brailsford and Ford [5, 1]	*ab initio* [4]	Present data	Brailsford and Ford [5]
11.3	11.46 t_2	11.61 t_2	11.40 t_2	11.12 b_g	10.96 [b]
12.7	12.81 t_1	13.13 t_1	13.71 t_1	11.67 a_g	11.60 [b]
14.1	14.15 e	13.75 e	15.03 e	11.95 a_g	12.38
15.4	15.62 t_2	15.22 t_2	16.39 t_2	12.50 a_u	12.63
17.5	17.17 a_1	17.95 a_1	19.49 a_1	12.99 b_u	13.51
—	22.26 t_2	22.21 t_2	24.56 t_2	14.48 b_g	13.66
—	25.04 a_1	24.43 a_1	28.66 a_1	14.65 b_u	14.38
				15.11 a_g	14.95
				16.3 a_u	16.20 [b]
				19.17 b_u	19.40 [b]
				20.82 a_g	20.46
				23.09 b_u	22.59
				24.89 a_g	24.74

experiment is more difficult because of the low resolution of levels in the experimental photoelectron spectrum (Fig. 5) [5]. One can see that the theoretical IP $\varepsilon_{b_u} = -19.2$ eV coincides with the experimental value -19.4 eV. The theoretical level $\varepsilon_{a_u} = -16.3$ eV agrees with the experimental value -16.2 eV. The single maximum between 15 and 16 eV is to be interpreted as the level $\varepsilon_{a_g} = -15.11$ eV. The two theoretical levels $\varepsilon_{b_u} = -14.65$ eV and $\varepsilon_{b_g} = -14.5$ eV correspond to one maximum between 14 and 15 eV. The theoretical level $\varepsilon_{a_u} = -12.5$ eV agrees with the experimental value 12.8 eV, and the weak peak below 13 eV is to be interpreted as the level $\varepsilon_{b_u} = -13.0$ eV.

The broad band with the two maxima -10.95 eV and -11.6 eV corresponds to the three levels $\varepsilon_{b_g} = -11.1$, $\varepsilon_{a_g} = -11.7$, and $\varepsilon_{a_u} = -11.95$ eV.

6. Polyethylene

There are many calculations of the electronic structure of polyethylene, but even the structure of the valence band of this polymer is not established definitively [6]. We shall apply the EO method to the valence band of polyethylene using the parameters of Table 1. Therefore we hope our data for this molecule are correct with the same accuracy as for the other alkanes calculated above. It is to be noted that the EO method permits to obtain the dispersion curves for polyethylene in the analytical form. It is not possible to obtain such a form by the LCAO method.

7. The Dispersion Law

Let us divide all the C atoms of the polyethylene chain into two classes {A} and {B} so that each atom of class {B} is surrounded by atoms of class {A} and each atom of class {A} by atoms of class {B}. We shall associate EO's for the C–C bonds with that atom B which takes part in the bonding. EO's for the C–H bonds
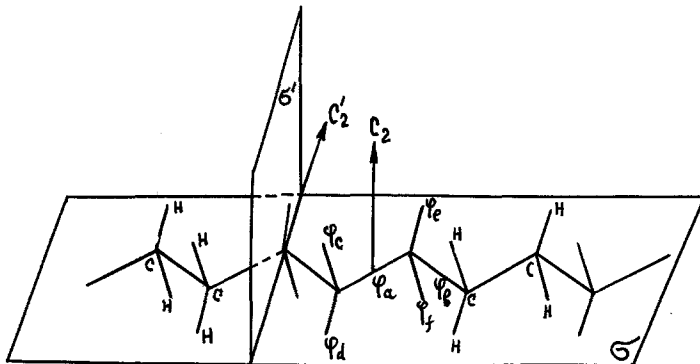
Fig. 6. The symmetry operations of the infinite polyethylene chain

we shall associate with the hydrogen atoms which take part in the bonding. The corresponding denotations are shown in Fig. 6. Thus, all the bonds are divided into six classes of bonds. Then we can write:

$$\psi_a(k|r) = \frac{1}{\sqrt{N}} \sum_n e^{iknR_0} \varphi_a(r - nR_0)$$

$$\psi_b(k|r) = \frac{1}{\sqrt{N}} \sum_n e^{iknR_0} \varphi_b(r - nR_0)$$

$$\psi_c(k|r) = \frac{1}{\sqrt{N}} \sum_n e^{iknR_0} \varphi_c(r - nR_0)$$

$$\psi_d(k|r) = \frac{1}{\sqrt{N}} \sum_n e^{iknR_0} \varphi_d(r - nR_0)$$

$$\psi_e(k|r) = \frac{1}{\sqrt{N}} \sum_n e^{iknR_0} \varphi_e(r - nR_0)$$

$$\psi_f(k|r) = \frac{1}{\sqrt{N}} \sum_n e^{iknR_0} \varphi_f(r - nR_0)$$

$$(2.30)$$

where $2N$ is the total number of C atoms, $n = 0, \pm 1, \pm 2 \ldots$, R_0 is the period of the one-dimensional lattice, and φ_a, $\varphi_b \ldots$ are corresponding EO's.

