533. *A Quantum-mechanical Treatment of Aliphatic Compounds. Part I. Paraffins.*

By R. D. Brown.

A new general quantum-mechanical treatment of molecular structure is described, applicable to all types of molecules, and especially to aliphatic compounds. It consists of a molecular-orbital treatment in which the orbitals are represented as linear combinations of united-atom orbitals, located in every bond in the molecule. The various parameters which arise in the theory are discussed; they are analogous to the parameters occurring in the LCAO molecular-orbital treatment of conjugated systems.

A convenient expansion for the total electronic energy of a molecule is obtained in powers of S, the overlap integral between orbitals in adjacent C–H bonds. The results are compared with experimental heats of formation of the paraffins and, by extension of the calculations to alkyl radicals, with various bond-dissociation energies. The agreement between theory and experiment is satisfactory.

It is shown that the electron densities in the various bonds are equal. This makes the theoretical treatment "self-consistent" and means that chemical reactivities must be discussed in terms of polarizabilities or activation energies rather than in terms of the charge distribution.

The application of quantum-mechanical approximations to problems of molecular structure and reactivity has been extensively developed in recent years for conjugated and aromatic compounds because it has been possible to focus attention solely on the π-electrons, any effects arising from the σ-electrons being regarded as unimportant or constant. Particularly in the case of the molecular-orbital approximation, a general theory of conjugated systems has been formulated (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; **192**, 16; 1948, *A*, **193**, 447; **195**, 188; Chirgwin and Coulson, *ibid.*, 1950, *A*, **201**, 196) and has had considerable success as a basis of theories of chemical reactivity (Brown, *Quart. Reviews*, 1952, **6**, 63). However no analogous general treatment has hitherto been published for saturated molecules. Such molecules are treated in the present paper.*

The approximations employed for conjugated systems, namely, the valence-bond and LCAO molecular-orbital approximations, ultimately stem from approximations developed for the treatment of simple diatomic molecules (Heitler and London, *Z. Physik*, 1927, **44**, 455; Hund, *ibid.*, 1928, **51**, 759; Mulliken, *Phys. Review*, 1928, **32**, 186, 761; Lennard-Jones, *Trans. Faraday Soc.*, 1929, **25**, 668) and have the common feature that the wave functions are built up from atomic orbitals centred on each atom in the system. This results in considerable complexity for larger molecules when the atomic interactions are in tetrahedral directions, although not for the simpler planar π-type interactions, and so it is not surprising that the theory has developed more rapidly for the latter systems. This defect has been overcome in the present method by rejecting atomic-centred orbitals as the basis of the molecular wave-functions. Instead, the basis is taken to be a set of orbitals situated in each bond of the molecule, so that in methane, for example, the eight σ-electrons are considered to move in molecular orbitals formed by appropriate linear combinations of more localized σ-orbitals situated in each of the C–H bonds. In the case of diatomic molecules these bond orbitals are simply the united-atom orbitals which would accommodate the molecular electrons if the nuclei could be united; indeed, the present approach was stimulated by a recent revival of interest in the united-atom viewpoint of molecular binding (Matsen, in the press; Brown and Matsen, in the press).

The molecular orbitals for the σ-electrons will therefore be written :

$$\psi_j = \sum_{r=1}^{N} c_{jr}\,\phi_r \qquad (1)$$

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* A similar treatment has also been investigated by Professor C. A. Coulson (personal communication).

where ϕ_r is a united-atom σ-orbital located in the rth bond of the molecule, the summation in (1) being taken over all N bonds in the molecule. The coefficients for the molecular orbitals, c_{rj}, may be determined by the variation method (*e.g.*, Kemble, "Fundamental Principles of Quantum Mechanics," McGraw-Hill, New York, 1937, p. 408), and lead to the familiar secular equations :

$$\sum_{r=1}^{N} c_{jr} \left(H_{jr} - eS_{jr}\right) = 0, j = 1 \ldots N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the N roots of which, e_j, correspond to the energies of the molecular orbitals. To solve expression (2) we require values for the matrix elements :

$$H_{jr} = \int \phi_j \mathcal{H} \phi_r \, d\tau \, ; \; S_{jr} = \int \phi_j \phi_r d\tau$$

which are analogous to the matrix elements in the molecular-orbital treatment of conjugated systems. The following analogous assumptions will be made. The coulomb integral, H_{mm}, of an orbital, ϕ_m, depends only on the type of bond in which it resides; thus all C–H bond orbitals will be assumed to have a coulomb integral α. The resonance integral, H_{mn}, between orbitals ϕ_m and ϕ_n will be assumed to be zero, unless m and n are adjacent bonds in which case it will be taken to depend only on the type of bonds m and n. When m and n are both C–H bonds the resonance integral will be taken to be β, and the resonance integrals for other pairs of bond orbitals will be assumed to have the values listed in Table 1. A similar set of values will be adopted for the overlap integrals, S_{mn} (see Table 1).

