Theoret. Chim. Acta (Berl.) 33, 323—328 (1974)

Electronic Structure of Saturated Hydrocarbons in the Semiempirical Equivalent Orbital Method

1. Matrix Elements in Valence Approximation from Data for CH_4, C_2H_6 and Diamond

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Received May 16, 1973/October 10, 1973

The problem of matrix elements of the Hartree-Fock Hamiltonian for saturated hydrocarbons in the EO method is considered. It is stated, that all the proposed scales of such parameters are incomplete or lead to an incorrect band structure of diamond. It is shown that the data on the band structure of diamond may be useful to obtain the full scale of the parameters for the calculations of the electronic structure of hydrocarbons.

Key words: CH_4 – C_2H_6 – Diamond – Saturated hydrocarbons, electronic structure of ~

Introduction

Progress in the photoelectron spectroscopy revived an interest to equivalent orbital (EO) method proposed by Hall [1, 2], because the experimental data on the ionization potentials permit to determine matrix elements of the Hartree-Fock operator in the EO basis. The EO method depends on the fact that a total wave function of a ground state is invariant to a unitary transformation and thus it is always possible to transform a molecular orbital basis to the equivalent orbitals in a solution of a particular problem. The EO basis gives a classically localized picture of a molecule.

Recently Brailsford and Ford [3], Murrell and Schmidt [4], and Nefedov [5] tried to determine the parameters of Hall's method from the experimentally known ionization potentials of a series of molecules. The authors of the two latter papers obtained the matrix elements of interactions of the C–H bonds only, because it was difficult to obtain the parameters for different C–C bonds. The paper of Brailsford and Ford [3] is more complete from this point of view. Nevertheless, this paper has the following deficiencies.

1. All the parameters (except those for CH_4 and C_2H_6) are obtained from the photoelectron spectra without reliable symmetry assignment.
2. We believe the parameters β_A, β_t[1] obtained from C_3H_8 (β_A) and C_4H_{10} (β_t) to be not sufficiently reliable, because these parameters are small and occur in the corresponding secular determinants only once.

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[1] All the labellings see below.

3. The whole scale of parameters [3] is somewhat uncertain because of the t_2 level splitting in CH_4.

4. Nonvalent interactions are not accurately taken into account.

These deficiencies become obvious if one uses the parameters from the paper [3] for diamond. Let us calculate the upper *sp*-subband bandwidth with the "best" parameters from [3]: $\beta_A = -1.31$, $\beta_t = -1.03$. Using the equivalent orbital method [10] we obtain [8]: $\varepsilon(\Gamma^v_{25'}) - \varepsilon(X^v_1) = -4\beta_A + 8\beta_t = -3$ eV. Thus, with these parameters we obtain that the valence band level X^v_1 lies in diamond above the $\Gamma^v_{25'}$ level. This result is in drastic contradiction with all the experimental and theoretical data [9]. It is known that the X^v_1 level lies below the $\Gamma^v_{25'}$ level, the difference $\varepsilon(\Gamma^v_{25'}) - \varepsilon(X^v_1)$ being $(+12)$ eV.

The Calculation of Parameters

All the notations are taken from the paper [3] except β_A, β_g, and β_t, where

$$\beta_A = \langle 1|\mathscr{F}|2\rangle$$
$$\beta_g = \langle 1|\mathscr{F}|3\rangle$$
$$\beta_t = \langle 1|\mathscr{F}|4\rangle .$$

Here $\mathscr{F}$ is the Hartree-Fock operator, and 1, 2 ... are EOs (Fig. 1).

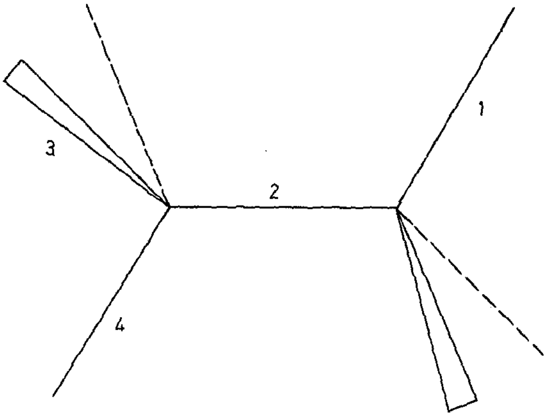

Fig. 1. Designation of (C–C) – (C–C) interactions

Methane

For methane one can write [1]:

$$\begin{aligned} \varepsilon_{t_2} &= a - b \\ \varepsilon_{a_1} &= a + 3b . \end{aligned} \tag{1.1}$$

Because of the large (0.8 eV) Jahn-Teller splitting [6] of the t_2 level we shall not calculate the parameters a and b from the Eq. (1.1). On the other hand the vertical ionisation potential from the a_1 level is well defined and $\varepsilon_{a_1} = -23$ eV [7]. Thus we obtain $a + 3b = -23$ eV.

