The molecular orbital theory of chemical valency
VIII. A method of calculating ionization potentials

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An analysis of the 'linear combination of atomic orbitals' approximation using the accurate molecular orbital equations shows that it does not lead to equations of the form usually assumed in the semi-empirical molecular orbital method. A new semi-empirical method is proposed, therefore, in terms of equivalent orbitals. The equations obtained, which do have the usual form, are applicable to a large class of molecules and do not involve the approximations that were thought necessary. In this method the ionization potentials are calculated by treating certain integrals as semi-empirical parameters. The value of these parameters is discussed in terms of the localization of equivalent orbitals and some approximate rules are suggested. As an illustration the ionization potentials of the paraffin series are considered and good agreement between the observed and calculated values is found.

1. Introduction

Both the electron pair and the molecular orbital theories of valency lead to equations whose solutions, even for simple molecules, involve heavy numerical computation. To avoid this, semi-empirical theories have been developed in which the integrals are not calculated directly, but determined by comparison with experiment. Molecules containing the same atoms, or groups of atoms, can usually be described in terms of the same integrals, so that the values of the integral parameters can be extensively checked. Such methods may be regarded as linking together a large number of experimental results by means of a small number of empirical parameters and the theoretically derived equations.

The particular theory that uses molecular orbitals has been very fruitful. It has been used by Hückel (1931) and others to discuss the mobile electrons of conjugated molecules. The symmetry of the orbitals of these electrons, which enables them to be considered apart from the rest of the molecule, and the fact that orbitals of carbon atoms only are needed, mean that two parameters, usually called α and β, are sufficient for the description of a large number of these molecules. Despite its undoubted success in predicting and correlating various properties of molecules, there are a number of features of the theory which cannot be considered satisfactory. The scheme of calculation that is used was based originally on arguments partly mathematical and partly physical, and so could only be justified by its agreement with experiment. Attempts have been made, particularly by Mulliken (1949), to lay a more rigorous foundation using the 'linear combination of atomic orbitals' approximation but, as yet, the precise definition of the integrals and the reasons for the limitations of the theory have not been given. This means that any attempt to extend the theory to other molecules or to other types of bond is difficult. Some of the difficulties have been discussed in a recent paper by Moffitt (1949) and have led him to propose a method of calculation for heteronuclear molecules using equations of a rather different form.

The explicit molecular orbital equations which have been obtained by Lennard-Jones (1949) open up the possibility of examining the foundations of the semi-empirical method rigorously. In this paper it will be shown that this examination leads to a new semi-empirical method founded on ionization potentials rather than total energies and applicable to any saturated molecule.

2. The 'linear combination of atomic orbitals' approximation

The 'linear combination of atomic orbitals' approximation, developed by Lennard-Jones (1929, 1937), Mulliken (1935 a) and others, has been considered the best foundation for the semi-empirical method. It seeks to find the molecular orbitals by expanding them in terms of a number of atomic orbitals centred on each atom in the molecule. Ideally, this set of orbitals should include a complete ortho-normal set, but in practice it is assumed that a linear combination of a finite number of atomic orbitals will be a close approximation to a molecular orbital.

The molecular orbital equations (Lennard-Jones 1949) for a molecule in a singlet ground state may be written in the variational form*

$$\sum_i \int \delta \overline{\psi}_i \{(H + V + A)\psi_i - E_{ii}\psi_i\} dx = 0, \tag{2.01}$$

where $\psi_i (i = 1, ..., N)$ are the doubly-occupied molecular orbitals, H is the Hamiltonian for an electron in the field of the bare nuclei,

$$V = 2\sum_n \int \overline{\psi}_n (1/r_{12})\psi_n dx_2, \tag{2.02}$$

$$A\psi_i = -\sum_n \int \overline{\psi}_n (1/r_{12})\psi_i dx_2 \psi_n \tag{2.03}$$