TABLE 1. *Fundamental bond and interaction parameters.*

Coulomb parameters		Resonance parameters		Overlap integrals	
Bond	Assumed val.	Bonds	Assumed val.	Bonds	Assumed val.
C–H	α	C–H ; C–H	β	C–H ; C–H	S
C–C	$\alpha + h\gamma$	C–H ; C–C	$\theta\beta$	C–H ; C–C	θS
		C–C ; C–C	$\eta\beta$	C–C ; C–C	ηS

The proportionality of resonance and overlap integrals has been assumed in order that the secular determinants may be simplified by means of manipulations due to Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900) in which energies are expressed in terms of the parameter $\gamma = \beta - S\alpha$, and the coulomb integrals of orbitals associated with bonds other than C–H are expressed in terms of α and γ (see Table 1).

The above assumptions, all of which correspond to assumptions made in the MO treatment of conjugated systems, are more satisfactory in the present instance. Thus it is recognized (Lennard-Jones, *Proc. Roy. Soc.*, 1937, *A*, **158**, 280; Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41; Coulson and Altmann, *Trans. Faraday Soc.*, 1952, **48** 293) that the resonance integral between a given pair of orbitals will vary with their distance apart; but bond lengths in unsaturated systems are known to vary considerably, while in saturated molecules very little relative variation is found experimentally, so that the actual variation in, say, β(C–H:C–H) will be much less than, say, the variation of β(C–C) in conjugated systems. It is also considered that the coulomb integral of a given kind of orbital will depend strongly on the electron density at that point in the molecule, and "self-consistent" procedures have been devised (Wheland and Mann, *J. Chem. Phys.*, 1949, **17**, 264; Laforgue, *J. Chim. phys.*, 1949, **46**, 568) to allow for this in those cases where the molecular charge distribution is not uniform. In the present treatment of saturated systems however it may be shown (see Appendix) that the electron distribution is uniform for all kinds of systems (not just for hydrocarbons), and so a treatment based on the above assumptions will always be "self-consistent."

If the values listed in Table 1 are inserted into the secular equations (2) it is a straightforward calculation to obtain the orbital energies, e_j, and hence the total electronic energy :

$$E = \sum_{j=1}^{N} 2e_j \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is convenient to expand E in powers of S. It is then possible to obtain the first few terms of the expansion quite simply, as described in the Appendix, the simplification arising mainly because in the case of saturated systems all the molecular orbitals are doubly filled with σ-electrons. The results for the first few paraffins are collected in Table 2.

TABLE 2. *Electronic energies of the paraffins.*

Paraffin	E	H_f (kcal.) [*]
Methane	$8\alpha - 24S\gamma$	$-17{\cdot}9$
Ethane	$14\alpha + 2h\gamma - (24 + 24\theta^2)S\gamma$	$-20{\cdot}2$
Propane	$20\alpha + 4h\gamma - (28 + 40\theta^2 + 4\eta^2)S\gamma$	$-24{\cdot}8$
Butane	$26\alpha + 6h\gamma - (32 + 56\theta^2 + 8\eta^2)S\gamma$	$-29{\cdot}8$
*iso*Butane	$26\alpha + 6h\gamma - (36 + 48\theta^2 + 12\eta^2)S\gamma$	$-31{\cdot}5$
Pentane	$32\alpha + 8h\gamma - (36 + 72\theta^2 + 12\eta^2)S\gamma$	$-35{\cdot}0$
*iso*Pentane	$32\alpha + 8h\gamma - (40 + 64\theta^2 + 16\eta^2)S\gamma$	$-36{\cdot}9$
*neo*Pentane	$32\alpha + 8h\gamma - (48 + 48\theta^2 + 24\eta^2)S\gamma$	$-39{\cdot}7$
Hexane	$38\alpha + 10h\gamma - (40 + 88\theta^2 + 16\eta^2)S\gamma$	$-40{\cdot}0$
2-Methylpentane	$38\alpha + 10h\gamma - (44 + 80\theta^2 + 20\eta^2)S\gamma$	$-41{\cdot}7$
3-Methylpentane	$38\alpha + 10h\gamma - (44 + 80\theta^2 + 20\eta^2)S\gamma$	$-41{\cdot}0$
2 : 3-Dimethylbutane	$38\alpha + 10h\gamma - (48 + 72\theta^2 + 24\eta^2)S\gamma$	$-42{\cdot}5$
2 : 2-Dimethylbutane	$38\alpha + 10h\gamma - (52 + 64\theta^2 + 28\eta^2)S\gamma$	$-44{\cdot}4$