Let us introduce Born-von Kárman cyclic conditions and obtain the symmetrized combinations of the basic Bloch functions (2.30). Then the combinations

$$\Psi_1 = \frac{1}{\sqrt{2}} \{\psi_a + \psi_e\}$$

$$\Psi_2 = \frac{1}{2} \{\psi_c + \psi_d + \psi_e + \psi_f\}$$

$$(2.31)$$

are invariant under every symmetry operation. The function

$$\Psi_3 = \frac{1}{\sqrt{2}} \{\psi_a - \psi_b\} \qquad (2.32)$$

is antisymmetric under the operations σ' and C_2' (Fig. 6). The function

$$\Psi_4 = \frac{1}{2}\{\psi_c + \psi_d - \psi_e - \psi_f\} \tag{2.33}$$

is antisymmetric under the operation C_2. The function

$$\Psi_5 = \frac{1}{2}\{\psi_c - \psi_d + \psi_e - \psi_f\} \tag{2.34}$$

is antisymmetric under operations σ and C_2'. And the function

$$\Psi_6 = \frac{1}{2}\{\psi_c - \psi_d - \psi_e + \psi_f\} \tag{2.35}$$

is antisymmetric under operations σ, C_2', and C_2. Therefore the dispersion law $\varepsilon = \varepsilon(k)$ for identical representation (2.30) is to be obtained from secular equation

$$\begin{vmatrix} \mathscr{H}_{11} - \varepsilon(q) & \mathscr{H}_{12} \\ \mathscr{H}_{21} & \mathscr{H}_{22} - \varepsilon(q) \end{vmatrix} = 0 \tag{2.36}$$

where $\mathscr{H}_{ij} = \langle \Psi_i | \mathscr{F} | \Psi_j \rangle$ and $q = kR$. Then from Eqs. (2.36), (2.31), and (2.30) we have

$$\mathscr{H}_{11} = c + \beta_A + \{\beta_A + 2\beta_t + \beta_w\}\cos q + \beta w \cos 2q$$

$$\mathscr{H}_{22} = a + b + g + f + \{g + f + 2k + 2p\}\cos q \tag{2.37}$$

$$\mathscr{H}_{12} = \frac{1}{\sqrt{2}}\{3d + s + 2(s + m)\cos q + (d + s)e^{iq} + me^{-iq} + me^{i2q}\}$$
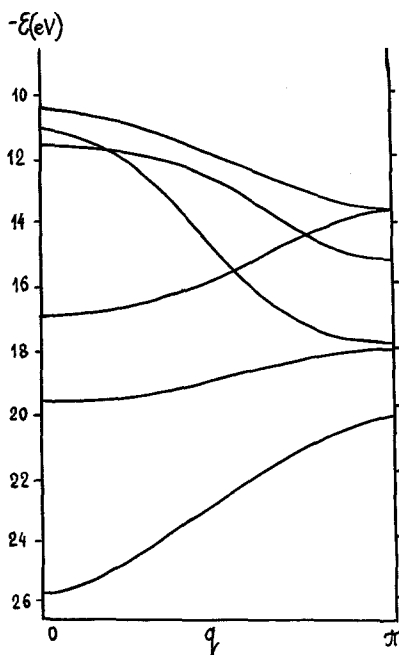

Fig. 7. Band structure of polyethylene valence band

The symmetrized Bloch functions (2.32)–(2.35) correspond to the different one dimensional representations, and therefore we obtain

$$\varepsilon_3(q) = \mathcal{H}_{33} = c - \beta_A + \{2\beta_t - \beta_A - \beta_w\} \cos q - \beta_w \cos 2q, \qquad (2.38)$$

$$\varepsilon_4(q) = \mathcal{H}_{44} = a + b - g - f - \{g + f + 2k - 2p\} \cos q, \qquad (2.39)$$

$$\varepsilon_5(q) = \mathcal{H}_{55} = a - b + g - f + \{g - f + 2k - 2p\} \cos q, \qquad (2.40)$$

$$\varepsilon_6(q) = \mathcal{H}_{66} = a - b - g + f - \{g - f - 2k + 2p\} \cos q. \qquad (2.41)$$

Using the parameters of Table 1 we obtain the valence band structure of polyethylene. The corresponding dispersion curves are shown in Fig. 7. The calculated IP from the upper occupied level is 10.2 eV. This value agrees with the trend in series of linear alkanes. (The neglect of the work function makes the estimation 8.6 eV [9] unreliable). The calculated total valence bandwidth $E_v \approx 16$ eV seems to be reasonable too. The photoelectron spectrum shape [10] does not allow to obtain any definite value of E_v. (The approximate value (about 20 eV) given in [10] seems to be the upper limit, because this value corresponds to the total valence bandwidth in diamond [8] with its much more branched bond system.)

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