ELECTRON INTERACTION IN UNSATURATED HYDROCARBONS

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An approximate form of the molecular orbital theory of unsaturated hydrocarbon molecules in their ground states is developed. The molecular orbital equations rigorously derived from the correct many-electron Hamiltonian are simplified by a series of systematic approximations and reduce to equations comparable with those used in the semi-empirical method based on an incompletely defined one-electron Hamiltonian. The two sets of equations differ, however, in that those of this paper include certain important terms representing electronic interaction. The theory is used to discuss the resonance energies, ionization potentials, charge densities, bond orders and bond lengths of some simple hydrocarbons. The electron interaction terms introduced in the theory are shown to play an important part in determining the ionization potentials. It is also shown that the uniform charge density theorem, proved by Coulson and Rushbrooke [1] for the simpler theory, holds also for the self-consistent orbitals derived by the method of this paper.

1. INTRODUCTION.—One of the methods most extensively used in the quantum-mechanical study of the mobile electrons of conjugated molecules is the semi-empirical molecular orbital theory developed by Hückel,[2] Lennard-Jones,[3] Coulson and Longuet-Higgins [4] and others. According to this well-known theory, the mobile electrons can be treated as occupying a set of delocalized molecular orbitals (not more than two electrons in each), these orbitals being eigenfunctions of a one-electron Hamiltonian representing the kinetic energy, the field of the nuclei and the smoothed-out distribution of the other electrons. The total energy of the mobile electrons is then obtained by adding together the energies of the individual electrons. By approximating the orbitals as linear combinations of atomic orbitals centred on the various atoms and estimating certain integrals empirically, the theory can be put in a simple form enabling it to be applied to a wide range of molecules.

Although it has the merit of great simplicity, the Hückel procedure has serious defects. These are connected with the difficulty of giving a precise definition of the one-electron Hamiltonian. Strictly the problem should be formulated in terms of the complete many-electron Hamiltonian in which the interelectronic repulsions are included explicitly. If the one-electron Hamiltonian is supposed to include a term allowing for the screening effect of other electrons, then interelectronic interactions will be counted twice in the total energy. These considerations have led some authors to develop more precise theories of mobile electrons based on the correct many electron Hamiltonian. Hall [5] has proposed an alternative interpretation of the empirical theory in which the parameters are closely related to the ionization potentials of an excited state in which all mobile electrons have the same spin. Most of the more refined theories, however, have been of a non-empirical nature, obtaining energy levels and other molecular properties by direct calculation from approximate analytical forms for the wave function. The molecular orbital calculations of Goeppert-Mayer and Sklar [6] on benzene and of Parr and Mulliken [7] on butadiene are based on a single configuration wave-function, that is, a single way of allocating electrons to orbitals. Other detailed calculations [8,9] indicate, however, that different configurations cannot always be treated independently and that the interaction of configurations often leads

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to important changes in molecular properties, notably excitation levels. The significance of configuration interaction in conjugated molecules has been fully discussed by Coulson, Craig and Jacobs.[10]

The aim of this paper is to present a simplified molecular orbital theory of the ground states of hydrocarbons which is correctly based on the many-electron Hamiltonian but which is simple enough to be directly comparable with the Hückel procedure. The method is based on a single configuration wave function, the molecular orbitals being chosen as the best possible linear combinations of given atomic orbitals. The method starts from the self-consistent orbital equations given by Lennard-Jones,[11] Hall[12] and Roothaan.[13] These are simplified by systematic approximation of the integrals and reduce to expressions involving empirical parameters analogous to those of the Hückel theory, together with certain electron interaction terms given directly in terms of the geometrical dimensions of the molecule. The resulting wave functions can then be used in a discussion of resonance energies, ionization potentials and bond orders of some simple hydrocarbons.

The interaction of configurations can be included at a similar level of approximation.[14] This must eventually lead to an improved wave function, but in view of the difficulty of enumerating all configurations and the even greater difficulty of deciding which will interact most strongly, it is important to find out just how successful a single-determinant function can be. Only such a simple wave function will be considered in this paper.

