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Commentationes

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Pariser and Parr Type Calculations on Saturated Hydrocarbons I

By

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A Pariser and Parr-type approximation is proposed for saturated paraffinic hydrocarbons and is applied to methane, ethane and propane.

The choice of the integrals is discussed in detail. One center electron repulsion integrals are determined from atomic spectral data by deducing empirical Z numbers in Bingel's manner. Two center electron repulsion integrals are obtained according to the procedure used by Pariser and Parr. Resonance integrals are computed so that only the $(p:pp)$ type core-integrals therein are adjusted empirically.

A preliminary attempt is made to interpret the electronic spectra due to valence-shell transitions. The trend toward lower energies with increasing chain length of both the first ionization potential and the first excitation energy is successfully interpreted. Diagrams of electronic charge densities and bond orders are also given.

Une approximation du type Pariser et Parr pour le calcul des propriétés des hydrocarbures saturés est décrite et appliquée au méthane, l'éthane et le propane.

Le choix des intégrales est discuté en détail. Les intégrales de répulsion électronique à un centre ont été tirées des spectres atomiques en déduisant des nombres Z empiriques à la manière de Bingel. Les intégrales de répulsion à deux centres ont été obtenues par la procédure utilisée par Pariser et Parr. En calculant les intégrales de résonance seules les intégrales du type $(p:pp)$ étaient ajustées d'une manière empirique.

On rapporte une tentative à l'interprêtation du spectre électronique dû aux transitions dans la couche de valence. Les résultats interprêtent correctement le glissement vers les grandes longueurs d'onde du premier potentiel d'ionisation et de l'énergie d'excitation de la première transition singulet-singulet avec l'allongement de la chaîne carbonique. Des diagrammes des charges électroniques et des indices de liaison sont également présentés.

Für gesättigte Kohlenwasserstoffe wird ein Verfahren, analog dem von Pariser und Parr entwickelten, vorgeschlagen und auf Methan, Äthan und Propan angewendet. Dabei werden die Einzentren-Coulombintegrale nach der Methode von Bingel aus den Atomspektren errechnet, die Zweizentren-Coulombintegrale gemäß dem Verfahren von Pariser und Parr geschätzt, die Resonanzintegrale berechnet und die Rumpfintegrale als Justierungsparameter verwendet.

In einem ersten Versuch werden die der Anregung von Valenzelektronen zugeordneten Banden interpretiert. Ferner läßt sich das Absinken von Ionisierungs- und erster Anregungsenergie mit zunehmender Kettenlänge verstehen. Schließlich werden Diagramme für Ladungsdichte der Elektronen sowie für die Bindungsordnung gegeben.

Introduction

Quantum chemical literature related to larger molecules exhibits a rather pronounced preference for π-electronic systems and much work should be done in order to do justice to saturated molecules.

Early workes on saturated hydrocarbons used bond or group orbitals. Their results have been reviewed by various authors [*5, 19, 37*] and will not concern us here.

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An improved method of this type was recently given by LORQUET [*28*]. DEL RE [*7, 8*] described a method for the calculation of σ charges and σ energies which is based on the idea that the σ bonds are normally fully localized and they interact with each other through inductive effects representable by changes in the value of the Coulomb integrals.

The simple Hückel molecular orbital method was first applied to saturated hydrocarbons and their substituted derivatives by SANDORFY and DAUDEL [*41*] who based it uniquely on sp^3 hybrid orbitals bonding together carbon atoms (the "C" approximation) and by SANDORFY [*42*] who included all sp^3 hybrids whether they form C-C or C-H bonds and the hydrogen $1s$ orbitals (the "H" approximation).

These methods were improved by YOSHIZUMI [*48*] and were successfully used by FUKUI, KATO, and YONEZAWA [*10, 11*] for computing ionization potentials, heats of formation and certain quantities characterizing chemical reactivity.

Subsequently KLOPMAN [*19, 20, 21*] obtained an even better simultaneous fit of experimental values for heats of formation and ionization potentials, with a more suitable choice of parameters based on heats of formation.

HOFFMANN [*13*] used a parametrization based on valence-state ionization potentials, included overlap integrals and interactions between non-neighbors and was able to interprete many conformational problems. A more complete treatment was given by POPLE and SANTRY [*37*] who studied the causes of the non-additivity of certain properties of the hydrocarbons treating the factors causing delocalization as a perturbation.

The obvious next step in the evolution of treatments related to saturated molecules is to apply the semiempirical Pariser and Parr method, either in its original form [*31, 32*] with or without configuration interaction or with self-consistent orbitals as proposed by POPLE [*3, 37*]. In recent papers KLOPMAN gave [*18*] a self-consistent semiempirical method of this sort applied to diatomic and some small polyatomic molecules where all integrals involved are directly deduced from atomic spectra or bond distances. Another self-consistent approach with complete neglect of differential overlap was given by POPLE et al. [*36*], and still another by KAUFMAN [*17*]*.

In the present paper a somewhat different method is outlined which is closer to the original Pariser and Parr method. Our efforts were directed mostly toward the interpretation of ionization potentials and electronic spectra of saturated hydrocarbons, a problem what none of the previous authors have attacked. Electronic charge distribution will also be considered, however.

Outline of the Method

The procedure we have followed is essentially the same as the one originally introduced by PARISER and PARR [*31, 32*]. As it is well known in this method the wavefunctions are antisymmetrized products of molecular orbitals (12) and we neglect differential overlap in electron repulsion integrals and treat the core integrals as parameters. In the following we discuss in some detail the choice of the integrals we have made.

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* These papers appeared after our manuscript was submitted and are not considered in detail.

The basic atomic orbitals we used were carbon sp^3-tetrahedral hybrid orbitals and hydrogen $1s$ orbitals. Only the carbon $1s$ orbitals were included in the core.

a) Carbon One-Center Repulsion Integrals

For reasons given below we did not use Pariser's $(pp \mid pp) = I - A$ formula where p stands for a carbon sp^3-orbital and I and A are the valence state ionization potential and electron affinity respectively. Instead we chose to adjust the effective nuclear charges Z_{2s} and Z_{2p} empirically in the following way.

In Slater's theory of atoms [*45*] (one-center) Coulomb and exchange integrals involving no more than two atomic orbitals are expressed, apart from a spin factor, as:

$$J\,(nlm_l;\, n'l'm_l') = \sum_k a^k\,(lm_l;\, l'm_l')\, F^k\,(nl;\, n'l') \tag{1}$$

and

$$K\,(nlm_l;\, n'l'm_l') = \sum_k b^k\,(lm_l;\, l'm_l')\, G^k\,(nl;\, n'l') \tag{2}$$

where F^k and G^k are expressions introduced into the integrals by the radial parts of the wave functions:

$$F^k\,(nl;\, n'l') = R_k\,(nl,\, n'l';\, nl,\, n'l') \tag{3}$$

$$G^k\,(nl;\, n'l') = R_k\,(nl,\, n'l';\, n'l',\, nl) \tag{4}$$

and a^k and b^k by their angular parts. The summation is over the appropriate Legendre polynomials (4). For a pair of equivalent electrons

$$F^k\,(nl,\, nl) = G^k\,(nl,\, nl)\,. \tag{5}$$

The a^k and b^k were tabulated by Condon and Shortley (ref. [*4*], p. 178) for all possible sets of quantum numbers for s, p, d and f orbitals. The F^k and G^k are given in the extensive work of Bingel [*2*] who used Slater orbitals to compute them. They are expressed as functions of the orbital exponent $\zeta = Z/2$. Since, on the other hand, the F^k and G^k can be determined from observed atomic spectra we have a means for deducing empirical Z values for given cases.