[*] Heat of formation at 25° (Rossini *et al.*, "Selected Values of Properties of Hydrocarbons" (circular c-461, Nat. Bur. Stand., Washington, 1947).

Some interesting deductions may be made from the results in Table 2, independent of the six [*] parameters in terms of which the energies are expressed. The most significant result is that to the first approximation ($S = 0$) *the total energy is the sum of the individual bond energies.* In the present case the energy of an isolated bond is equal to its coulomb term multiplied by the number of electrons present (*i.e.*, 2), so the C–H energy is 2α, and the C–C energy is $2\alpha + 2h\gamma$. The same general result can be established for all types of compound, not just for hydrocarbons (see Appendix). It is important that in the present treatment all the electrons are assigned to molecular orbitals embracing the whole molecule and possessing a wide range of orbital energies. The simple additivity property, more characteristic of a localized orbital treatment, arises "accidentally" because all orbitals happen to be fully occupied.

TABLE 3.

Isomeric pair	δE (kcal.) [*]	Isomeric pair	δE (kcal.) [*]
Butane : *iso*butane	$-1{\cdot}7$	Hexane : 3-methylpentane	$-1{\cdot}0$
Pentane : *iso*pentane	$-1{\cdot}9$	Hexane : 2 : 3-dimethylbutane	$2 \times 1{\cdot}3$ [†]
Hexane : *iso*hexane	$-1{\cdot}7$		

[*] Differences in heats of formation at 25°.

[†] The corresponding theoretical difference is $2(\Gamma - \Phi)$.

When the energies are calculated to the second approximation (*i.e.*, with terms to the first power of S) the strict additivity no longer holds, and certain differences in energy are predicted for isomers. Thus the pairs of isomers, *n*-pentane–2 : 2-dimethylpropane and *n*-hexane–2 : 2-dimethylbutane, are predicted to have the same difference in electronic energies, namely $-(12 - 24\theta^2 + 12\eta^2)S\gamma$, which is conveniently written (cf. Table 5) $3(\Gamma - \Phi)$. Furthermore the pairs of isomers listed in Table 3 are predicted to have a constant energy difference of $\Gamma - \Phi$, *i.e.*, one-third of the preceding difference. We may test these predictions by using the experimental heats of formation of the hydrocarbons for their electronic energies [†] (see Table 2). The differences corresponding to $3(\Gamma - \Phi)$ are, respectively, $-4{\cdot}7$ and $-4{\cdot}4$ kcal., showing acceptable agreement between theory and experiment, and from these values we may predict that the differences $\Gamma - \Phi$ will be about $-1{\cdot}5$ kcal. The experimental differences are listed in Table 3, and are gratifyingly near this figure, with a mean value of $-1{\cdot}5$ kcal.

The present theory may be extended to deal with alkyl radicals. The simplest procedure, and the only one to be considered in detail here, is to suppose that the orbitals in the (planar) bonds around the carbon atom carrying the odd electron have the same

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[*] Six parameters occur also in the analogous LCAO treatment of the energies of conjugated systems containing one heteroatom or monoatomic substituent.

[†] Since we are considering isomers, differences are also the differences in intrinsic energies, but the comparison with theory is not entirely satisfactory since the experimental data will include vibrational and rotational energy contributions. However similar comparisons have frequently been made for conjugated and aromatic compounds.

coulomb and resonance parameters as the corresponding orbitals for tetrahedral bonds, and to assign the odd electron to the customary $2p\pi$-orbital on this atom. The resonance integrals between this π-orbital and the adjacent σ-bond orbitals vanish in virtue of the antisymmetry of the π-orbital, and the σ-electrons can again be assigned to fill completely the molecular orbitals formed from the σ-bond orbitals, so that the convenient method of calculating total electronic energies, as described in the Appendix, is again applicable. A more refined procedure would be to introduce parameters for the orbitals in the bonds around the sp^2-carbon atom, differing from those of the corresponding tetrahedral orbitals, but this has the disadvantage of increasing the number of parameters appearing in the results, and so will not be considered here.