2. THE DETERMINATION OF SELF-CONSISTENT MOLECULAR ORBITALS FOR CONJUGATED MOLECULES.—According to the molecular orbital theory, the wave function for the ground state of a molecule with $2N$ electrons is obtained by allocating one electron of each spin to each of a set of space orbitals $\psi_1 \ldots \psi_N$ and combining the products into a complete determinantal wave function

$$\overline{\Psi} = \det\{\psi_1(1)\alpha(1) \ldots \psi_N(N)\alpha(N)\psi_1(N+1)\beta(N+1) \ldots \psi_N(2N)\beta(2N)\}. \quad (2.1)$$

Explicit equations for the functions ψ_i can be derived from the variational principle.[11]

If it is not practicable to use the best possible ψ_i, it is usual to use some approximate analytical forms containing adjustable parameters, these parameters being determined by the variational principle. The most convenient way of doing this is by writing the molecular orbitals as a linear combination of given atomic orbitals ϕ_μ centred on the various atoms of the molecule

$$\psi_i = \sum_\mu x_{i\mu}\phi_\mu. \quad (2.2)$$

Throughout this paper, Greek suffixes will be used for atomic orbitals and italics for molecular orbitals. The equations for the coefficients $x_{i\mu}$ are

$$\sum_\nu F_{\mu\nu}x_{i\nu} = E_i \sum_\nu S_{\mu\nu}x_{i\nu}, \quad (2.3)$$

where

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}\{(\mu\lambda \mid G \mid \nu\sigma) - \tfrac{1}{2}(\mu\lambda \mid G \mid \sigma\nu)\}, \quad (2.4)$$

$$H_{\mu\nu} = \int \overline{\phi}_\mu\{-\tfrac{1}{2}\nabla^2 - \sum_\alpha V_\alpha(\mathbf{r})\}\phi_\nu d\mathbf{r}, \quad (2.5)$$

$$(\mu\lambda \mid G \mid \nu\sigma) = \iint \overline{\phi}_\mu(1)\overline{\phi}_\lambda(2)(1/r_{12})\phi_\nu(1)\phi_\sigma(2)d\mathbf{r}_1 d\mathbf{r}_2, \quad (2.6)$$

$$S_{\mu\nu} = \int \overline{\phi}_\mu\phi_\nu d\mathbf{r}, \quad (2.7)$$

$$P_{\lambda\sigma} = 2 \sum_i \overline{x}_{i\lambda}x_{i\sigma}. \quad (2.8)$$

In these expressions $V_\alpha(\mathbf{r})$ is the potential due to nucleus α, so that $H_{\mu\nu}$ is the matrix element of the one-electron Hamiltonian for motion in the field of the bare nuclei.   The E_i in (2.3) are the N lowest roots of the secular equation

$$| F_{\mu\nu} - ES_{\mu\nu} | = 0, \tag{2.9}$$

and are the molecular orbital theory approximations to the ionization potentials.[15] Equations of this type for the coefficients $x_{i\mu}$ were given by Hall [12] and Roothaan.[13] It should be noted that they are not linear since $F_{\mu\nu}$ itself depends on $x_{i\mu}$.   The expression for the total electronic energy using these orbitals can be written

$$\mathscr{E} = \tfrac{1}{2} \sum_{\mu\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}). \tag{2.10}$$

This follows from the energy expression corresponding to the wave function (2.1) [16] if the molecular orbitals are written in the LCAO form (2.2).   The total energy of the molecule is obtained by adding the nuclear repulsion terms to (2.10).

Strictly the above equations should be applied to all electrons in a molecule including inner shells.   For conjugated molecules with a planar nuclear framework, however, it is possible to separate the orbitals into non-combining classes π and σ according as they have or have not a node in the nuclear plane.   Since a complete treatment would be very difficult, it is usual to suppose that the effect of the σ-electrons on the π-structure can be represented by a rigid non-polarizable core whose potential can then be included in the $H_{\mu\nu}$ matrix elements.   The only investigation of the effect of the details of π—σ interaction [17] indicates that this approximation is reasonable, at least for the ground state.   If only one atomic orbital of π symmetry is used for each atom $(2p\pi)$ then eqn. (2.3) lead to a set of self-consistent coefficients for the LCAO orbitals.   The theory in this form has been applied to butadiene by Parr and Mulliken [7] and by Coulson and Jacobs.[9] As outlined in the introduction, we shall endeavour to simplify these equations by a series of approximations so that the method becomes comparable with the Hückel procedure but yet retains the important qualitative features of electron interaction.   These approximations are as follows.

A. The σ-system is treated as a non-polarizable core and its effect included in the $H_{\mu\nu}$ terms as described above.   This means that $V_\alpha(\mathbf{r})$ now represents the potential due to the nuclear charge and all the σ-electrons associated with atom α.