and

$$E_{ii} = \int \overline{\psi}_i (H + V + A)\psi_i dx. \tag{2.04}$$

Let us now assume, in accordance with the linear combination of atomic orbitals method, that each molecular orbital can be expressed approximately as a series of atomic orbitals

$$\psi_i = \sum_{j=1}^M a_{ij}\omega_j \quad (i = 1, ..., N) \tag{2.05}$$

where M, the number of the atomic orbitals ω_j, is in general larger than N. Although it might be possible to decide, for a given value of M, which atomic orbitals gave the most accurate approximation, it is usual to consider the ω_j as a set of known ortho-normal functions. The problem, therefore, is to determine the coefficients a_{ij} which yield the most accurate approximation to the molecular orbitals. It can be solved by varying these coefficients and using the calculus of variations. The variation takes the form

$$\delta \overline{\psi}_i = \sum_l^M \overline{\omega}_l \delta \overline{a}_{il} \tag{2.06}$$

and the functions V and A become

$$V = 2\sum_n \sum_{jk}^M \overline{a}_{nj} a_{nk} \mathscr{G}_{ik}, \tag{2.07}$$

* All summations, unless otherwise indicated, are over the occupied orbitals $i = 1, 2, ..., N$.

$$A\psi_i = -\sum_n \sum_{opq} \bar{a}_{no} a_{nq} a_{ip} \mathscr{G}_{op} \omega_q, \tag{2.08}$$

where

$$\mathscr{G}_{jk} = \int \bar{\omega}_j (1/r_{12}) \omega_k \, dx_2. \tag{2.09}$$

This leads to equations determining the coefficients

$$\sum_r a_{ir} \left\{ \mathscr{H}_{lr} + \sum_{jk}^M \sum_n \bar{a}_{nj} a_{nk} \left[2(lj \,|\, \mathscr{G} \,|\, rk) - (lj \,|\, \mathscr{G} \,|\, kr) \right] \right\} - E_{ii} a_{il} = 0$$

$$(i = 1, ..., N; \; l = 1, ..., M), \tag{2.10}$$

where

$$\mathscr{H}_{lr} = \int \bar{\omega}_l H \omega_r \, dx, \tag{2.11}$$

$$(l_j \,|\, \mathscr{G} \,|\, rk) = \int \bar{\omega}_l(1) \, \bar{\omega}_j(2) \, (1/r_{12}) \, \omega_r(1) \, \omega_k(2) \, dx_1 dx_2. \tag{2.12}$$

The form of these equations is of particular interest. They are cubic in the coefficients and there are NM of them.

Equations (2.10) do not have the form that the semi-empirical theory has always assumed. Instead, this theory has used linear equations leading to a single secular equation for all the molecular orbitals. This failure of the atomic orbital approximation to lead to equations of the expected form is due to the fact that the matrix a_{ij} is rectangular. This means that it does not have a left inverse and, consequently, that the factor

$$\sum_n \bar{a}_{nj} a_{nk} \tag{2.13}$$

in equations (2.10) does not simplify. This can be avoided by using only N atomic orbitals and making a_{ij} square, for then equations (2.10) become

$$\sum_r a_{ir} \{ \mathscr{H}_{lr} + \sum_j [2(lj \,|\, \mathscr{G} \,|\, rj) - (lj \,|\, \mathscr{G} \,|\, jr)] \} - E_{ii} a_{il} = 0 \tag{2.14}$$

or

$$\sum_r a_{ir} \mathscr{E}_{lr} - E_{ii} a_{il} = 0, \tag{2.15}$$

where

$$\mathscr{E}_{lr} = \int \bar{\omega}_l (H + V + A) \omega_r \, dx. \tag{2.16}$$

Equations (2.15) are linear and homogeneous and, therefore, can be solved only if the consistency equation

$$| \mathscr{E}_{lr} - E_{ii} \delta_{lr} | = 0 \tag{2.17}$$

is satisfied. Since E_{ii} has not yet been determined, the roots of this equation are the values of E_{ii} corresponding to the approximate molecular orbitals ψ_i. For each of these E_{ii}, equations (2.15) can be solved and the matrix a_{ij} found.