The energies to the second order for various paraffin radicals are given in Table 4.

TABLE 4. *Hydrocarbon radicals and* R–H *dissociation energies.*

Radical	E	D(R–H) Theor.		Exp.*
Methyl	$6\alpha - 12S\gamma$	$F + 3\Phi$	$101{\cdot}_4$	102
Ethyl	$12\alpha + 2h\gamma - (16 + 20\theta^2)S\gamma$	$F + 2\Phi$	$97{\cdot}_7$	97
n-Propyl	$18\alpha + 4h\gamma - (24 + 32\theta^2 + 4\Phi^2)S\gamma$	$F + 2\Phi$	$97{\cdot}_7$	—
*iso*Propyl	$18\alpha + 4h\gamma - (24 + 32\theta^2 + 4\eta^2)S\gamma$	$F + \Phi$	$94{\cdot}_0$	94
n-Butyl	$24\alpha + 6h\gamma - (24 + 52\theta^2 + 8\eta^2)S\gamma$	$F + 2\Phi$	$97{\cdot}_7$	—
*iso*Butyl	$24\alpha + 6h\gamma - (28 + 44\theta^2 + 12\eta^2)S\gamma$	$F + 2\Phi$	$97{\cdot}_7$	—
sec.-Butyl	$24\alpha + 6h\gamma - (28 + 48\theta^2 + 8\eta^2)S\gamma$	$F + \Phi$	$94{\cdot}_0$	—
tert.-Butyl	$24\alpha + 6h\gamma - (36 + 36\theta^2 + 12\eta^2)S\gamma$	F	$90{\cdot}_3$	90

* Stevenson, *Discuss. Faraday Soc.*, 1951, **10**, 35, 113; Trotman-Dickenson, *ibid.*, p. 112.

Theoretical values for various dissociation energies, D(R–H), may be obtained by subtraction of the relevant hydrocarbon energies from Table 2, and these are also included in Table 4. They are conveniently expressed in terms of the parameters F and Φ, which are defined in Table 5. Table 5 also lists two other parameters, G and Γ, and all the theoretical results discussed in the present paper depend only upon these four parameters. They are discussed further below (p. 2619).

TABLE 5. *Derived energy parameters.*

Parameter	Definition	Assumed val. (kcal.)	Parameter	Definition	Assumed val. (kcal.)
F	$-2\alpha + 12\theta^2 S\gamma$	$90{\cdot}_3$	Φ	$4(1 - \theta^2)S\gamma$	$3{\cdot}_7$
G	$-2\alpha - 2h\gamma + 24\eta^2 S\gamma$	$71{\cdot}_7$	Γ	$4(\theta^2 - \eta^2)S\gamma$	$2{\cdot}1_3$

It will be observed that the present theory (to the second order) groups R–H dissociation energies into four classes (methane-type, primary, secondary, tertiary), and predicts, independently of the values of any parameters, a uniform variation in the values from class to class. The uniform variation is confirmed experimentally by Stevenson's data for methane, ethane, propane, and *iso*butane (see Table 4), while the constancy of various primary D(R–H) and of various secondary D(R–H) has been remarked, *e.g.*, by Trotman-Dickenson (*Discuss. Faraday Soc.*, 1951, **10**, 112).

The theoretical dissociation energies, D(R–R′), for various C–C bonds are similarly derived from the data of Tables 2 and 4. They are conveniently expressed in terms of the parameters G and Γ of Table 5, *e.g.*, $D(C_2H_5{-}C_2H_5) = G + 4\Gamma$. Experimental dissociation energies may be derived from heats of formation of paraffin radicals (cf., *e.g.*, Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339; Szwarc, *Chem. Reviews*, 1950, **47**, 75), and comparison with theory may be made by using the assumed values of G and Γ listed in Table 5. For this purpose we have preferred to recalculate the heats of formation of paraffin radicals using Stevenson's more recent data (*loc. cit.*), and thence D(R–R′) for various bonds, rather than to employ the earlier tabulations of Roberts and Skinner or of Szwarc (*locc. cit.*). The latter are based on dissociation energies obtained from pyrolysis studies, and the data for *tert.*-butyl, and to some extent for *iso*propyl, are unreliable (see, *e.g.*, discussion by Szwarc, *loc. cit.*). The theoretical dissociation energies are compared with the experimental values (in parentheses) in Table 6. The two sets of figures agree extremely well, discrepancies being appreciably less than the uncertainty in the experimental figures, with the exception of D(R–R′) for 2 : 2 : 3 : 3-tetramethylbutane