B. The overlap integral $S_{\mu\nu}$ will be neglected unless $\mu = \nu$, in which case it is unity.   This approximation is not quantitatively accurate, but it simplifies the treatment considerably and is unlikely to alter the general features of the electronic distribution.   The condition that the molecular orbitals ψ_i are normalized now becomes

$$\sum \bar{x}_{i\mu} x_{i\mu} = 1. \tag{2.11}$$

C. All two-electron integrals which depend on the overlapping of charge distributions of different orbitals are neglected.   This means that $(\mu\lambda \,|\, G \,|\, \nu\sigma)$ is neglected unless $\mu = \nu$ and $\lambda = \sigma$.   Approximations B and C are really consistent with one another for if the magnitude $S_{\mu\nu}$ of the charge distribution $\bar{\phi}_\mu \phi_\nu$ is neglected, its interaction with other distributions should also be left out of account.   In fact, if approximation B were made without approximation C it would be equivalent to counting the interactions of more electrons than are actually present.   With these simplifications the $F_{\mu\nu}$ can be written

$$F_{\mu\mu} = H_{\mu\mu} + \tfrac{1}{2}P_{\mu\mu}(\mu\mu \,|\, G \,|\, \mu\mu) + \sum_{\sigma(\neq\mu)} P_{\sigma\sigma}(\mu\sigma \,|\, G \,|\, \mu\sigma), \tag{2.12}$$

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}(\mu\nu \,|\, G \,|\, \mu\nu), \qquad (\mu \neq \nu). \tag{2.13}$$

The $H_{\mu\mu}$ in (2.12) are the diagonal matrix elements of the core Hamiltonian for all atoms and will therefore include the interaction with distant cores.   These distant interactions will not be small (in fact their sum diverges for a long polyene)

but they will be largely cancelled by corresponding terms in the last part of (2.12). In order to replace $H_{\mu\mu}$ by something which may reasonably be taken as constant from molecule to molecule, it is convenient to rearrange (2.12). The matrix element $H_{\mu\mu}$ is

$$H_{\mu\mu} = (\mu \mid -\tfrac{1}{2}\nabla^2 - V_\mu \mid \mu) - \sum_{\alpha(\neq\mu)} (\mu \mid V_\alpha \mid \mu) = U_{\mu\mu} - \sum_{\alpha(\neq\mu)} (\mu \mid V_\alpha \mid \mu), \quad (2.14)$$

where $U_{\mu\mu}$ is now the diagonal matrix element of ϕ_μ with respect to the one-electron Hamiltonian containing the kinetic energy and the interaction with the core of atom μ. $U_{\mu\mu}$ may reasonably be taken as the same for all hydrocarbons.

D. To allow some of the cancelling mentioned above to be carried out explicitly we now replace all electron interaction integrals $(\mu\nu \mid G \mid \mu\nu)$ between electrons on different centres and also $(\mu \mid V_\alpha \mid \mu)$, $(\alpha \neq \mu)$, by the interaction energy of point charges at the nuclear centres.

$$(\mu\nu \mid G \mid \mu\nu) = R_{\mu\nu}^{-1}, \tag{2.15}$$

$$(\mu \mid V_\alpha \mid \mu) = -Z_\alpha R_{\mu\alpha}^{-1}, \tag{2.16}$$

where Z_α is the " effective charge " of the σ-core of atom α. For hydrocarbons $Z_\alpha = 1$ but in the extension of the theory to systems where one atom contributes two electrons to the π-system, it may take other values.

This set of approximations is similar to those suggested by Pariser and Parr.[14] These authors neglect all but the Coulomb-type two-electron integrals $(\mu\nu \mid G \mid \mu\nu)$ and approximate these by the interaction of suitably chosen uniformly charged spheres.