These equations are undoubtedly of the form that was expected, but the sacrifice of all but N of the atomic orbitals means that the approximation is very poor. The expansion (2.05) with $M = N$ suggests adopting a rather different approach. It has the form of the transformations already discussed (Hall & Lennard-Jones 1950)

$$\psi_i = \sum_l T_{il} \chi_l, \tag{2.18}$$

where the ψ_i are now the accurate molecular orbitals determined by (2.01). These transformations leave invariant the determinantal wave function, from which

equations (2·01) were derived, and express, therefore, the degrees of freedom of the orbitals among themselves. The χ_l cannot be chosen arbitrarily but must satisfy the equation

$$(H + V + A)\chi_l - \sum_m e_{ml}\chi_m = 0, \tag{2·19}$$

where

$$e_{ml} = \int \bar{\chi}_m (H + V + A) \chi_l \, dx. \tag{2·20}$$

Under such a transformation it is not possible to transform the molecular orbitals into orbitals strictly localized around one atom, but it is possible to transform them into equivalent orbitals approximately localized around one or two atoms according as they correspond to inner shells or lone pairs or bonds. A description of the properties of these equivalent orbitals has been given in part VII (Hall & Lennard-Jones 1951).

This leads to the conclusion that, although the 'linear combination of atomic orbitals' approximation is of very great value for the qualitative description of molecules and may lead to a useful semi-empirical method (Moffitt 1949), it is not closely related to the existing semi-empirical method. On the other hand, the form of the equations suggests the formulation of an equivalent orbital semi-empirical method.

3. The equivalent orbital method

The equivalent orbital method is based on the properties of the matrix e_{mn}, as discussed by Hall & Lennard-Jones (1950). In the molecular orbital description of a molecule this matrix is diagonal and, indeed, it is this property which defines a molecular orbital. The diagonal elements E_{nn} then have the physical significance of being nearly equal to the negative of the vertical ionization potentials of electrons in the corresponding molecular orbitals. The matrix elements in an equivalent orbital description do not have the same physical significance. They are defined as the matrix elements, with respect to two equivalent orbitals χ_m and χ_n, of the self-consistent Hamiltonian, which is the same for all occupied orbitals and invariant under transformations of these orbitals,

$$e_{mn} = \int \bar{\chi}_m (H + V + A) \chi_n \, dx. \tag{3·01}$$

Consequently, if two equivalent orbitals χ_m and χ_n bear the same relation to each other as do another pair χ_x and χ_y, then their matrix elements will be identical,

$$e_{mn} = e_{xy}. \tag{3·02}$$

For a molecule composed of a small number of sets of equivalent orbitals this reduces the number of independent matrix elements very considerably.

Let us now consider the problem of finding the ionization potentials and the molecular orbitals from known equivalent orbitals and their matrix elements e_{mn}. Since the transformation matrix T_{il}, for which

$$\psi_i = \sum_l T_{il}\chi_l, \tag{3·03}$$

also transforms the matrix e_{mn}

$$E_{ij} = \sum_{mn} T_{mi}^{-1} e_{mn} T_{jn}, \tag{3·04}$$

the problem is to find the matrix T_{il} for which E_{ij} is in diagonal form. This can be done by solving the eigenvalue equations

$$\sum_m e_{lm} x_m = E x_l. \tag{3·05}$$

For these homogeneous linear equations to be consistent they must satisfy the condition

$$| e_{lm} - E \delta_{lm} | = 0. \tag{3·06}$$

The roots of the equation are the required molecular orbital quantities E_{nn}. The corresponding eigenvectors $x_m^{(n)}$ are found by solving equation (3·05). These eigenvectors determine the required matrix T_{il} according to the relation

$$T_{il} = x_l^{(i)}, \tag{3·07}$$

so that the molecular orbitals can be found. These equations are similar to those obtained in the previous section for the specially simple case $M = N$, despite the fact that this is an accurate method whereas any 'linear combination of atomic orbitals' method involves approximation.