For the present work we need integrals over $2s$ and $2p$ orbitals. From eq. (1) and (2) we obtain the following relations:

$$\begin{aligned}
(2s\,2s \mid 2s\,2s) &= F^0\,(2s,\, 2s)\\
(2p\,2p \mid 2p\,2p) &= F^0\,(2p,\, 2p) + \frac{4}{25}\, F^2\,(2p,\, 2p)\\
(2s\,2s \mid 2p\,2p) &= F^0\,(2s,\, 2p)\\
(2s\,2p \mid 2s\,2p) &= \tfrac{1}{3}\, G^1\,(2s,\, 2p)
\end{aligned} \tag{6}$$

where all the p occuring in the same integral have the same index x or y or z and the equality:

$$F^2\,(2p,\, 2p) = G^2\,(2p,\, 2p)$$

is taken into account. Now, according to Bingel [*2*] and with the symbols used by him and previously by Pritchard and Skinner [*39, 44*],

$$G_2\,(2p,\, 2p) = \frac{1}{25}\, G^2\,(2s,\, 2p) = \frac{9}{1280}\,\zeta_{2p}\ \text{a.u.} = 0.191314\,\zeta_{2p}\ \text{e.V.} \tag{7}$$

$$G_1\,(2s,\, 2p) = \tfrac{1}{3}\, G^1\,(2s,\, 2p) = \frac{\zeta_{2s}^5\,\zeta_{2p}^5}{\zeta^9}\ \text{a.u.} \tag{8}$$

where:

$$\zeta = \zeta_{2s} + \zeta_{2p}$$

$$\zeta_{2p} = Z_{2p}/2 \quad \text{and} \quad \zeta_{2s} = Z_{2s}/2 \, .$$

The experimental values of G_1 and G_2 are given in Tab. 1, expressed in electron volts. They are taken from Pilcher and Skinner [*35*].

Table 1

	C+	C	C−
$G_2\,(2p, 2p)$	0.2311	0.2138	0.1810
$G_1\,(2s, 2p)$	2.8278	2.5868	2.2204

Substituting these into eq. (7) yields empirical effective nuclear charges for the $2p$ electrons of the neutral carbon atom and its positive and negative ions respectively.

$$Z^0_{2p} = 2.2306 \qquad \text{for the neutral C atom}$$
$$Z^-_{2p} = 1.8922 = Z^0_{2p}\,(1 - \varepsilon^-_p) \qquad \text{for the } C^- \text{ ion}$$
$$Z^+_{2p} = 2.4159 = Z^0_{2p}\,(1 + \varepsilon^+_p) \qquad \text{for the } C^+ \text{ ion}$$

with $\varepsilon^-_p = 0.1534_1$ and $\varepsilon^+_p = 0.0809_2$.

Similarly for $2s$ electrons we obtain, from eq. (8):

$$Z^0_{2s} = 2.2585 \quad \text{for the neutral C atom}$$
$$Z^+_{2s} = 2.4461 \quad Z^0_{2s}\,(1 + \varepsilon^+_s) \qquad \text{for the } C^+ \text{ ion}$$
$$Z^-_{2s} = 1.9170 \quad Z^0_{2s}\,(1 - \varepsilon^-_s) \qquad \text{for the } C^- \text{ ion}$$

with $\varepsilon^-_s = 0.1512_3$ and $\varepsilon^+_s = 0.08305$.

In Tab. 2 we compare these empirical effective nuclear charges with those calculated previously by Bingel [*2*] (who used spectral term values given by Skinner and Pritchard [*44*]) and by Kohlrausch [*22*]. The number corresponding to Slater's rules is also included.

Table 2

Z Slater	Z Bingel	Z Kohlrausch	Z This work
3.25	2.1	2.03	2.23

In this work we used the theoretical one-center repulsion integrals obtained from equations (1) and (2) with these empirical Z values. They are listed in Tab. 3 in the columns headed by C^-, C, and C^+. In the same table under "Theoretical, $Z = 3.25$", we give the theoretical integrals computed with the conventional Slater Z value. The values marked with an asterisk were computed with orthogonalized $2s$ functions. Under P-P are the Pariser and Parr values obtained from the $I - A$ formula with valence state ionization potentials and electron affinities based on spectral terms found in [*35*]. Under "Valence state method" are values of the integrals computed from data given by the same authors using methods due

Table 3

	Theoretical $Z = 3.25$	C^-	C	C^+	Empirical			
					P-P Method	Valence State Method	Julg's Method	Leroy's Method
$(2p\,2p \mid 2p\,2p)$	17.306	10.076	11.902	12.865	10.44	10.44	9.21	8.97
$(2s\,2s \mid 2s\,2s)$	16.063 15.661 *	9.585	11.161	12.090	11.89	11.89	8.89	8.31
$(2s\,2s \mid 2p\,2p)$	16.063 15.837 *	9.410	11.105	12.014	–	11.74		
$(2p_\pi\,2p_\pi \mid 2p_\sigma\,2p_\sigma)$	15.441	8.990	10.600	11.478	–	9.18		
$(2p_\pi\,2p_\sigma \mid 2p_\pi\,2p_\sigma)$	0.933	0.543	0.641	0.693	–	0.63		
$(2s\,2p \mid 2s\,2p)$	3.550	2.220	2.585	2.828	–	2.59		
$(tt \mid tt)$	19.425	11.461	13.497	14.618	12.78		11.13	10.81

to Mulliken [*30*]. For comparison some integrals were also computed from formulas deduced by Julg [*16*] and by Leroy [*26*] using the valence state energies given in [*35*]. p_σ and p_π are oriented in a bond direction and perpendicular to each other and the integral over the tetrahedral orbitals is given by

$$(tt \mid tt) = \frac{1}{16}\,[(2s\,2s \mid 2s\,2s) + 12\,(2s\,2p \mid 2s\,2p) + 9\,(2p\,2p \mid 2p\,2p) + 6\,(2s\,2s \mid 2p\,2p)]$$

where

$$t = \tfrac{1}{2}\,(2s + \sqrt{3}\;2p)\,.$$

(see below)

It now becomes apparent why we did not choose the $I - A$ method of Pariser and Parr. In fact we cannot obtain by this procedure the important $(2s\,2s \mid 2p\,2p)$ or $(2p_\pi\,2p_\sigma \mid 2p_\pi\,2p_\sigma)$ integrals and others whose place was left vacant in Tab. 3.

Since one center Coulomb repulsion integrals originate – using the valence-bond language – from polar structures that is, from negatively charged carbon atoms, we used the Z values related to C^- to compute them.

b) Hydrogen one-center repulsion integrals

For the H^- ion the variational method gives $Z'_h = 11/16 = 0.69$ [*46*]. This value, however, leads to a negative electron affinity which is contrary to the result of the exact calculations of Pekeris [*34*]. We shall use Pekeris' electron affinity value in order to estimate $(hh \mid hh)$ where h stands for an $1s$ orbital of the hydrogen atom.

The ionization potential in atomic units is equal to:

$$-\,I = \int h\,(1)\,(-\nabla^2 + V_h^+)\,h\,(1)\,d\tau_1 = \tfrac{1}{2}\,Z_h^2 - Z_h \qquad (9)$$

with $Z_h = 1$.