Using (2.15) and (2.16), eqn. (2.12) and (2.13) now reduce to

$$F_{\mu\mu} = U_{\mu\mu} + \tfrac{1}{2}P_{\mu\mu}(\mu\mu \mid G \mid \mu\mu) + \sum_{\sigma(\neq\mu)} (P_{\sigma\sigma} - Z_\sigma)R_{\mu\sigma}^{-1}, \tag{2.17}$$

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}R_{\mu\nu}^{-1}, \qquad (\mu \neq \nu). \tag{2.18}$$

$(P_{\sigma\sigma} - Z_\sigma)$ may be described as the resultant electronic charge on atom σ. $H_{\mu\nu}$ ($\mu \neq \nu$) is now a non-diagonal matrix element representing the fact that electrons can move in levels of lower energy by virtue of being in the field of two σ-cores simultaneously. This is the primary cause of chemical binding. If all the terms in (2.17) and (2.18) except $H_{\mu\mu}$ and $H_{\mu\nu}$ for nearest neighbours are omitted, the method reduces to the Hückel theory where the parameters are usually called α and β. In the present work we shall continue to treat $U_{\mu\mu}$ and $H_{\mu\nu}$ as empirical parameters, neglecting $H_{\mu\nu}$ for all but nearest neighbours, but shall also include the electron interaction terms in the forms given in (2.17) and (2.18).

To get an expression for the total π-electron energy, it is convenient to add to (2.10) an " effective nuclear interaction " term

$$\mathscr{E}' = \sum_{\mu < \nu} Z_\mu Z_\nu R_{\mu\nu}^{-1}. \tag{2.19}$$

This is really part of the energy of the σ-core itself, but it is convenient to include it as it leads to a simply additive expression. All expressions for resonance energies, ionization potentials and excitation energies, however, occur as the difference of two quantities both including $\mathscr{E}'$. The total π-electron energy is then given by

$$\mathscr{E}_\pi = \mathscr{E}' + \tfrac{1}{2}\sum_{\mu\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu})$$

$$= \sum_\mu P_{\mu\mu}[U_{\mu\mu} + \tfrac{1}{4}P_{\mu\mu}(\mu\mu \mid G \mid \mu\mu)] + 2\sum_{\mu < \nu} P_{\mu\nu}H_{\mu\nu}$$

$$+ \sum_{\mu < \nu} (P_{\mu\mu} - Z_\mu)(P_{\nu\nu} - Z_\nu)R_{\mu\nu}^{-1} - \tfrac{1}{2}\sum_{\mu < \nu} P_{\mu\nu}^2 R_{\mu\nu}^{-1}. \tag{2.20}$$

3. RESONANCE ENERGIES AND IONIZATION POTENTIALS OF CONJUGATED HYDRO-CARBONS.—The expression (2.20) for the π-electron energy can be used for comparing the resonance or delocalization energies of simple conjugated hydrocarbons. In the simplest molecules (ethylene, benzene) the coefficients $x_{i\mu}$ are determined by symmetry and will be the same in this theory as in the Hückel method. For ethylene, which is treated as the standard double bond, there is only one occupied π-molecular orbital $(\phi_1 + \phi_2)/\sqrt{2}$ so that

$$P_{11} = P_{12} = P_{22} = Z_1 = Z_2 = 1. \tag{3.1}$$

The expression $\mathscr{E}_\pi$ then becomes

$$\mathscr{E}_\pi \text{ (ethylene)} = 2U_{11} + \tfrac{1}{2}(11 \mid G \mid 11) + 2H_{12} - \tfrac{1}{2}R_{12}^{-1}. \tag{3.2}$$

For benzene the orbitals are

$$\left.\begin{aligned}
\psi_1 &= (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)/\sqrt{6}, \\
\psi_2 &= (\phi_2 + \phi_3 - \phi_5 - \phi_6)/\sqrt{2}, \\
\psi_3 &= (\phi_1 + \tfrac{1}{2}\phi_2 - \tfrac{1}{2}\phi_3 - \phi_4 - \tfrac{1}{2}\phi_5 + \tfrac{1}{2}\phi_6)/\sqrt{3},
\end{aligned}\right\} \tag{3.3}$$

the atoms being numbered cyclically round the ring. It then follows that

$$P_{11} = 1, \quad P_{12} = \tfrac{2}{3}, \quad P_{13} = 0, \quad P_{14} = -\tfrac{1}{3}, \tag{3.4}$$

and $$\mathscr{E}_\pi \text{ (benzene)} = 6U_{11} + \tfrac{3}{2}(11 \mid G \mid 11) + 8H_{12} - \tfrac{4}{3}R_{12}^{-1} - \tfrac{1}{6}R_{14}^{-1}. \tag{3.5}$$

If it is now assumed that U_{11} may be taken as constant from molecule to molecule and if the bond lengths are assumed the same, the resonance energy of benzene is

$$\mathscr{E}_\pi \text{ (benzene)} - 3\mathscr{E}_\pi \text{ (ethylene)} = 2H_{12} + \tfrac{1}{6}R_{12}^{-1} - \tfrac{1}{6}R_{14}^{-1} = 2H_{12} + \tfrac{1}{12}R_{12}^{-1}. \tag{3.6}$$

The simpler theory gives $2H_{12}$ (usually written 2β). Eqn. (3.6) indicates that the positive electron interaction energy in the benzene molecule is greater than in one of its Kekulé structures where the electrons are paired in localized bonds.