($R = R' = \mathrm{Bu^t}$). The experimental value in this case is about 5 kcal. less than the theoretical figure, and a plausible explanation immediately suggests itself. The theoretical treatment is based solely on the connectivity of all neighbouring bonds, and so does not include energy terms arising from the interactions of orbitals in different portions of the molecule which happen to approach one another because of the geometry of the molecule, *i.e.*, steric compressions of the van der Waals type. Such steric interactions will be greatest in the molecule under consideration, where the C–C bond concerned carries three methyl groups at each end. It is tempting to conclude from the present analysis that the compressional energy arising from the mutual repulsions of the six methyl groups amounts to about 5 kcal. The dissociation energy D ($\mathrm{Pr^i}$–$\mathrm{Bu^t}$) is also slightly lower than predicted, although in this case the two values agree within the experimental uncertainty.

TABLE 6. *Dissociation energies of* C–C *bonds.**

	R′			
R	Methyl	Ethyl	*iso*Propyl	*tert.*-Butyl
Methyl	84·5 $(84{\cdot}_{4})$	82·4 $(81{\cdot}_{7})$	80·2 $(80{\cdot}_{8})$	78·1 $(78{\cdot}_{3})$
Ethyl	—	80·2 $(79{\cdot}_{4})$	78·1 $(78{\cdot}_{9})$	76·0 $(75{\cdot}_{7})$
*iso*Propyl	—	—	76·0 $(76{\cdot}_{9})$	73·8 $(72{\cdot}_{7})$
tert.-Butyl	—	—	—	71·7 $(67{\cdot}_{0})$

* Dissociation energies derived from heats of formation of alkyl radicals are given in parentheses.

The treatment just discussed for alkyl radicals is equally applicable to the corresponding carbonium ions and carbanions, since the odd electron of the radical residues in a different " shell " from the σ-electrons, as discussed above. However, the resultant charge on the sp^2-carbon atom in these ions will doubtless affect the σ-bond orbitals immediately surrounding this carbon atom, just as in the simple LCAO treatment of conjugated systems a heteroatom is considered to affect the coulomb integrals of adjacent atoms. It is hoped to discuss these paraffin ions in terms of the present theory in a subsequent communication.

The preceding discussion of electronic energies is not complete without some further remarks concerning the parameters F, G, Φ, Γ. These four parameters have been used to interpret a considerable number of independent experimental measurements of dissociation energies and heat-content differences, and the values assigned to them in Table 5 have been chosen to give the best fit with experiment. The parameter G arises in the treatment of C–C dissociation energies, and its value simply determines the origin of the energy scale for these dissociation energies. The parameter F plays an analogous part in the treatment of C–H dissociation energies. Clearly the selection of values of F and G to fit the observational data will help to eliminate any systematic error in the calculation of electronic energies of radicals in the present theory, *e.g.*, errors such as might arise from neglect of π–σ interactions.

The differences in the dissociation energies and in heats of formation are obtained solely in terms of Φ and Γ, so only two parameters are involved if we restrict considerations to differences rather than absolute values. It should perhaps be pointed out that the present treatment provides an acceptable prediction of energy differences of three essentially distinct types in terms of only two parameters.

It has already been mentioned that the first-order theory constitutes a theoretical justification for the additivity of bond energies. The second-order terms in the theory may also be interpreted quite simply. They arise from interactions of adjacent bonds. It can can be established generally (see Appendix) that the total energy to the second order consists of a sum of bond-energy terms and interaction-energy terms for adjacent bonds; the parameters $S\gamma$, $\theta^2 S\gamma$ and $\eta^2 S\gamma$ representing interactions of C–H with C–H, C–H with C–C, and C–C with C–C, respectively. The third-order terms (coefficient of S^2) which contain terms corresponding to mutual interactions of three adjacent bonds, include additional terms which are no so simply interpreted. The present theory thus constitutes a theoretical justification for the empirical analysis of heats of formation of the paraffins by Platt (*J. Phys. Chem.*, 1952, **56**, 328), who included corrections to the simple additivity rule in terms of a parameter, *f*, representing the number of adjacent pairs of C–C bonds. The present analysis suggests that smaller corrections might be expressed in terms of mutual interactions of three adjacent bonds, rather than pairs of next-but-nearest neighbours, as was considered by Platt.