The electron affinity A may be expressed using Goeppert-Mayer and Sklar's [*12*] potential involving the neutral Hamiltonian:

$$-\,A = \int h'\,(1)\,(-\nabla_1^2 + V_h^0)\,h'\,(1)\,d\tau_1 \qquad (10)$$

where

$$V_h^0 = V_h^+ + \int h'(2)\, h'(2) \frac{1}{r_{12}}\, d\tau_2 . \tag{11}$$

Substituting (11) into (10) we obtain

$$\begin{aligned} -A &= \int h'(1)\,(-\nabla_1^2 + V_h^+)\, h'(1)\, d\tau_1 + (h'\, h' \mid h'\, h') \\ &= \tfrac{1}{2} Z_{h'}^2 - Z_{h'} + (h'\, h' \mid h'\, h') . \end{aligned} \tag{12}$$

Substracting (12) from (9) yields

$$(h'\, h' \mid h'\, h') = I - A + \tfrac{1}{2} (Z_h^2 - Z_{h'}^2) + (Z_{h'} - Z_h) . \tag{13}$$

This would be equal to $I - A$ if we had $Z_{h'} = Z_h$. If we take $Z_h = 1$ and $Z_{h'} = 0.69$ we have:

$$\begin{aligned} (h'\, h' \mid h'\, h') &= I - A + (0.69 - 1) + \tfrac{1}{2} (1 - 0.69^2) \\ &= I - A - 0.04805 \text{ a.u.} \\ &= I - A - 1.307 \text{ eV} . \end{aligned} \tag{14}$$

Introducing $I = 13.605$ eV

and $A = 0.755$ eV

we obtain that

$$(h'\, h' \mid h'\, h') = 11.542 \text{ eV} .$$

The theoretical value of $(hh \mid hh)$ with

$$Z = 0.69 \text{ is } 11.734 \text{ eV} .$$

The Pariser and Parr value $I - A$ is equal to $13.605 - 0.755 = 12.85$ eV.

We adopted 11.542 eV.

We did not use the method applied to carbon in the previous section because of lack of spectral data on the H^- ion. Also the method used in the present section would be more dangerous to apply to carbon because of the more complicated character of its core.

c) Two Center Electron Repulsion Integrals

For internuclear distances larger than 2,8 Å we used the uniformly charged sphere model of PARR [*33*] with $Z = 3.25$ for carbon $2p$ orbitals. For $2s$ and H$1s$ orbitals we used the point charge model.

For distances shorter than 2.8 Å we applied the well know formulas given in PARISER and PARR's second paper obtained by extrapolating to $r = 0$ the equation:

$$ar + br^2 = \tfrac{1}{2} [(pp \mid pp) + (qq \mid qq)] - (pp \mid qq) \tag{15}$$

after determining the constants a and b by fitting (15) for $r = 2.80$ Å and $r = 3.80$ Å by the values obtained from the uniformly charged sphere model.

Then we have the following types of two-center electronic repulsion integrals for distances shorter than 2.8 Å:

$$\begin{aligned}
(hh \mid h' h') &= 11.542 - 2.9730\, r + 0.2455\, r^2 \\
(hh \mid s' s') &= 10.564 - 2.3660\, r + 0.1535\, r^2 \\
(hh \mid p'_\sigma p'_\sigma) &= 10.809 - 2.1643\, r + 0.0945\, r^2 \\
(hh \mid p'_\pi p'_\pi) &= 10.809 - 2.6822\, r + 0.2153\, r^2 \\
(p_\pi p_\pi \mid p'_\pi p'_\pi) &= 10.076 - 2.3098\, r + 0.1644\, r^2 \\
(p_\sigma p_\sigma \mid p'_\sigma p'_\sigma) &= 10.076 - 1.1437\, r - 0.1124\, r^2 \qquad (16) \\
(ss \mid s' s') &= 9.585 - 1.7590\, r + 0.0615\, r^2 \\
(ss \mid p'_\pi p'_\pi) &= 9.410 - 1.8144\, r + 0.0839\, r^2 \\
(ss \mid p'_\sigma p'_\sigma) &= 9.410 - 1.2777\, r - 0.0437\, r^2 \\
(p_\pi p_\pi \mid p'_\sigma p'_\sigma) &= 8.990 - 1.2785\, r - 0.0192\, r^2 \\
(p_\pi p_\pi \mid p'_\pi p'_\pi) &= 8.990 - 1.7275\, r + 0.0858\, r^2 \,.
\end{aligned}$$

Here h and h' are hydrogen $1s$ orbitals on two different hydrogen nuclei, s is a carbon $2s$ orbital on the same nucleus as the one to which the other orbital involved with the given integral and $2s'$ on a different one; $2p_\sigma$ is an orbital directly linked to the other orbital in the integral and $2p_\pi$ is a $2p$ orbital perpendicular to $2p_\sigma$; $2p'_\sigma$ is lying an another bond axis and $2p'_\pi$ perpendicular to the latter: $2p'_{\pi'}$ is perpendicular to $2p'_\pi$ and $2p'_\sigma$.

The C-H distance was taken for 1.09 Å, the C-C distance for 1.54 Å and all angles for 109°28′.

The overlap integrals between hydrogen and carbon were calculated numerically while those between carbon atoms were obtained by interpolating from KOTANI's tables [*23*].

d) Core Integrals

For the resonance integral β_{pq} we took MULLIKEN's definition [*29*] as was done by PARISER and PARR [*31, 32*] which takes account of overlap integrals.

$$\beta_{pq} = \tfrac{1}{2}\,(H^{\mathrm{C}}_{pq} + H^{\mathrm{C}}_{qp}) - \frac{S_{pq}}{2}\,(H^{\mathrm{C}}_{p} + H^{\mathrm{C}}_{q}) \text{ where the index C stands for ``Core''} \,. \qquad (17)$$

Here

$$\alpha_p = H^{\mathrm{C}}_p = -\, I_p - \sum_{p \neq q} [(pp \mid qq) + (q{:}pp)] - \sum_{l \neq p} [(pp \mid ll) + (l{:}pp)] \qquad (18)$$

and

$$\gamma_{pq} = H^{\mathrm{C}}_{pq} = -\, I_p\, S_{pq} - \sum_{p \neq q} [(pq \mid qq) + (q{:}pq)] - \sum_{l \neq p,\, q} [(pq \mid ll) + (l{:}pq)] \qquad (19)$$

where I_p is the ionization potential for orbital p, $(pp \mid ll)$ is a Coulomb repulsion integral and $(l{:}pp)$ a Coulomb penetration integral and p and q are "chemically" bonded together.

Substitution of (18) and (19) into (17) yields:

$$\begin{aligned}
\beta_{pq} = \sum_{l \neq p,\, q} \frac{S_{pq}}{2} \Big\{[(ll \mid pp) + (ll \mid qq) + (l{:}pp) + (l{:}qq)]\Big\} - [(pq \mid ll) + \\
+ (l{:}pq)] + \frac{S_{pq}}{2}\,[2\,(pp \mid qq) + (p{:}qq) + (q{:}pp)] - \tfrac{1}{2}\,[(pp \mid pq) + (qq \mid pq) + \\
+ (p{:}pq) + (q{:}pq)] \text{ (see SIMMONS [43])} \,. \qquad (20)
\end{aligned}$$

Application of MULLIKEN's approximations [*29*] to non-neighbour interactions makes the first term zero and further application of MULLIKEN's approximation to the second term finally gives

$$\beta_{pq} = -\frac{S_{pq}}{2}\left\{\tfrac{1}{2}\left[(pp \mid pp) + (qq \mid qq) + (p{:}pp) + (q{:}qq)\right] - (pp \mid qq)\right\} + \frac{S_{pq}}{2}\,\tfrac{1}{2}\left[(p{:}qq) + (q{:}pp)\right]. \qquad (21)$$

The second term in (21) is small since terms like $(p{:}qq)$ are approximately proportional to the overlap integral and therefore the second term in (21) may be taken as multiplied by the square of the overlap integral and we neglect it. Then we have

$$\beta_{pq} = -\frac{S_{pq}}{2}\left[c_{pq} + \tfrac{1}{2}(pp \mid pp) + \tfrac{1}{2}(qq \mid qq) - (pp \mid qq)\right] \qquad (22)$$

where

$$c_{pq} = \tfrac{1}{2}\left[(p{:}pp) + (q{:}qq)\right]. \qquad (23)$$

c_{pq} only contains one center penetration integrals whose values are difficult to estimate. For this reason and in order to remedy at least partially to the approximations made in the above deductions we prefer to keep c_{pq} as a parameter. We kept $(pp \mid qq)$ separate since this is expressed by formulas depending on the internuclear distance.