Following Lennard-Jones [3] and others, the resonance energy (3.6) has to be compared with the difference between the energy of benzene and of one of its Kekulé structures with bond lengths equal to those in benzene (frequently called the vertical resonance energy). An experimental value for this can be obtained by adding the thermochemical resonance energy to an estimate of the energy required to distort a Kekulé structure with normal single and double bond lengths into the corresponding structure with equal bond lengths. The best available estimate obtained in this way is 78·4 kcal/mole.[18] * As R_{12} is 1·39 Å or 2·63 atomic units, $\tfrac{1}{12}R_{12}^{-1}$ is 19·8 kcal/mole, so the empirical value H_{12} is $-49·1$ kcal/mole.

If the symmetry of the molecule is insufficient to determine the coefficients $x_{i\mu}$, it is necessary either to solve the self-consistent equations (2.3), (2.17) and (2.18) exactly or to accept the orbitals calculated by the Hückel method as approximations and use these in the energy expression (2.20). In this section the latter course will be followed, but the solution of the self-consistent equations is further discussed in § 4.

The orbitals for butadiene are well known [9] and when used together with the assumption of equal bond lengths, the vertical resonance energy is found to be

$$\mathscr{E}_\pi \text{ (butadiene)} - 2\mathscr{E}_\pi \text{ (ethylene)} = 0.4722 H_{12} + 0.1 \, (R_{12}^{-1} - R_{14}^{-1}). \tag{3.7}$$

Again assuming $R_{12} = 1·39$ Å as an average, the vertical resonance energy is calculated by this formula using the same value of H_{12} as for benzene, 11·3 kcal/mole for *cis*-butadiene and 8·4 kcal/mole for *trans*-butadiene. The experimental estimate for the vertical resonance energy of the equilibrium configuration

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* Mulliken and Parr indicate that other small terms should be added to this estimate. But as the exact values are uncertain they are omitted here.

is 9·3 kcal/mole.[18]   In view of the many approximations involved, it is unlikely
that much significance can be attributed to the prediction that the *cis* isomer
will be more stable.   The physical reason behind this prediction is discussed in
the final section.   Parr and Mulliken,[7] making fewer approximations, obtain
the opposite result.   Other similar calculations of resonance energies could be
carried out, but since these are already fairly well correlated by the simpler theory,
it is unlikely that any significant results would emerge.

The molecular orbital theory expression for the ionization potential corre-
sponding to the orbital i is

$$- I_i = \sum_{\mu\nu} \bar{x}_{i\mu} F_{\mu\nu} x_{i\nu}. \tag{3.8}$$

Given the coefficients $x_{i\mu}$, these can easily be calculated from eqn. (2.17) and
(2.18).   For ethylene,

$$\left.\begin{array}{l} F_{11} = F_{22} = U_{11} + \tfrac{1}{2}(11 \mid G \mid 11), \\ F_{12} = H_{12} - \tfrac{1}{2}R_{12}^{-1}, \end{array}\right\} \tag{3.9}$$

so that the lowest ionization potential is given by

$$- I \text{(ethylene)} = U_{11} + \tfrac{1}{2}(11 \mid G \mid 11) + H_{12} - \tfrac{1}{2}R_{12}^{-1}. \tag{3.10}$$

For benzene the orbitals are given by (3.3) and

$$F_{11} = U_{11} + \tfrac{1}{2}(11 \mid G \mid 11), \quad F_{12} = H_{12} - \tfrac{1}{3}R_{12}^{-1}, \quad F_{13} = 0, \quad F_{14} = \tfrac{1}{6}R_{14}^{-1}, \tag{3.11}$$

so that

$$- I \text{(benzene)} = U_{11} + \tfrac{1}{2}(11 \mid G \mid 11) + H_{12} - \tfrac{1}{3}R_{12}^{-1} - \tfrac{1}{6}R_{14}^{-1}. \tag{3.12}$$

If the difference between bond lengths is neglected, comparison of (3·10) and
(3·12) shows that the ionization potential of benzene should be smaller than that
of ethylene by an amount $\tfrac{1}{6}(R_{12}^{-1} - R_{14}^{-1})$ or $\tfrac{1}{12}R_{12}^{-1}$.   This is 0·86 eV to be com-
pared with the experimental difference of 1·19 eV (table 1).   The calculated
difference, which does not appear at all in the Hückel theory, is independent of
choice of the empirical parameters U_{11} and H_{12}.