Equation (3·06) enables us to calculate ionization potentials knowing only the equivalent orbitals quantities e_{lm}. This can be made the basis of a semi-empirical method by treating these matrix elements as parameters to be found from the observed ionization potentials. Since the character of the representation spanned by the equivalent orbitals is easily found from the corresponding inner shells, lone pairs or bonds, it is often possible to simplify these calculations by using group theory.

Although this semi-empirical method is of a familiar form it differs in many respects from that used hitherto. In the first place, it has been rigorously deduced from the quantum mechanical equations. Apart from the assumption that the electrons can be assigned to orbitals, there are no approximations made. In particular, since the determinantal wave function, from which the orbital equations were deduced, satisfies the Pauli principle, all the exchange effects are included. This also means that the quantities involved are precisely defined and can be calculated theoretically once the molecular orbital equations are solved. Furthermore, the method can be applied to the ground state of any molecule, provided that this state is a singlet and that the molecular orbitals are doubly occupied and can be transformed into a number of sets of equivalent orbitals. The latter condition has been discussed in part VI (Hall 1950) and it is probable that all saturated molecules having a singlet ground state will satisfy it. It is intended in a further paper to propose an extension of the method applicable to conjugated molecules. Thus the scope of this method is very much greater than that of the previous method. Another difference is in the connecting link between theory and experiment. Hitherto it has been customary to use thermo-chemical quantities such as resonance energies for this purpose but, in this theory, the total energy of a molecule is equal to

$$\sum_n (H_{nn} + E_{nn}), \tag{3·08}$$

and so is not simply related to the quantities in the secular equation. Instead, the vertical ionization potentials are used, because a calculation of these quantities (Hall & Lennard-Jones 1950) shows that they are approximately equal to the negative of the molecular orbitals quantities E_{nn}.

4. Experimental Ionization Potentials

Ionization potentials are obtained experimentally from two sources, electron impact experiments and spectra in the vacuum ultra-violet. Results from these sources do not quite agree, for the electron impact potentials are always a little higher than those derived from spectra. This has been explained (Honig 1948) by saying that the electron impact potential is a vertical potential, whereas the spectral transitions are not quite vertical. Since the theoretical quantities are vertical ionization potentials, we must, therefore, prefer the electron impact values. This is unfortunate, since these experiments are not of an accuracy comparable with the measurements on spectra. In identifying the observed and theoretical ionization potentials the assumption is made that the vibrational energy is the same in the neutral and the ionized states of the molecule. This is a good approximation for many molecules, but corrections may have to be applied for some smaller molecules.

A further difficulty is that, except for one or two special cases, we have no experimental information about any ionization potential other than that of the most loosely bound electron in each molecule. This leads to complications when we wish to determine the semi-empirical parameters, but once these are known, the remaining ionization potentials can be deduced from them and used to interpret experimental results.

5. Methane and Ethane

To illustrate the method we shall now discuss the ionization potentials of the methane and ethane molecules. The ten electrons of the methane molecule can be assigned to five doubly occupied orbitals. In a molecular orbital description of the molecule these occupied orbitals are the carbon $1s$ orbital, a molecular orbital of symmetry A_1 and three molecular orbitals spanning the triply degenerate T_1 representation. This carbon inner shell may also, without loss of generality, be taken as a single equivalent orbital. The remaining four molecular orbitals can be transformed into four equivalent orbitals corresponding to the CH bonds. The various matrix elements e_{lm} for these equivalent orbitals can have only two distinct values. If a is the matrix element for a CH bond, and b for the interaction between two bonds, the matrix is of the form

$$e_{lm} = \begin{pmatrix} a & b & b & b \\ b & a & b & b \\ b & b & a & b \\ b & b & b & a \end{pmatrix}. \tag{5.01}$$