The present theory of saturated systems may be used to deal with the problem of chemical reactivities. It is natural, by analogy with the theory of conjugated systems, to suppose that the reactivity of a bond in heterolytic reactions might be correlated with the " bond charge density," which is defined by

$$Q_r = 2 \sum_{j=1}^{N} c_{rj}^2 \quad (S = 0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for orthogonal orbitals, with a suitably modified definition for non-zero S (see Appendix). However, it can be shown (Appendix) that all bonds have $Q_r = 2$, independently of S, *i.e.*, the σ-electron distribution over the bonds is uniform. Consequently the most promising approach to the problem of chemical reactivities appears to be by calculation of energies of activation. This application of the theory will be discussed in later papers.

APPENDIX

In order to solve the secular equations (2), with the values of the matrix elements as set out in the preceding discussion, it is expedient to use the substitution (cf. Wheland, *loc. cit.*) :

$$(\alpha - e)/(\beta - S\alpha) = x/(1 - Sx) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The secular determinant then involves the numerical parameters h, θ, and η of Table 1, and the energy parameter, x, appears only in the leading diagonal. As an example, the resulting determinant for ethane is shown ($\delta = 1 - Sh$). The $N \times N$ determinant reduces to an Nth degree polynomial in x, the zeros of which, x_j, correspond to the energies of the molecular orbitals :

$$e_j = \alpha - \frac{x_j}{1 - Sx_j}\gamma = \alpha - y_j\gamma, \text{ say,} \quad . \quad (6)$$

$$\begin{vmatrix} x & 1 & 1 & \theta & — & — & — \\ 1 & x & 1 & \theta & — & — & — \\ 1 & 1 & x & \theta & — & — & — \\ \theta & \theta & \theta & (\theta x + h) & \theta & \theta & \theta \\ — & — & — & \theta & x & 1 & 1 \\ — & — & — & \theta & 1 & x & 1 \\ — & — & — & \theta & 1 & 1 & x \end{vmatrix}$$

and the total electronic energy is :

$$E = 2N\alpha - 2\gamma \sum_{j=1}^{N} y_j \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

To obtain explicit values for a particular x_j (and so y_j) it is in general necessary to assign specific numerical values to h, θ, and η, but it is possible to obtain $\sum_{j=1}^{N} y_j$ explicitly in terms of h, θ, and η, as a power series in S, by employing some well-known formulæ of the theory of equations (see, *e.g.*, Turnbull, " Theory of Equations," Oliver and Boyd, Edinburgh, 1946). Thus if the polynomial in x is

$$a_0x^N + a_1x^{N-1} + a_2x^{N-2} + \ldots\ldots$$

then we have :

$$\begin{aligned} \Sigma y_j &= \Sigma\, x_j + S\, \Sigma\, x_j^2 + S^2\, \Sigma\, x_j^3 + \ldots\ldots \\ &= \frac{-a_1}{a_0} + \frac{a_1^2 - 2a_0a_2}{a_0^2} S - \frac{a_1^3 - 3a_0a_1a_2 + 3a_0^2a_3}{a_0^3} S^2 + \quad . \quad . \quad . \quad (8) \end{aligned}$$

and it remains to determine the coefficients, a_n.

Specific formulæ for the coefficients up to a_6 have been given by Coulson (*Proc. Camb. Phil. Soc.*, 1949, **46**, 202) for the particular case when $h = 0$, and $\theta = \eta = 1$. The formulæ we require may be obtained by an extension of his analysis. The main difference in the present case arises from terms involving powers of h from the diagonal elements of the secular determinant. The coefficients a_0 and a_1 arise from only one term in the expansion of the determinant, namely, the product of the leading diagonal elements. These clearly comprise an element $(\delta x + h)$ for each C–C bond, and an element x for each C–H bond. The paraffin