Corresponding expressions for the ionization potentials of other conjugated
hydrocarbons are fairly easily derived if it is assumed that the coefficients given
by the Hückel theory are adequate.   For even alternant hydrocarbons (that is
hydrocarbons with an even number of carbon atoms which can be divided into
two groups, no member of one group being directly bonded to another of the
same group) it can be shown [1] that $P_{\mu\mu} = 1$ if the coefficients are calculated by
the Hückel procedure.   It follows that

$$F_{\mu\mu} = U_{11} + \tfrac{1}{2}(11 \mid G \mid 11). \tag{3.13}$$

Since $\sum_{\mu} \bar{x}_{i\mu} x_{i\mu} = 1$, this term is common to the calculated ionization potentials
of all even alternant hydrocarbons and it is simplest to compare the differences
between the ionization potentials of the conjugated molecules and that of ethylene.
Some examples derived in this way are (assuming all carbon-carbon bonds to be
of the same length R_{12} and using the geometry of the molecule to express $R_{\mu\nu}^{-1}$
in terms of R_{12}^{-1}):

$$\left.\begin{array}{lll} cis\text{-butadiene,} & I - I \text{(ethylene)} = 0{\cdot}3820\ H_{12} - 0{\cdot}0809\ R_{12}^{-1}, \\ trans\text{-butadiene,} & I - I \text{(ethylene)} = 0{\cdot}3820\ H_{12} - 0{\cdot}1006\ R_{12}^{-1}, \\ \text{naphthalene,} & I - I \text{(ethylene)} = 0{\cdot}3820\ H_{12} - 0{\cdot}1474\ R_{12}^{-1}, \\ \text{anthracene,} & I - I \text{(ethylene)} = 0{\cdot}5858\ H_{12} - 0{\cdot}1929\ R_{12}^{-1}, \\ \text{hexatriene,} & I - I \text{(ethylene)} = 0{\cdot}5550\ H_{12} - 0{\cdot}1652\ R_{12}^{-1}. \end{array}\right\} \tag{3.14}$$

Taking $R_{12} = 2.63$ a.u. and $H_{12} = -49.1$ kcal/mole $= -2.130$ eV as before, these formulae have been used to calculate the vertical ionization potentials of the molecules using the observed value for ethylene. The results are given in the second column of table 1. The first column contains the results of a similar calculation based on the simple theory without the electron interaction terms. Here the value of H_{12} has been taken as -39.2 kcal/mole (the vertical resonance energy of benzene being $2H_{12}$ in the simple theory).

TABLE 1.—IONIZATION POTENTIALS OF CONJUGATED HYDROCARBONS (eV)

	calc. (without electron interaction)	calc. (with electron interaction)	obs.
ethylene	(10·62)	(10·62)	10·62 a
benzene	10·62	9·76	9·43 a
cis-butadiene	9·97	8·97	—
trans-butadiene	9·97	8·77	9·07 b
trans-hexatriene	9·68	7·73	8·23 c
naphthalene	9·97	8·28	8·30 d
anthracene	9·62	7·38	—

a Honig [19]; b Price and Walsh [20]; c Price and Walsh [21]; d Birge [22]. The values for butadiene and hexatriene are obtained spectroscopically and are not truly vertical. The corresponding vertical ionization potentials will be slightly larger.

The agreement between the calculated and experimental ionization potentials where the latter exist is encouraging. It is clear that the introduction of electron interaction terms leads to a marked improvement in the theory. In fact, the R_{12}^{-1} terms in (3.14) are the dominant parts and it is impossible to understand ionization potentials without them.