From this matrix the values of the molecular orbital quantities E_{nn} may be obtained using equation (3.06), which now becomes

$$\begin{vmatrix} a-E & b & b & b \\ b & a-E & b & b \\ b & b & a-E & b \\ b & b & b & a-E \end{vmatrix} = 0. \tag{5.02}$$

Since the $1s$ shell is already a molecular orbital, it factorizes out of the equation and so may be omitted. The triple root of this equation $(a-b)$ corresponds to the three T_1 orbitals, and the single root $(a+3b)$ to the A_1 molecular orbital. Thus the molecular orbital matrix, into which e_{lm} can be transformed, is

$$E_{lm} = \begin{pmatrix} a+3b & \cdot & \cdot & \cdot \\ \cdot & a-b & \cdot & \cdot \\ \cdot & \cdot & a-b & \cdot \\ \cdot & \cdot & \cdot & a-b \end{pmatrix}. \tag{5.03}$$

Of the two ionization potentials

$$I_1 = -(a-b), \quad I_2 = -(a+3b), \tag{5.04}$$

the triply degenerate I_1 will be the smaller.

The experimental ionization potential is 13.04 ± 0.02 (Honig 1948) but there is no experimental value available for the other potential. Mulliken (1935 b) estimated this second potential at 22.0 on the basis of a first potential of 14.4. With our present more accurate value for the first potential, a second potential of 20.0 would be a better estimate. Thus we have

$$a-b = -13, \quad a+3b = -20, \tag{5.05}$$

so that

$$a = -14.75, \quad b = -1.75. \tag{5.06}$$

Because of the uncertainty in the second potential, these values for a and b can only be taken as showing their order of magnitude.

TABLE 1. MATRIX ELEMENTS FOR THE EQUIVALENT ORBITALS OF ETHANE

	C_1C_2	$C_1H^{(1)}$	$C_1H^{(2)}$	$C_2H^{(1)}$
C_1C_2	c	d	d	d
$C_1H^{(1)}$	d	a	b	f
$C_1H^{(2)}$	d	b	a	g
$C_2H^{(1)}$	d	f	g	a

The ethane molecule can be treated in much the same way. The $1s$ orbitals factorize out leaving six equivalent CH bond orbitals and a CC bond orbital. If we assume the D_{3d} model of the molecule, six parameters are required to set up the equation for the ionization potential. These are most conveniently defined in the form of table 1. In this table, the equivalent orbital corresponding to $C_1H^{(1)}$ transforms into the one corresponding to $C_2H^{(1)}$ under the inversion operation. Using these parameters we can set up the matrix e_{lm} and hence the equation for the molecular orbital E_{nn}

$$\begin{vmatrix} c-E & d & d & d & d & d & d \\ d & a-E & b & b & f & g & g \\ d & b & a-E & b & g & f & g \\ d & b & b & a-E & g & g & f \\ d & f & g & g & a-E & b & b \\ d & g & f & g & b & a-E & b \\ d & g & g & f & b & b & a-E \end{vmatrix} = 0. \tag{5.07}$$

The solution of (5·07) is simplified by the symmetry of the molecule. These seven orbitals span a reducible representation of the group which splits up according to the reduction

$$2A_{1g} + A_{2u} + E_g + E_u. \tag{5·08}$$

Now, if we transform the orbitals according to a transformation

$$\phi_n = \sum_l T_{nl} \chi_l, \tag{5·09}$$

the elements of the secular equations transform to

$$E_{mn} = \sum_{ij} T_{im}^{-1} e_{ij} T_{nj}$$

$$= \sum_{ij} \bar{T}_{mi} T_{nj} e_{ij}. \tag{5·10}$$

The matrix T_{nl}, which transforms equivalent orbitals to symmetry orbitals, is easily written down from the irreducible representations (5·08)