Finally then we have from (22) and (15)

$$\beta_{pq} = -S_{pq}\left(C_{pq} + Ar + Br^2\right) \qquad (24)$$

with

$$C_{pq} = \tfrac{1}{4}\left[(p{:}pp) + (q{:}qq)\right]$$

and

$$A = \frac{a}{2} \text{ and } B = \frac{b}{2}\ .$$

If $p = q$ then the last formula reduces to

$$C_p = \tfrac{1}{2}(p{:}pp)$$

and we may write for $p \neq q$ that

$$C_{pq} = \tfrac{1}{2}(C_p + C_q)\,. \qquad (25)$$

We choose the value of C_h so that $\beta_{hh'}$ is equal to its value computed by Mulliken [29] for H_2 $1s - 1s$ bonds for the related internuclear distance which in methane is equal to 1.78 Å. We obtained

$$C_h = 4.628 \text{ eV for this distance.}$$

C_{ht} was chosen to fit the first singlet-singlet transition energy of methane taken to be equal to 10.21 eV (approximate location of the O-O band). It turned out to be

$$C_{ht} = 8.35 \text{ eV}\,.$$

Using C_h and C_{ht} we computed C_t from equation (25) obtaining:

$$C_t = 12.07 \text{ eV}\,.$$

These values were used for computing resonance integrals.

e) Integrals over Hybrid Orbitals

For two tetrahedral orbitals we obtain using equations (16).

$$(t_1\,t_1 \mid t_1\,t_1) = \frac{1}{16}\,[(ss \mid ss) + 9\,(pp \mid pp) + 6\,(ss \mid pp) + 12\,(sp \mid sp)]$$
$$= \frac{1}{16}\,(9.585 + 9 \times 10.076 + 6 \times 9.410 + 12 \times 2.220) = 11.461 \text{ eV}$$

and

$$(t_1\,t_1 \mid t_2\,t_2) = \frac{1}{16}\,[(s_1\,s_1 \mid s_2\,s_2) + 9\,(p_{\sigma 1}\,p_{\sigma 1} \mid p_{\sigma 2}\,p_{\sigma 2}) + 6\,(s_1\,s_1 \mid p_{\sigma 2}\,p_{\sigma 2})$$
$$= 9.7956 - 1.2324\,r - 0.0758\,r^2 = 7.718 \text{ eV}$$

with

$$r = 1.54 \text{ Å}\,.$$

Here we kept the term $(sp \mid sp)$ in computing $(t_1\,t_1 \mid t_1\,t_1)$ though it contains differential overlap since without it the integral turned out to be too low [close to $(pp \mid pp)$]. We only did this on computing mono-center integrals, however, to which MULLIKEN's approximations do not apply. Differential overlap was neglected in computing $(t_1\,t_1 \mid t_2\,t_2)$.

We have to treat separately the β_{pq} related to two hybrids on the same carbon atom.

Starting from the definition

$$\beta_{tt'} = H^{\mathrm{C}}_{tt'} - S_{tt'}\,H^{\mathrm{C}}_{t} \tag{26}$$

we see that the second term is zero since the two hybrids are mutually orthogonal.

Then

$$\beta_{tt'} = H^{\mathrm{C}}_{tt'} = -\sum_{k \neq t,\,t'} (tt' \mid kk) - \sum_{l \neq t,\,t',\,k} [(tt' \mid ll) + l\!:\!tt')] \tag{27}$$

where the first sum is extended to the same atom and the second one to the other atoms, both carbon and hydrogen. Applying MULLIKEN's approximations makes the second sum vanish, however, and there remains

$$\beta_{tt'} = -\sum_{k \neq t,\,t'} (tt' \mid kk)\,. \tag{28}$$

Writing out (28) in detail we have that:

$$\beta_{tt'} = -\,[(t_1\,t_2 \mid t_2\,t_2) + (t_1\,t_2 \mid t_3\,t_3) + (t_1\,t_2 \mid t_4\,t_4)]\,. \tag{29}$$

In this work, however, we preferred using an empirical value for this integral which is close to the one used by POPLE and SANTRY [*38*]:

$$\beta_{tt'} = -\,1.32 \text{ eV}\,.$$

f) The Minimization Process

If differential overlap is neglected then the matrix elements entering the secular determinant can be written down in the manner of POPLE [*37*], BRICKSTOCK and POPLE [*3*] and KON [*24*] and we have, for the diagonal ones:

$$F_{pp} = \alpha_p + \tfrac{1}{2}\,Q_p\,(pp \mid pp) + \sum_{p \neq q} Q_q\,(pp \mid qq)$$
$$= -\,I_p + \tfrac{1}{2}\,Q_p\,(pp \mid pp) + \sum_{p \neq q} (Q_q - 1)\,(pp \mid qq) \tag{30}$$

and for the non-diagonal ones

$$F_{pq} = \beta_{pq} - \tfrac{1}{2} P_{pq} (pp \mid qq) \qquad (31)$$

where P_{pq} and Q_p are the bond order of bond $p - q$ and the electronic charge density of orbital p respectively. Then using Hückel molecular orbitals the roots of the secular equation are

$$\varepsilon_i = \sum_p C_{ip} F_{pp} + 2 \sum_{p>q} C_{ip} C_{iq} F_{pq} \qquad (32)$$

and we can use the following formulas [with notations by JACOBS [*15*], for computing the total energies, ionization potentials and excitation energies (see [*6*], p. 468 – 486)]

$$E = 2 \sum_i \varepsilon_i + \sum_{i,j} (2 J_{ij} - K_{ij})$$

$${}^2E - E_0 = - \varepsilon_n - \sum_{i=1}^{n-1} (2 J_{in} - K_{in}) - J_{nn} = - \varepsilon_n \qquad (34)$$

where the ionization potential corresponds to the removal of an electron from orbital φ_n and it is supposed that the same Z value can be used for the neutral molecule and for its positive ion*;

$${}^1E_1^{ij} - E_0 = \varepsilon_j - \varepsilon_i - J_{ij} + 2 K_{ij} \qquad (35)$$

and

$${}^3E_1^{ij} - E_0 = \varepsilon_j - \varepsilon_i - J_{ij} = ({}^1E_1^{ij} - E_0) - 2 K_{ij} \, .$$

We introduced the following further approximations in computing the matrix elements which seem to be justified due to the highly localized character of the bonds in saturated hydrocarbons:

1. $Q_p = 1$
2. $P_{pq} = 1$ for neighbouring atoms
3. $P_{pq} = 0$ for non-neighbours.

Thus is our case,

$$\varepsilon_i' = \sum_p C_{ip}^2 \left[- I_p + \tfrac{1}{2} (pp \mid pp) \right] + \\ + 2 \sum_{\text{neigh}} C_{ip} C_{iq} \left[\beta_{pq} - \tfrac{1}{2} (pp \mid qq) \right] + \sum_{\text{non neigh}} C_{ip} C_{iq} \beta_{pq} \, . \qquad (37)$$

(see eq. (5) of the Appendix)

We computed our coefficients in this way and used equations (34 – 36) for obtaining ionization potentials and excitation energies. No iterations were made at this stage.

For methane and ethane we also computed these quantities without making the last approximations. The differences are very slight. The calculation of the correction terms is given in the Appendix.

We recall that differencial overlap was neglected throughout this work both between pure atomic and hybrid orbitals except in computing one center integrals. MULLIKEN's approximation was used to take care of non-neighbor interactions. Overlap integrals were neglected in solving the secular equation.

Details of the calculations are given in the Appendix.