Ethane

For ethane one can write the following equations [1, 3].

$$\begin{aligned} a-b+f-g &= -12.0\\ a-b-f+g &= -15.2\\ a+2b-f-2g &= -20.4 \end{aligned} \tag{1.2}$$

and

$$\begin{vmatrix} c-\varepsilon & \sqrt{6}\,d \\ \sqrt{6}d & a+2b+f+2g-\varepsilon \end{vmatrix} = 0 \tag{1.3}$$

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

From the Eq. (1.2) and the a_1-level of methane we have $a = -15.95$, $b = -2.35$, $f = 0.98$, $g = -0.62$ eV. And from (1.3):

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

$$d = \pm 2.09\ \text{eV}\,.$$

The sign of the parameter d will be derived below.

Diamond

We have calculated the interactions of C–H bonds from CH_4 and C_2H_6, i.e. from those compounds where these parameters determine almost the whole electron spectrum. By analogy, we have to derive the parameters of the interactions between C–C bonds from diamond, because just in this substance the electron structure is completely determined by interactions of the C–C bonds. From the dispersion law for diamond in the EO method [10] we may find [8]:

$$\begin{aligned} E_v &= -8\beta_A - 16\beta_g\\ \Delta E_p &= 8\beta_t - 8\beta_g\\ \Delta E_1 &= -4\beta_A + 8\beta_t \end{aligned} \tag{1.4}$$

where E_v, is the total bandwidth of the valence band,

$$\Delta E_p = \varepsilon(\Gamma^v_{25'}) - \varepsilon(X^v_4)$$

is the bandwidth of its p-subband, and

$$\Delta E_1 = \varepsilon(\Gamma^v_{25'}) - \varepsilon(X^v_1)$$

is the bandwidth of the upper sp-subband. According to the most reliable Herman's data [9], obtained by the empirically adjusted OPW method, we have $E_v = 21$, $\Delta E_1 = 12$ and $\Delta E_p = 6$ eV. It is to be noted that even if the value E_v were erroneous by 2 eV, the value $\beta_A + 2\beta_g$ would be obtained with fairly good accuracy about 0.2 eV. That is why we suppose that all the parameters $\beta_A = -2.06$, $\beta_g = -0.28$ and $\beta_t = 0.47$ eV are obtained from the system (1.4) with an accuracy of about 0.1 eV.

C–H- and C–C-Bonds Interactions

Now let us obtain the sign of the (C–H) – (C–C) nearest neigbour interaction d. Using the EO-LCAO approximation one can write:

$$\varphi_{A-B} = \frac{1}{\sqrt{2}}\{\chi_A + \chi_B\}$$

$$\varphi_{A-H} = \frac{1}{\sqrt{2}}\{\chi_A + \chi_H\}^{2}$$

where φ_{A-B}, φ_{A-H} are EOs, χ_H is the Is hydrogen orbital, and χ_A and χ_B are sp^3 hybrid orbitals of carbon (Fig. 2). Then one can write:

$$\begin{aligned} b &= \tfrac{1}{2}\langle\chi_A|\mathscr{F}|\chi'_A\rangle + \langle\chi_A|\mathscr{F}|\chi'_H\rangle + \tfrac{1}{2}\langle\chi_H|\mathscr{F}|\chi'_H\rangle \\ \beta_A &= \tfrac{1}{2}\langle\chi_A|\mathscr{F}|\chi'_A\rangle + \langle\chi'_A|\mathscr{F}|\chi_B\rangle + \tfrac{1}{2}\langle\chi'_B|\mathscr{F}|\chi_B\rangle \\ 2d &= \langle\chi_A|\mathscr{F}|\chi'_A\rangle + \langle\chi'_A|\mathscr{F}|\chi_B\rangle + \langle\chi_A|\mathscr{F}|\chi'_H\rangle + \langle\chi_B|\mathscr{F}|\chi'_H\rangle \end{aligned} \tag{1.5}$$

and

$$d = \tfrac{1}{2}\{b + \beta_A\} + \tfrac{1}{4}\{2\langle\chi_B|\mathscr{F}|\chi'_H\rangle - \langle\chi'_B|\mathscr{F}|\chi_B\rangle - \langle\chi_H|\mathscr{F}|\chi'_H\rangle\}\,.$$

Thus we have $d = \frac{1}{2}\{b + \beta_A\}$ the second term being neglected.

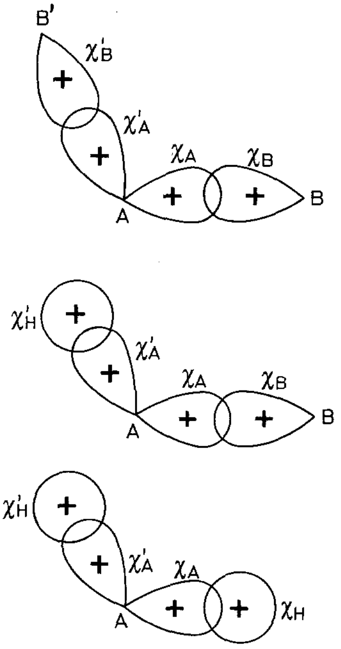

Fig. 2. Interactions of AOs in b, d, and β_A-configurations

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[2] Indeed $\varphi_{AH} = \frac{1}{\sqrt{1+\lambda^2}}\{\lambda\chi_A + \chi_H\}$, but it is not important below.