$$T_{nl} = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} \\ \cdot & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \\ \cdot & \sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{12}} & -\sqrt{\frac{1}{12}} & \sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{12}} & -\sqrt{\frac{1}{12}} \\ \cdot & \cdot & \frac{1}{2} & -\frac{1}{2} & \cdot & \frac{1}{2} & -\frac{1}{2} \\ \cdot & \sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{12}} & -\sqrt{\frac{1}{12}} & -\sqrt{\frac{1}{3}} & \sqrt{\frac{1}{12}} & \sqrt{\frac{1}{12}} \\ \cdot & \cdot & \frac{1}{2} & -\frac{1}{2} & \cdot & -\frac{1}{2} & \frac{1}{2} \end{pmatrix}. \tag{5·11}$$

By means of this matrix and equation (5·10), the secular equation can be factorized and the result written down immediately

$$\begin{vmatrix} c - E & \sqrt{6}d \\ \sqrt{6}d & a + 2b + f + 2g - E \end{vmatrix} = 0, \quad (2A_{1g}), \tag{5·12}$$

$$E = a + 2b - f - 2g, \quad (A_{2u}), \tag{5·13}$$

$$E = a - b + f - g, \quad (E_g), \tag{5·14}$$

$$E = a - b - f + g, \quad (E_u). \tag{5·15}$$

Since f and g are probably small, this means that there are two doubly degenerate potentials, one on each side of $(-a+b)$, two singly degenerate potentials in the neighbourhood of $(-a-2b)$ and one potential near $-c$. From our knowledge of the relative strength of these bonds we expect the lowest ionization potential to be that of an electron concentrated around the carbon atoms, so that the smaller root of the equation (5·12) will give the observed ionization potential. The observed potential is 11·76 (Honig 1948) but, since no others are known, we cannot solve the equations without further simplification.

6. A THEORY OF THE PARAMETERS

Since there are not enough experimental data available to determine all the parameters necessary in the exact theory, we must reduce the number of independent parameters by introducing various approximations. Theoretical considerations

suggest particular approximations, but these can only be justified if they give agreement with experiment. As the empirical theory of the values of the parameters develops it should be possible to test these approximations and suggest better ones.

In parts IV and VI (Lennard-Jones & Pople 1950; Hall 1950) the nature of equivalent orbitals has been discussed, and arguments have been given for regarding them as almost localized. This has several implications for the values of the parameters. In the first place, the interaction parameters between two almost localized orbitals will decrease rapidly as the orbitals become further apart. This means, for a saturated molecule in which there are no strong polar groups, that the interactions between orbitals which are not immediate neighbours are small compared with the interactions of neighbours.

Localization implies also that an equivalent orbital is determined by the nature of the atom or atoms around which it is concentrated. This means that the matrix elements between two orbitals will be invariant if the atoms concerned are the same chemically. Since the localization is not strict, neighbouring atoms influence the parameters and the invariance is only an approximation. The largest effect on an orbital is that due to other orbitals on the same atom or atoms. These may, for example, change the effective field around the nucleus and so alter the parameters. A change in the value of a parameter due to an alteration of a neighbouring orbital may be called an inductive effect. To avoid these complications we shall adopt the more accurate approximation that chemically equivalent orbitals give rise to the same equalities of parameters as if they were mathematically equivalent. Orbitals, in the same or in different molecules, are called *chemically equivalent* if they are concentrated around similar atoms and have the same immediate neighbours.

Thus, in the ethane molecule, we should expect the parameters f and g to be small and the parameters a and b to be nearly equal to the corresponding parameters a and b for methane. The latter is probably not a good approximation, for there may be an inductive effect due to the difference in neighbouring orbitals.