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* For a discussion of this see I'HAYA [*14*].

Results and Discussion

The ionization potentials obtained through equation (35) are compared with their experimental values [*47*, *9*] in Tab. 4. The experimental values were determined by electron impact measurements.

As is seen the calculated values are about 2 eV higher than the experimental ones. This is a familiar situation known for π-electronic systems and it could be very probably remedied by using for the positive ion resulting from ionization a Z number different from the one used with the neutral molecule.

Table 4

		Calc.	Obs.
CH_4		15.85	13.12
C_2H_6	staggered	13.26	11.65
	eclipsed	13.19	
C_3H_8		12.62	11.21

The lower electronic energy levels are shown in Fig. 1 and in Tab. 5. They are in electron volts with the energy of the ground state taken as zero.

In methane (T_d symetry) the lowest energy transition is from the degenerate orbital $\varepsilon_{2,\,3,\,4}$ to the non-degenerate orbital ε_5 that is, from an A_1 ground state to an F_2 excited state and it is allowed according to all coordinates. The next highest transition, from $\varepsilon_{2,\,3,\,4}$ to $\varepsilon_{6,\,7,\,8}$ leads from an A_1 ground state to a degenerate stat which is expected to split according to $F_2 \times F_2 = A_1 + E + F_1 + F_2$ the transition to F_2 being allowed and the others forbidden. The latter may be made allowed by non-totally symetrical vibrations of suitable symetry (F_2) which are, of course, available.

Transitions from ε_1 to ε_5 would be $A_1 \rightarrow A_1$ and forbidden and from ε_1 to $\varepsilon_{6,\,7,\,8}$ $A_1 \rightarrow F_2$ and allowed. Transitions from ε_1 would have much higher frequencies than those departing from $\varepsilon_{2,\,3,\,4}$ as is seen from the data of Tab. 5.

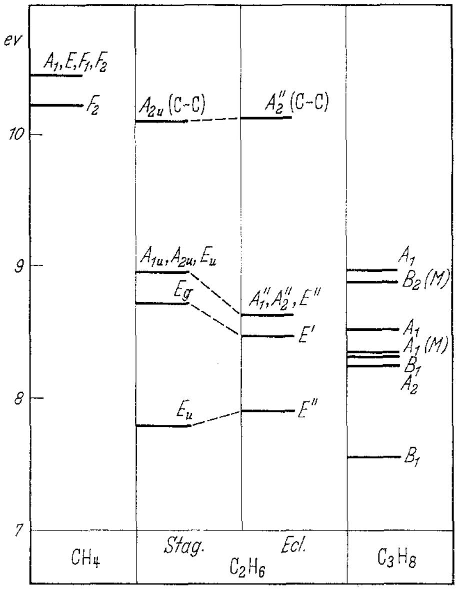

Fig. 1. Energies of the lower singlet-singlet electronic levels of methane, ethane and propane. C-C means that the orbital from which the transition departs (in absorption) has a high population in the C-C bonds; M (mixed), that it has a fairly large population in the C-C bonds. If the state is unmarked then all the charge is in C-H bonds in the orbital of departure

It is not intended here to give a thorough discussion of the spectra of saturated hydrocarbons. This we should like to reserve to our next publication after introducing certain refinements into our calculations and extending them to some other molecules. It should be pointed out that, naturally, our calculations cover valenceshell transitions only and not Rydberg transitions and that configuration interaction between levels of the same symmetry could change our energy scheme appreciably.

In staggered ethane (D_{3d}) the lowest frequency transition would be the one from $\varepsilon_{6,\,7}$ (e_g) to ε_8 (a_{2u}) and it would be $A_{1g} \rightarrow E_u$ and allowed according to the

Table 5

	Singlet-singlet		Singlet-triplet		I pot.	
	I	II	I	II		
Methane	10.21	10.26	9.26	9.31	15.93	15.85
	10.45	10.48	10.07	10.11		
Ethane	7.80	7.81	7.36	7.37	13.33	13.16
(staggered)	8.70	8.78	7.97	8.05		
	8.94	8.84	8.11	8.01		
	10.07	10.15	9.30	9.38		
Ethane	7.83	7.84	7.25	7.26	13.25	13.08
(eclipsed)	8.44	8.51	7.87	7.95		
	8.61	8.56	7.89	7.82		
	10.04	10.12	9.27	9.35		
Propane	7.53		7.00		12.68	
C_{2v}	8.22		7.96			
	8.28		7.79			
	8.49		7.77			
	8.31		7.79			
	8.91		8.66			
	8.98		8.61			

The lower transition energies of methane, ethane and propane. The values given in columns indicated by I were obtained in making the approximations described in section *F*. The values given in columnus II were computed without these approximations.

x and y axes, z being taken along the C-C bond. The transitions of next higher energy would be the ones from $\varepsilon_{6,7}$ (e_g) to ε_9 (a_{1g}) that is, $A_{1g} \to E_g$ (forbidden); from $\varepsilon_{6,7}$ (e_g) to $\varepsilon_{10,11}$ (e_u) whose excited state splits into $A_{1u} + A_{2u} + E_u$ of which the transition to A_{1u} is forbidden, A_{2u} is allowed according to z and E_u according to x and y. Then would follow transitions departing from ε_5 (a_{1g}) to ε_8 (a_{2u}) which is $A_{1g} \to A_{2u}$ and allowed for z, to ε_9 (a_{1g}) which is $A_{1g} \to A_{1g}$ and forbidden, and to $\varepsilon_{10,11}$ (e_u) which is $A_{1g} \to E_u$ and allowed for x and y.

For eclipsed (D_{3h}) ethane the situation is similar with

$$\begin{array}{lcc} e_g & \text{becomming} & e'' \\ a_{2u} & ,, & a_2'' \\ a_{1g} & ,, & a_1' \\ \text{and } e_u & ,, & e' . \end{array}$$

The selection rules are the same except for the $\varepsilon_{6,7}$ (e'') to $\varepsilon_{10,11}$ (e') transition whose excited state splits into $A_1'' + A_2'' + E''$ with only the transition to A_2'' allowed (z).

There would be, naturally many other transitions at shorter wavelengths.

The difference between related transition energies of staggered and eclipsed ethane turns out to be somewhat larger than expected and varies between a few hundreds and 3 or 4 tenth of an electron volt. If this is correct there should be a detectable change in the spectrum of ethane when temperature is varied.

Propane has a much lower symetry than either methane or ethane and only the results pertaining to all-trans propane C_{2v} are included here. The first five transitions are ε_{10} (b_1) to ε_{11} (a_1) which is $A_1 \to B_1$ and allowed according to the x axis which is perpendicular to the plane of the carbon atoms, ε_9 (a_1) to ε_{11} (a_1) which is

$A_1 \rightarrow A_1$ and allowed according to the z axis which lies in the molecular plane and bisects the CCC angle; ε_{10} (b_1) to ε_{13} (a_1) which is $A_1 \rightarrow B_1$ and allowed for x; ε_{10} (b_1) to ε_{14} (b_1) which is $A_1 \rightarrow A_1$ and ε_{10} (b_1) to ε_{12} (b_2) which is $A_1 \rightarrow A_2$ and forbidden.

The following conclusions may be drawn from this preliminary account.

1. Except for (perhaps) the lowest frequency band system the spectra of paraffinic hydrocarbons are likely to contain many overlapping band systems and are probably much more complicated than it is usually admitted, even if Rydberg transitions are disregarded.

2. Spectral differences between conformers may be significant.

3. Singlet-triplet transitions are usually to less than 1 eV at the low frequency side of the related singlet-singlet transitions.