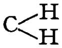
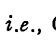
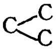
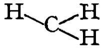
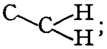
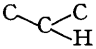
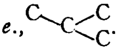
C_nH_{2n+2} contains $(n-1)$ C–C bonds and $(2n+2)$ C–H bonds, and the coefficients a_0 and a_1 are, respectively :

$$a_0 = \delta^{n-1};\ a_1 = (n-1)\delta^{n-2}h$$

Subsequent coefficients $a_2, a_3, \ldots, a_N$, contain contributions from other terms of the secular determinant, and we find :

$$a_2 = \frac{(n-1)(n-2)}{2}\delta^{n-3}h^2 - (b_1\delta^{n-1} + b_2\theta^2\delta^{n-2} + b_3\eta^2\delta^{n-3})$$

$$a_3 = \frac{(n-1)(n-2)(n-3)}{6}\delta^{n-4}h^3 - (b_1'\delta^{n-2} + b_2'\theta^2\delta^{n-3} + b_3'\eta^2\delta^{n-4})h + 2(c_1\delta^{n-1} + c_2\theta^2\delta^{n-2} + c_3\eta\theta^2\delta^{n-3} + c_4\eta^3\delta^{n-4})$$

where b and c are the numbers of adjacent pairs or trios of bonds as follows : b_1, C–H ; C–H, *i.e.*, ; b_2, C–H ; C–C, *i.e.*, ; b_3, C–C ; C–C, *i.e.*, ; c_1, C–H ; C–H, *i.e.*, ; c_2, C–H; C–H; C–C, *i.e.*, ; c_3, C–H; C–C; C–C, *i.e.*, ; c_4, C–C; C–C; C–C, *i.e.*, .

$$b_1' = (n-1)b_1;\ b_2' = \sum_{r=1}^{n-1} A_r;\ b_3' = \sum_{r=1}^{n-1} B_r$$

where A_r and B_r are properties of the rth C–C bond and the summations are over all C–C bonds in the molecule. A_r is the number of adjacent pairs of C–H ; C–C bonds which do not involve r, and B_r is the number of adjacent C–C ; C–C bonds which do not involve r.

When these values are substituted in (8), the result is :

$$\Sigma y_j = -(n-1)h + 2(b_1 + b_2\theta^2 + b_3\eta^2)S - \{[(3n-5)b_2 - 3b_2']h\theta^2 + [(3n-7)b_3 - 3b_3']h\eta^2 + 6(c_1 + c_2\theta^2 + c_3\eta\theta^2 + c_4\eta^3)\}S^2 \quad . \quad . \quad (9)$$

and the total electronic energy, obtained by substituting (9) in (7), is then the sum of first-order terms which are additive properties of the bonds present in the molecule, together with second-order terms which represent sums of interactions of adjacent bond pairs, and third-order terms corresponding to interaction energies for structural features of the kinds shown opposite the definitions of $c_1, \ldots, c_4$, together with terms in h which correspond to certain structural features which are not so easily visualised as interactions of bond orbitals.

Although the above results were derived specifically for hydrocarbons they apply equally to any other types of molecule when suitable additional parameters are included to represent the properties of orbitals for other kinds of bonds. The general result for the total energy still holds, *i.e.*, first-order additivity of " bond energies " with second-order correction terms from bond interaction energies.

Electron Densities.—In the general case where S is not zero the formula (4) for electron densities must be modified, and, as shown by Lowdin (*J. Chem. Phys.*, 1950, **18**, 365), it is convenient to transform the coefficients of the molecular orbitals, c_{rj}, into another set, C_{rj}, by the relationship :

$$(\mathbf{1} + \mathbf{S})^{1/2}\mathbf{c} = \mathbf{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where the bold-face symbols represent the appropriate matrices, and the matrix $(\mathbf{1} + \mathbf{S})$ is the matrix of the overlap integrals. The modified definition for the electron density in the rth bond is then :

$$Q_r = 2\sum_{j=1}^{N} C_{rj}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which coincides with the definitions employed by Wheland, by Chirgwin and Coulson, and by Lowdin (*locc. cit.*) for the charge densities on atoms in the analogous treatment of conjugated systems.

As Lowdin observed, the matrix $\mathbf{C}$ is unitary, so the summation in (11) is unity, and all bonds thus have $Q_r = 2$. This uniformity of the charge distribution is again a consequence of all the molecular orbitals' being doubly filled; in the case of the analogous treatment of conjugated systems where the molecular orbitals are not all filled, the uniformity of electron densities is no longer obtained, except in the special case of alternant hydrocarbon systems. In the present treatment the uniformity is valid for all types of molecules.

William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.

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