7. The paraffin series

As a further illustration of the method and as an empirical justification for some of the approximations suggested above, we shall now consider the series of saturated hydrocarbons. It is necessary first to discuss an infinite chain of CH_2 groups staggered about a line but having all the carbon atoms in one plane. We shall include all the first and second neighbour interactions and neglect all others. The parameters required are defined in table 2. In this table the $C_nH^{(1)}$ equivalent orbital inverts into the $C_{n+1}H^{(2)}$ orbital. The equation for the molecular orbital quantities is infinite but has a periodic form consisting of blocks along the diagonal such as

$$
\left.
\begin{array}{cccccccccccccccc}
. & f & g & d & b & a-E & d & f & g & k & . & . & . & . & . & . \\
h & k & k & e & d & d & c-E & d & d & e & . & . & h & . & . & . \\
. & . & . & . & d & f & d & a-E & b & d & g & f & k & . & . & . \\
. & . & . & . & f & g & d & b & a-E & d & f & g & k & . & . & . \\
. & . & . & h & k & k & e & d & d & c-E & d & d & e & . & . & .
\end{array}
\right\}
\quad (7\cdot01)
$$

TABLE 2. MATRIX ELEMENTS FOR THE EQUIVALENT ORBITALS OF A PARAFFIN

	$C_{n-1}C_n$	$C_nH^{(1)}$	$C_nH^{(2)}$	C_nC_{n+1}	$C_{n+1}H^{(1)}$	$C_{n+1}H^{(2)}$	$C_{n+1}C_{n+2}$
$C_{n-1}C_n$	c	d	d	e	.	.	h
$C_nH^{(1)}$	d	a	b	d	g	f	k
$C_nH^{(2)}$	d	b	a	d	f	g	k
C_nC_{n+1}	e	d	d	c	d	d	e
$C_{n+1}H^{(1)}$	.	g	f	d	a	b	d
$C_{n+1}H^{(2)}$	.	f	g	d	b	a	d

A secular equation of this kind is most easily solved by substituting in the linear equations from which it arises. If we denote by p_n, q_n and r_n the coefficients of the CC equivalent orbital and the two CH equivalent orbitals respectively of the nth CH_2 group, then the substitution is

$$p_n = p\,e^{in\theta}, \quad q_n = q\,e^{in\theta}, \quad r_n = r\,e^{in\theta}, \tag{7.02}$$

where p, q and r remain to be determined and θ is arbitrary. This reduces the infinite set of equations to the finite set

$$(c + 2e\cos\theta + 2h\cos 2\theta - E)p + (d + 2k\cos\theta)q + (d + 2k\cos\theta)r = 0, \tag{7.03}$$

$$(d + 2k\cos\theta)p + (a + 2g\cos\theta - E)q + (b + 2f\cos\theta)r = 0, \tag{7.04}$$

$$(d + 2k\cos\theta)p + (b + 2 + \cos\theta)q + (a + 2g\cos\theta - E)r = 0, \tag{7.05}$$

and hence to the secular equation

$$\begin{vmatrix} c + 2e\cos\theta + 2h\cos 2\theta - E & d + 2k\cos\theta & d + 2k\cos\theta \\ d + 2k\cos\theta & a + 2g\cos\theta - E & b + 2f\cos\theta \\ d + 2k\cos\theta & b + 2f\cos\theta & a + 2g\cos\theta - E \end{vmatrix} = 0. \tag{7.06}$$

The substitution is equivalent to using the irreducible representations of the translation subgroup of the symmetry group of the molecule. Equation (7.06) can be simplified by using the symmetry plane of the molecule. This is equivalent to using the transformation matrix

$$\begin{pmatrix} 1 & . & . \\ . & \sqrt{\tfrac{1}{2}} & \sqrt{\tfrac{1}{2}} \\ . & \sqrt{\tfrac{1}{2}} & -\sqrt{\tfrac{1}{2}} \end{pmatrix} \tag{7.07}$$

to give

$$\begin{vmatrix} c + 2e\cos\theta + 2h\cos 2\theta - E & \sqrt{2}(d + 2k\cos\theta) \\ \sqrt{2}(d + 2k\cos\theta) & a + b + 2g\cos\theta + 2f\cos\theta - E \end{vmatrix} = 0, \tag{7.08}$$

$$E = a - b + 2g\cos\theta - 2f\cos\theta. \tag{7.09}$$

From these equations the general distribution of the potentials is easily deduced. There is a band of potentials around the value $(a - b)$ and two interacting bands around c and $(a + b)$. The observed potential, as before, is expected to be the smallest appearing in (7.08).