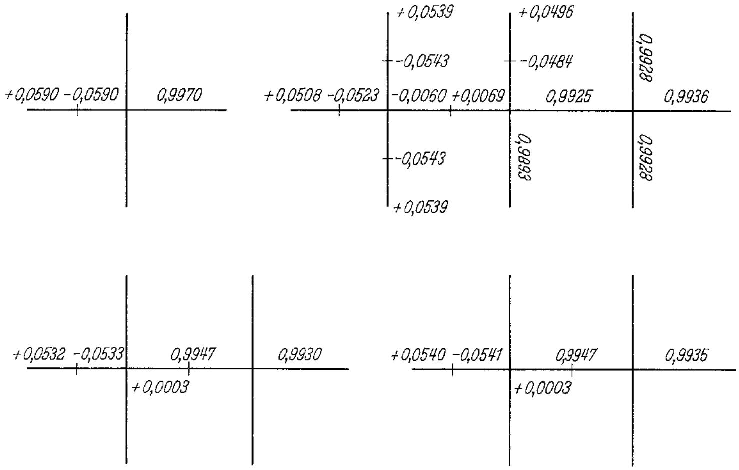

Fig. 2. Electronic charge densities and bond orders for methane, staggered and eclipsed ethane and propane

4. Our Pariser-Parr type calculations interpret well the trend toward lower energies with increasing chain length of both the first ionization potentials and the first singlet-singlet transition. Actually we find a linear relationship between the two quantities and the variation of the ionization potential turns out to be about 1.14 times that of the first excitation energies.

5. According to our calculations the first excitation in methane, ethane and propane is departing from an orbital where the electronic charge is in the C-H bonds. However, as shown in Fig. 1, the lowest mainly C-C type transition shifts considerably to lower frequencies from ethane to propane and is likely to become the first band from *n*-butane on (In Fig. 1 C-C means that the electronic charge in the orbital of departure is essentially in the C-C bonds and *M* that it is divided between both C-C and C-H bonds.)

This conclusion concerning the three first paraffines is contrary to the results obtained by SIMPSON by his independent system method [*40*]. We prefer delaying further discussion at this point too, however.

Electronic charge densities calculated by the method described in this paper are shown in Fig. 2. It is seen that the hydrogen atoms loose negative charges

Table 6. *Charge Densities*

	Q (H)		Q (C)	
	This work	HOFFMANN	This work	HOFFMANN
Méthane	+ 0.0590	+ 0.133	− 0.2360	− 0.532
Ethane	+ 0.0532	+ 0.119	− 0.1596	− 0.356
Propane				
CH_3-	+ 0.0539		− 0.1669	− 0.373
	+ 0.0508			
—CH_2-	+ 0.0496	+ 0.105	− 0.0828	− 0.185

amounting to about 0.05 electronic charges. These are picked up by the Csp^3 orbitals directly bonded to the hydrogens. Hydrogens on secondary carbons loose slightly less charge than those on primary ones.

Bond orders are close to but not equal to unity both for C-C and C-H bonds. Tab. 6 compares the electronic charge densities obtained in this work with those computed by HOFFMANN [*13*]. Our values areu sually about two times lower but the signs and trends are the same. The bond orders follow well the experimental bond lengths [*1*, *25*, *27*]. The differences are very slight, however, and the agreement may be coincidental (Tab. 7).

Table 7. *Relation between Bond Orders and Bond Lengths of* C-H *bonds*

	Bond Order	Bond Length (Å)
Methane	0.9970	1.085 [*1*]
Ethane	0.9930	1.092 [*25*]
Propane	0.9931	1.091 [*27*]
	0.9936	
	0.9893	1.096 [*27*]

The authors intend to present some refinements and applications to further molecules in subsequent papers. They believe that the usefulness and validity of the Pariser-Parr approximation will prove to be of the same order for saturated molecules as for π-electronic systems.

We express our sincere thanks to the National Research Council of Canada for financial support and for granting a fellowship to one of us (S. K.).

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Appendix I

The Correction Term K_i

See Section F

Within the antisymmetrized MO approximation the total electronic energy can be written as

$$E_0 = 2 \sum_i \varepsilon_i^C + \sum_{ij} (2\, J_{ij} - K_{ij}) = \sum_i (\varepsilon_i^C + \varepsilon_i) \qquad (1)$$

where

$$\varepsilon_i = \varepsilon_i^{\mathrm{C}} + \sum_j (2\,J_{ij} - K_{ij})\,. \tag{2}$$

The MO's φ_i are written as a linear combination of AO's:

$$\varphi_i = \sum_k C_{ik}\,X_k\,. \tag{3}$$

Then eq. (2) is written in terms of AO's

$$\varepsilon_i = \sum_k C_{ik}^2\,F_{kk} + 2\sum_{k>l} C_{ik}\,C_{il}\,F_{kl} \tag{4}$$

with

$$F_{kk} = I_k + \tfrac{1}{2}\,Q_k\,(kk\,|\,kk) + \sum_{l\neq k} (Q_l - 1)\,(kk\,|\,ll)$$

$$F_{kl} = \beta_{kl} - \tfrac{1}{2}\,P_{kl}\,(kk\,|\,ll)\,.$$

Here the zero differential overlap and the Goeppert-Mayer and Sklar potential are assumed and all the penetration integrals are neglected.

Eq. (4) is further rewritten as:

$$\varepsilon_i = \varepsilon_i' + K_i\,. \tag{5}$$

Here

$$\varepsilon_i' = \sum_k C_{ik}^2\,[I_k + \tfrac{1}{2}\,(kk\,|\,kk)] + 2\sum_{k>l}^{\text{bond}} C_{ik}\,C_{il}\,[\beta_{kl} - \tfrac{1}{2}\,(kk\,|\,ll)]$$

$$+\,2\sum_{k>m}^{\text{non bond}} C_{ik}\,C_{im}\,\beta_{km} \tag{6}$$

and

$$K_i = \sum_k C_{ik}^2[\tfrac{1}{2}\,(Q_k - 1)\,(kk\,|\,kk) + \sum_{l\neq k} (Q_l - 1)\,(kk\,|\,ll)] +$$

$$+ \sum_{k>l}^{\text{bond}} C_{ik}\,C_{il}\,(1 - P_{kl})\,(kk\,|\,ll) - \sum_{k>m}^{\text{non bond}} C_{ik}\,C_{im}\,P_{km}\,(kk\,|\,mm)\,.$$

Eq. (6) corresponds to one of the roots of our secular equation. Accordingly the term K_i represents the deviation from the ASMO calculation where the approximations mentioned in section F are not made.

Appendix II

a) Two center repulsion integral formulas

$$\begin{aligned}
(hh\,|\,h'\,h') &= 11.542 - 2.9730\,r + 0.2455\,r^2\\
(hh\,|\,ss) &= 10.564 - 2.3660\,r + 0.1535\,r^2\\
(hh\,|\,\pi\pi) &= 10.609 - 2.6822\,r + 0.2153\,r^2\\
(hh\,|\,\sigma\sigma) &= 10.609 - 2.1643\,r + 0.0945\,r^2\\
(\sigma\sigma\,|\,\sigma'\,\sigma') &= 10.076 - 1.1437\,r - 0.1124\,r^2\\
(\pi\pi\,|\,\pi'\,\pi') &= 10.076 - 2.3098\,r + 0.1644\,r^2\\
(ss\,|\,s'\,s') &= 9.585 - 1.7590\,r + 0.0615\,r^2\\
(ss\,|\,\pi'\,\pi') &= 9.410 - 1.8144\,r + 0.0839\,r^2\\
(ss\,|\,\sigma'\,\sigma') &= 9.410 - 1.2777\,r + 0.0437\,r^2\\
(\pi\pi\,|\,\sigma'\,\sigma') &= 8.990 - 1.2785\,r + 0.0192\,r^2\\
(\pi\pi\,|\,\pi''\,\pi'') &= 8.990 - 1.7275\,r + 0.0858\,r^2\,.
\end{aligned}$$