Finally we have from the last equation $d = -|d| = -2.09$. In the same way one can write[3]:

$$r = \tfrac{1}{2}\{f + \beta_t\} = 0.72\,\text{eV}$$

$$s = \tfrac{1}{2}\{f + \beta_g\} = -0.45\,\text{eV}\,.$$

We have summarized the results of the consideration given above in Table 1. One can compare our parameters with those reported by Brailsford and Ford [3] in this table too.

Calculation of the Propane and Neopentane

We have calculated the vertical IPs of propane and neopentane in order to examine the parameters of Table 1. The results are summarized in Tables 2 and 3. We compare our results with the experimental data [3, 4], with *ab initio* results reported by Murrell and Schmidt and with the EO calculations applying the parameters from paper [3].

It is obvious from Table 2 that the parameters derived from methane, ethane and diamond are in good agreement with the experimental data, the agreement being as good as that with the parameters of paper [3]. But the parameters reported by Brailsford and Ford are obtained from the photoelectron spectra of linear alkanes including propane.

In this paper we have restricted ourselves with computation of the matrix elements of the valence interactions. However, the t_1/e splitting of 1.4 eV depends exclusively on "through space" [11] interactions and cannot be calculated within

Table 1. Matrix elements of the Hartree-Fock operator in the EO basis

	a	b	c	d	β_A	f	g	r	s	β_g	β_t
Present data	−15.95	−2.35	−16.39	−2.09	−2.06	0.98	−0.62	0.72	−0.45	−0.28	0.47
Brailsford, Ford	−15.92	−2.43	−16.33	−1.87	−1.31	0.88	−0.73	0.98	−0.45	—	−1.03

Table 2. Theoretical and experimental IPs for propane

Experiment	Present data		Brailsford		*Ab initio* [4]	
11.4	11.34	b_2	11.24	b_2	11.83	b_1
12.1	11.95	a_1	12.08	a_1	12.37	a_1
12.6	12.21	b_1	12.40	b_1	12.69	b_2
13.65	13.6	a_2	13.44	a_2	14.32	a_2
14.2	14.14	b_1	14.25	b_1	14.66	b_1
15.3	14.87	a_1	15.19	a_1	15.99	a_1
15.8	15.86	b_2	15.97	b_2	17.07	b_2
19.4	19.36	a_1	19.33	a_1	21.38	a_1
22.2	22.23	b_1	21.97	b_1	24.49	b_1
24.3	24.82	a_1	24.32	a_1	27.55	a_1

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[3] Really, $r = \frac{1}{2}\left\{f\frac{\sqrt{1+\lambda^2}}{\lambda\sqrt{2}} + g\frac{\sqrt{2}\lambda}{\sqrt{1+\lambda^2}}\right\}$, but in terms of the C–H bond dipole moment 0.4 D we have $\lambda = 0.924$ and our error is not large.

Table 3. Theoretical and experimental IPs for neopentane

Experiment	Present data	Brailsford	*Ab initio* [4]
11.3	11.37 t_2	11.61 t_2	11.40 t_2
12.7	13.60 t_1; e	13.13 t_1	13.71 t_1
14.1	13.60	13.75 e	15.13 e
15.4	14.93 t_2	15.22 t_2	16.39 t_2
17.5	17.56 a_1	17.95 a_1	19.46 a_1
—	22.29 t_2	22.21 t_2	24.56 t_2
—	25.66 a_1	24.43 a_1	28.66 a_1

our approximation ($\varepsilon_{t_1} = \varepsilon_e = a - b$). Except this splitting our results for neopentane are in good agreement with the experimental photoelectron spectrum too. (It is to be noted that the parameters of paper [3] give similar results, because the principal difference between both scales of parameters concerns the matrix element values of the (C–C) – (C–C) interactions β_t and β_g. One should not regard the t_1/e splitting of 0.6 eV occurring in neopentane when using the parameters of paper [3] as an advantage of this parameter scale. The splitting appears in any parameter scale which includes the "through space" interaction parameters.)

Conclusion

It is apparent from the foregoing sections that the data on diamond, methane and ethane really permit to obtain all the nearest neighbour bond interactions. As things turned out, the data on the well known electron structure of diamond are very useful for the calculations of the spectra of alkanes. That is why we are going to obtain the interactions "through space" [11] from diamond in our next paper.

We intend to use the t_1/e splitting in neopentane too.

It is to be noted that the parameter set reported here may also be useful. This scale has the parameter β_g which is essential for the calculations of molecules with cis C–C bonds (cyclohexane etc.). Therefore, one can consider this set of parameters to be more complete in comparison with any other one known.

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