The ionization potentials for a finite molecule containing s CC bonds can be deduced from these results if we impose the condition that the zeroth and the

$(s+1)$th equivalent orbitals have zero coefficients. This condition means that, instead of (7·02), we use the transformations

$$p_n = p\sin n\theta, \quad q_n = q\sin n\theta, \quad r_n = r\sin n\theta, \tag{7·10}$$

where θ satisfies the equation

$$\sin(s+1)\theta = 0, \tag{7·11}$$

and hence

$$\theta = m\pi/(s+1) \quad (m = 1, \ldots, s). \tag{7·12}$$

This leads to the equations (7·08) and (7·09) as before. For a finite molecule this method is not exact, because the number of CH bond interactions included is always four less than the correct number. This inaccuracy arises at the ends and means that the extreme carbon atoms have not their right number of CH bonds. For large molecules this should have little effect, but for a smaller molecule such as ethane the equations would not apply. There is also a small approximation involving the second neighbour CC-CC interaction only but since we shall be neglecting this interaction, it need not be discussed.

If we neglect the second neighbour interactions, equation (7·08) becomes

$$\begin{vmatrix} c + 2e\cos\theta - E & \sqrt{2}d \\ \sqrt{2}d & a+b-E \end{vmatrix} = 0. \tag{7·13}$$

Since c and e are negative, the smallest root occurs when $\theta = s\pi/(s+1)$. If we define ϕ as a function of s by

$$\phi = \pi/s + 1 \tag{7·14}$$

then the observed ionization potentials for the series should be the lower roots of the equation

$$\begin{vmatrix} c - 2e\cos\phi - E & \sqrt{2}d \\ \sqrt{2}d & a+b-E \end{vmatrix} = 0. \tag{7·15}$$

8. Numerical results

There are several difficulties in applying equation (7·15) to the experimental ionization potentials. The four parameters c, e, d and $a+b$ must first be determined using observed values of E. The equation can be written

$$c - 2e\cos\phi - 2d^2/(a+b-E) - E = 0, \tag{8·01}$$

but, even in this form, it is not linear in all the parameters and would be difficult to solve exactly. To avoid this difficulty a fixed value for $a+b$ was taken and the equations solved for the variables c, e and d^2. This was repeated for several values of $a+b$ and the best agreement with experiment was obtained using

$$a+b = -12·0. \tag{8·02}$$

Since the equations which were obtained were ill-conditioned, it was not possible to apply small corrections to this estimate, and it cannot be considered very accurate. With this value of $a+b$, three equations are needed to complete the solution. Since the differences between the ionization potentials are not large, it was thought better to use a least squares method and fit the parameters to the experimental results as a whole. Accordingly, the observed ionization potentials (Honig 1948) for the series

from propane to decane were used, each being assigned equal weight. The values obtained for the parameters were

$$c = -13 \cdot 2486, \quad e = -1 \cdot 4785, \quad d = \pm 0 \cdot 4678. \qquad (8 \cdot 03)$$

Of these, the value of d is the least reliable, since it depends sensitively on the value of $(a+b)$ assumed.

TABLE 3. EXPERIMENTAL AND CALCULATED IONIZATION POTENTIALS

	calculated	experimental
propane	11·214	11·21
butane	10·795	10·80
pentane	10·554	10·55
hexane	10·412	10·43
heptane	10·323	10·35
octane	10·265	10·24
nonane	10·224	10·21
decane	10·194	10·19

From these values of the parameters it is not difficult to deduce the ionization potentials. These are set out in table 3. Since the quoted experimental error is $\pm 0 \cdot 02$, this agreement is as good as can be expected and justifies the approximation of neglecting second neighbour interactions.

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