Here π'' represents the $2p\pi$ orbital perpendicular to π' and σ'.

b) *Numerical integral values*

1. *Methane* (T_d). The tetrahedral, hybridized atomic orbitals of carbon atom are written (Fig. 3):

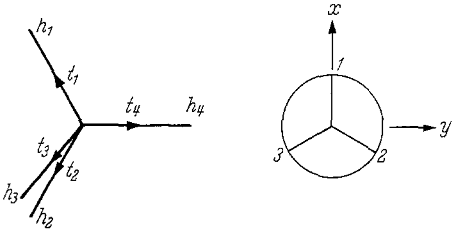

Fig. 3

$$X_{t1} = \tfrac{1}{2} X_{2s} - \frac{1}{2\sqrt{3}} X_{2p_z} + \sqrt{\frac{2}{3}} X_{2p_x}$$
$$X_{t2} = \tfrac{1}{2} X_{2s} - \frac{1}{2\sqrt{3}} X_{2p_z} - \frac{1}{\sqrt{6}} X_{2p_x} + \frac{1}{\sqrt{2}} X_{2p_y}$$
$$X_{t3} = \tfrac{1}{2} X_{2s} - \frac{1}{2\sqrt{3}} X_{2p_z} - \frac{1}{\sqrt{6}} X_{2p_x} - \frac{1}{\sqrt{2}} X_{2p_y}$$
$$X_{t4} = \tfrac{1}{2} X_{2s} + \frac{\sqrt{3}}{2} X_{2p_z}\,.$$

Overlap integrals

$S_{h_i h_j} = 0.283$ $S_{h_i t_i} = 0.688$ $S_{h_i t_j} = 0.150$ $S_{t_i t_j} = 0$.

Resonance integrals.

$\beta_{h_i h_j} = -1.948$ $\beta_{h_i t_i} = -6.531$ $\beta_{h_i t_j} = -1.445$ $\beta_{t_i t_j} = -1.32$

Electronic repulsion integrals.

$(h_i h_i \mid h_i h_i) = 11.542$ $(h_i h_i \mid h_j h_j) = 7.028$
$(t_i t_i \mid t_i t_i) = 11.461$ $(h_i h_i \mid t_i t_i) = 8.204$
$(t_i t_i \mid t_j t_j) = 8.143$ $(h_i h_i \mid t_j t_j) = 8.183$.

2. *Ethane* (Fig. 4). The integral values for the CH_3 group are the same as those for the methane molecule. For the interaction between the two methyl groups we have the following values.

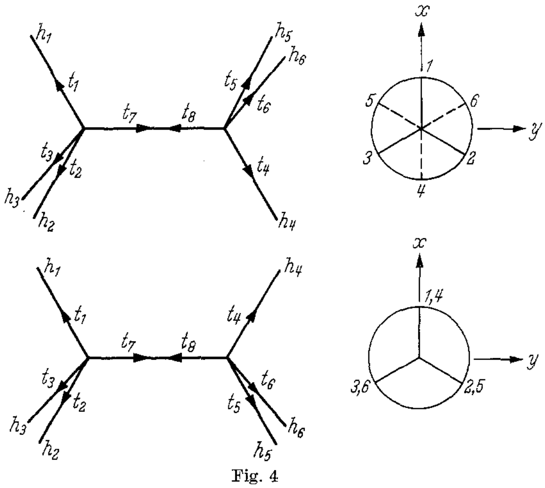

Fig. 4

Ethane (Fig. 4)

χ_i	χ_j	Overlap Integrals $S_{\chi_i \chi_j}$ Staggered	Overlap Integrals $S_{\chi_i \chi_j}$ Eclipsed	Resonance Integrals $\beta_{\chi_i \chi_j}$ Staggered	Resonance Integrals $\beta_{\chi_i \chi_j}$ Eclipsed	Electronic Repulsion Integrals $(\chi_i \chi_i \mid \chi_j \chi_j)$ Staggered	Electronic Repulsion Integrals $(\chi_i \chi_i \mid \chi_j \chi_j)$ Eclipsed
h_1	h_4	0.055	0.157	− 0.441	− 1.157	4.705	6.058
h_1	h_5	0.119	0.070	− 0.901	− 0.553	5.661	4.982
h_1	t_4	− 0.028	0.104	0.298	− 1.106	6.177	
h_1	t_5	0.071	0.005	− 0.757	− 0.053	6.114	
t_1	t_4	− 0.120	0.134	1.618	− 1.806	6.858	
t_1	t_5	0.071	− 0.057	− 0.947	0.760	6.793	
h_1	t_8	0.221		− 2.451		6.379	
t_1	t_8	0.108		− 1.420		7.094	
t_7	t_8	0.647		− 8.483		7.718	

3. Propane. (Fig. 5) The additional integrals are:

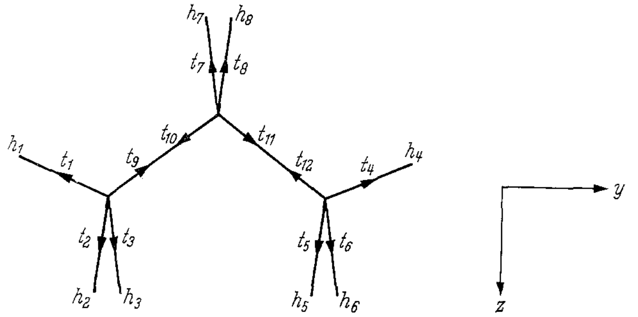

Fig. 5

Propane (Fig. 5)

χ_i	χ_j	Overlap Integrals $S_{\chi_i \chi_j}$	Resonance Integrals $\beta_{\chi_i \chi_j}$	Electronic Repulsion Integrals $(\chi_i \chi_i \mid \chi_j \chi_j)$
h_1	h_4	0.009	− 0.079	3.356
h_1	h_5	0.021	− 0.178	3.860
h_2	h_5	0.115	− 0.872	5.627
h_2	h_6	0.053	− 0.427	4.660
h_1	t_4	− 0.009	0.103	4.228
h_1	t_5	0.013	− 0.151	4.101
h_1	t_{12}	0.026	− 0.299	4.228
h_2	t_4	− 0.026	0.287	5.337
h_2	t_5	0.059	− 0.658	5.149
h_2	t_6	0.024	− 0.268	5.149
h_2	t_{12}	0.074	− 0.818	5.337
t_1	t_4	0.020	− 0.278	5.874
t_1	t_5	− 0.025	0.350	5.682
t_1	t_{12}	− 0.039	0.542	5.874
t_2	t_5	0.044	− 0.654	5.326
t_2	t_6	0.013	− 0.193	5.326
t_5	t-	0.050	− 0.700	5.682
t_9	t_{12}	0.169	− 2.347	5.874

c) *Molecular Orbitals and Orbital Energies*

1. *Methane*

MO	Sym.	Energy ε_i
$\varphi_8 = 0.36884\,(h_1 - h_2 - h_3 + h_4) - 0.33757\,(t_1 - t_2 - t_3 + t_4)$	f_2	$+\ 2.5231$
$\varphi_7 = 0.36884\,(h_1 - h_2 + h_3 - h_4) - 0.33757\,(t_1 - t_2 + t_3 - t_4)$		
$\varphi_6 = 0.36884\,(h_1 + h_2 - h_3 - h_4) - 0.33757\,(t_1 + t_2 - t_3 - t_4)$		
$\varphi_5 = 0.34838\,(h_1 + h_2 + h_3 + h_4) - 0.35865\,(t_1 + t_2 + t_3 + t_4)$	a_1	$+\ 1.7313$
$\varphi_4 = 0.33757\,(h_1 - h_2 - h_3 + h_4) + 0.36884\,(t_1 - t_2 - t_3 + t_4)$		
$\varphi_3 = 0.33757\,(h_1 - h_2 + h_3 - h_4) + 0.36884\,(t_1 - t_2 + t_3 - t_4)$	f_2	$-\ 15.9251$
$\varphi_2 = 0.33757\,(h_1 + h_2 - h_3 - h_4) + 0.36884\,(t_1 + t_2 - t_3 - t_4)$		
$\varphi_1 = 0.35865\,(h_1 + h_2 + h_3 + h_4) + 0.34838\,(t_1 + t_2 + t_3 + t_4)$	a_1	$-\ 28.2173$