4. CHARGE DENSITIES AND BOND ORDERS IN THE SELF-CONSISTENT THEORY.— In the previous section we have used the molecular orbitals determined by the Hückel procedure rather than the truly self-consistent ones obtained from eqn. (2.3). As already noted, for certain highly symmetrical molecules, the two sets of coefficients will be the same but in general they will be different. In this section we shall investigate differences between the values of $P_{\mu\nu}$ calculated by the two methods. The quantity $P_{\mu\mu}$ represents the mobile electron charge density on atom μ. $P_{\mu\nu}$ for neighbouring atoms μ and ν is the molecular orbital theory bond order and has been widely used in discussions of bond lengths.[23]

The most convenient general way of solving the self-consistent equations is by a cyclic method. If the coefficients obtained by the Hückel procedure are used as a first approximation, they can be used to calculate $P_{\mu\nu}$ and $F_{\mu\nu}$ and then a further set of coefficients (the second approximation) can be obtained by direct solution of (2.3) as linear equations. The process can be repeated an indefinite number of times and should converge to the final self-consistent solution.

Coulson and Rushbrooke [1] proved that for alternant hydrocarbons $P_{\mu\mu} = 1$ for all μ if the coefficients obtained by the Hückel procedure are used. This important result, which indicates that electron charge is uniformly distributed over the atoms of an alternant hydrocarbon, still holds in the self-consistent theory based on eqn. (2.17) and (2.18). The proof of this is given in the appendix.

This result only follows from the approximations that have been made in the evaluation of the integrals. More accurate calculations on butadiene [9] indicate that without the approximations, charge migrations of the order of $0.02\,e$ may be predicted. The theorem proved in the appendix does indicate, however, that any charge migrations that do occur will arise because of finer details in the integrals and not from the general features of electron distribution as retained in the present treatment.

It is not possible to prove any general result for the bond orders $P_{\mu\nu}$ but some idea of the trend can be obtained from an examination of the non-diagonal elements

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}R_{\mu\nu}^{-1}. \tag{4.1}$$

The Hückel coefficients are obtained by assuming that all non-diagonal matrix elements between neighbours are the same. This leads to a non-uniform set of bond-orders $P_{\mu\nu}$, the larger values corresponding to those bonds with most double bond character. Since $H_{\mu\nu}$ is negative, it follows that in the first cycle of the self-consistent calculation $|F_{\mu\nu}|$ will be largest for the strongest bonds. This will tend to make these bonds even stronger in the second approximation. It is probable, therefore, that the self-consistent theory will tend to accentuate the amount of double bond fixation compared with the simple theory.

We shall illustrate the changes in bond orders by calculations on *trans*-butadiene and naphthalene. A self-consistent calculation has been carried out for *trans*-butadiene and leads to the following occupied molecular orbitals

$$\begin{aligned}
\phi_1 &= 0\cdot4246\,(\phi_1 + \phi_4) + 0\cdot5655\,(\phi_2 + \phi_3),\\
\phi_2 &= 0\cdot5655\,(\phi_1 - \phi_4) + 0\cdot4246\,(\phi_2 - \phi_3),
\end{aligned} \tag{4.2}$$

The corresponding bond orders are $P_{12} = 0\cdot9604$ and $P_{23} = 0\cdot2790$, to be compared with values of $0\cdot8944$ and $0\cdot4472$ obtained from the simple theory. In this molecule the double bond character of the central bond is considerably diminished. The best experimental value for the length of this bond ($1\cdot46$ Å) is, in fact, considerably greater than the value ($1\cdot43$ Å) corresponding to a bond order of $0\cdot4472$.

For naphthalene
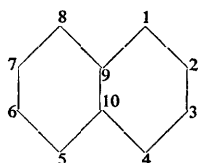
the self-consistent calculations lead to the bond orders ($P_{\mu\nu}$) given in table 2, where the values obtained by Coulson from the simple theory coefficients are also quoted.

TABLE 2.—BOND ORDERS FOR NAPHTHALENE

bond	1-2	9-10	2-3	1-9
bond order (Coulson)	1·725	1·518	1·603	1·554
bond order (self-consistent)	1·78	1·60	1·54	1·50

The naphthalene molecule is very suitable for a comparison with observed bond lengths for accurate experimental values are available.[24, 25] Previous methods for calculating the bond lengths in this molecule have been compared by Coulson, Daudel and Robertson.[26] The calculated values can be obtained from the bond orders using the Coulson [23] formula :

$$x = s - \frac{s - d}{1 + K(2 - p)/(p - 1)}, \tag{4.3}$$

where p is the bond order, s and d are the single and double bond lengths and K is a constant ($0\cdot765$). The results using the Coulson and self-consistent bond orders are given in the first two rows of table 3.