2. *Ethane*

α) Staggered

Symmetry a_{2u}

m. o.	$h_1 + h_2 + h_3 - h_4 - h_5 - h_6$	$t_1 + t_2 + t_3 - t_4 - t_5 - t_6$	$t_7 - t_8$	ε_i
φ_{14}	0.15152	−0.11724	0.62441	4.1807
φ_8	0.25689	−0.25374	−0.32994	1.3770
φ_2	0.27877	0.29755	−0.03534	−22.7507

Symmetry a_{1g}

m. o.	$h_1 + h_2 + h_3 + h_4 + h_5 + h_6$	$t_1 + t_2 + t_3 + t_4 + t_5 + t_6$	$t_7 + t_8$	ε_i
φ_9	0.28152	−0.29478	−0.03740	1.9721
φ_5	0.15410	0.17188	−0.58321	−15.6676
φ_1	0.25222	0.22412	0.39808	−33.2194

Symmetry e_u

m. o.	$2h_1 - h_2 - h_3 + 2h_4 + h_5 + h_6$	$2t_1 - t_2 - t_3 + 2t_4 + t_5 + t_6$	ε_i
φ_{11}	0.22168	−0.18491	2.1983
φ_3	0.18491	0.22168	−18.6253

m. o.	$h_2 - h_3 - h_5 + h_6$	$t_2 - t_3 - t_5 + t_6$	
φ_{10}	0.38395	−0.32028	2.1983
φ_4	0.32028	0.38395	−18.6253

Symmetry e_g

m. o.	$2h_1 - h_2 - h_3 + 2h_4 - h_5 - h_6$	$2t_1 - t_2 - t_3 + 2t_4 - t_5 - t_6$	ε_i
φ_{12}	0.20112	−0.20708	2.9480
φ_6	0.20708	0.20112	−13.3250

m. o.	$h_2 - h_3 + h_5 - h_6$	$t_2 - t_3 + t_5 - t_6$	
φ_{13}	0.34836	−0.35868	2.9480
φ_7	0.35868	0.34836	−13.3250

β) Eclipsed

Symmetry $\ddot{a}_2''$

m. o.	$h_1 + h_2 + h_3 - h_4 - h_5 - h_6$	$t_1 + t_2 + t_3 - t_4 - t_5 - t_6$	$t_7 - t_8$	ε_i
φ_{14}	0.15230	−0.11794	0.62345	4.1852
φ_8	0.25650	−0.25335	−0.33176	1.3919
φ_2	0.27871	0.29761	−0.03535	−22.7400

Symmetry a_1'

m. o.	$h_1 + h_2 + h_3 + h_4 + h_5 + h_6$	$t_1 + t_2 + t_3 + t_4 + t_5 + t_6$	$t_7 + t_8$	ε_i
φ_9	0.28156	−0.29483	−0.03738	1.9533
φ_5	0.15406	0.17178	−0.58333	−15.6710
φ_1	0.25230	0.22413	0.39790	−33.2274

Symmetry e''_{33}

m. o.	$2h_1 - h_2 - h_3 - 2h_4 + h_5 + h_6$	$2t_1 - t_2 - t_3 - 2t_4 + t_5 + t_6$	ε_i
φ_{13}	0.20203	−0.20620	3.0197
φ_6	0.20620	0.20203	−13.2517
	$h_2 - h_3 - h_5 + h_6$	$t_2 - t_3 - t_5 + t_6$	
φ_{12}	0.34993	−0.35714	3.0197
φ_7	0.35714	0.34993	−13.2517

Symmetry e'

m. o.	$2h_1 - h_2 - h_3 + 2h_4 - h_5 - h_6$	$2t_1 - t_2 - t_3 + 2t_4 - t_5 - t_6$	ε_i
φ_{11}	0.22105	−0.18566	2.1113
φ_3	0.18566	0.22105	−18.6833
	$h_2 - h_3 + h_5 - h_6$	$t_2 - t_3 + t_5 - t_6$	
φ_{10}	0.38287	−0.32157	2.1113
φ_4	0.32157	0.38287	−18.6833

Propane

Symmetry b_1

m. o.	$h_1 - h_2 + h_5 - h_6$	$h_7 - h_8$	$t_1 - t_2 + t_5 - t_6$	$t_7 - t_8$	ε_i
φ_{18}	−0.23195	0.34832	0.25395	−0.37696	3.1317
φ_{14}	−0.28037	−0.38030	0.23014	0.30370	2.0499
φ_{10}	0.24832	−0.38412	0.22286	−0.36027	−12.6846
φ_4	0.23650	0.29410	0.28789	0.36862	−20.2070

Symmetry a_2

m. o.	$h_1 - h_2 - h_5 + h_6$	$t_1 - t_2 - t_5 + t_6$	ε_i
φ_{16}	0.36935	−0.33702	2.5869
φ_7	0.33720	0.36935	−15.0829

Propane

Symmetry a_1

m. o.	$h_2 + h_3 + h_5 + h_6$	$h_1 + h_4$	$h_7 + h_8$	$t_2 + t_3 + t_5 + t_6$	$t_1 + t_4$	$t_7 + t_8$	$t_9 + t_{12}$	$t_{10} + t_{11}$	ε_i
φ_{19}	−0.05959	−0.16160	0.24613	0.02894	0.16669	−0.20579	0.41861	−0.39895	4.0511
φ_{15}	0.29059	−0.26206	0.10060	−0.27660	0.23109	−0.15326	−0.10431	0.10743	2.3856
φ_{13}	0.05401	0.36622	0.34195	−0.09043	−0.33423	−0.33248	−0.06698	−0.00506	1.9614
φ_{11}	0.18960	0.19893	−0.26690	−0.19511	−0.19073	0.25516	0.26281	−0.26573	1.2315
φ_9	−0.17073	0.23384	−0.26428	−0.16433	0.22904	−0.26639	0.25665	0.27181	−13.5002
φ_5	0.01384	0.38167	0.07286	0.00491	0.44770	0.10450	−0.26542	−0.25842	−18.5419
φ_3	−0.22977	−0.03814	0.33218	−0.25989	−0.01302	0.37071	0.03637	0.09283	−22.1053
φ_1	0.20251	0.17237	0.23588	0.17845	0.13289	0.19801	0.32046	0.33073	−35.8942

Symmetry b_2

m. o.	$h_2 + h_3 - h_5 - h_6$	$h_1 - h_4$	$t_2 + t_3 - t_5 - t_6$	$t_1 - t_4$	$t_{10} - t_{11}$	$t_9 - t_{12}$	ε_i
φ_{20}	0.13808	0.05470	−0.12175	−0.00814	−0.46486	0.46159	4.3580
φ_{17}	−0.15112	0.46137	0.14817	−0.43731	−0.03417	0.07176	2.7750
φ_{12}	0.29898	0.20261	−0.28544	−0.23077	0.16290	−0.19347	1.7795
φ_8	−0.11121	0.37589	−0.10893	0.37135	−0.27764	−0.30802	−13.5866
φ_6	0.24094	−0.09565	0.27632	−0.10701	−0.32883	−0.32009	−16.6586
φ_2	0.21932	0.30440	0.20863	0.32570	0.26643	0.21684	−26.7893

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