TABLE 3.—BOND LENGTHS FOR NAPHTHALENE (Å)

bond	1-2	9-10	2-3	1-9
calc. (Coulson)	1·384	1·424	1·406	1·416
calc. (self-consistent theory)	1·376	1·408	1·420	1·428
calc. (self-consistent theory with adjusted mean)	1·366	1·398	1·410	1·418
obs.	1·365	1·393	1·404	1·424

The lengths calculated by the method of this paper are in rather better agreement with experiment than are Coulson's values. The correct order of lengths

is now predicted and the central bond is no longer anomalous. The calculated values are all too large, but this may well be due to the inadequacy of the formula (4.3). If the calculated lengths are all reduced by $0·010$ Å to give the correct mean, the values shown in the third row of table 3 are obtained. These are very well correlated with the experimental values.

5. THE CORRELATION OF ELECTRONS IN UNSATURATED HYDROCARBONS.—In order to appreciate the physical significance of the electron interaction terms appearing in the expressions for the resonance energies and ionization potentials, it is useful to examine some details of the electron distribution functions. These give the probabilities of relative distributions of electrons in multidimensional space and are obtained by suitable integration of the complete function $\overline{\Psi}\Psi$ The total electron-electron interaction energy can be calculated directly from the two-electron distribution function (in six-dimensional space). This function can be simplified in ways analogous to the approximations of § 2 and leads to some insight into the origin of the interelectronic terms.

Considering the π-electrons separately, let us write $P^{\alpha\alpha}$ (1, 2) $dv_1 dv_2$ for the probability of there being two electrons of α spin simultaneously in volume elements dv_1 and dv_2 and define $P^{\alpha\beta}$ and $P^{\beta\beta}$ similarly. Then for the ground state in which there are N doubly occupied molecular orbitals $\psi_1 \ldots \psi_N$ it can be shown [11] that the single determinant wave function leads to expressions

$$P^{\alpha\alpha} (1, 2) = P^{\beta\beta} (1, 2) = \sum_{ij}^{N} \{[\psi_i(1)]^2 [\psi_j(2)]^2 - \psi_i(1)\psi_j(1)\psi_i(2)\psi_j(2)\}, \quad (5.1)$$

$$P^{\alpha\beta} (1, 2) = \sum_{ij}^{N} [\psi_i(1)]^2 [\psi_j(2)]^2. \quad (5.2)$$

If we now write these expressions in terms of atomic orbitals and omit all terms of the type $\phi_\mu(1)\phi_\nu(1)$, $(\mu \neq \nu)$, we obtain

$$P^{\alpha\alpha} (1, 2) = P^{\beta\beta} (1, 2) = \tfrac{1}{4} \sum_{\lambda\mu} [P_{\lambda\lambda}P_{\mu\mu} - P_{\mu\lambda}^2][\phi_\lambda(1)]^2 [\phi_\mu(2)]^2, \quad (5.3)$$

$$P^{\alpha\beta} (1, 2) = \tfrac{1}{4} \sum_{\lambda\mu} P_{\lambda\lambda}P_{\mu\mu}[\phi_\lambda(1)]^2 [\phi_\mu(2)]^2. \quad (5.4)$$

The omission of terms of the type $\phi_\mu\phi_\nu$ is strictly analogous to approximations B and C of the energy calculations.

The probability distributions (5.3) and (5.4) can now be interpreted with the assumption that different atomic orbitals do not significantly overlap. We shall say that electron 1 is at the atom λ if $\phi_\lambda(1) \neq 0$ and $\phi_\mu(1) = 0$ for all other μ. Once again this is an oversimplification of the real picture, but it does enable general features of the electron distribution to be examined. It is clear from (5.2) and (5.4) that $P^{\alpha\beta}$ is the product of a function of electron 1 with a function of electron 2 so that the two sets of electrons are uncorrelated with one another. Eqn. (5.3) enables us to find the probability of an α-electron being found on atom μ, given that there is one on atom λ. For alternant hydrocarbons for which $P_{\lambda\lambda} = P_{\mu\mu} = 1$, this is

$$\tfrac{1}{2}(1 - P_{\lambda\mu}^2), \quad (5.5)$$

whereas the corresponding probability of finding a β-electron is $\tfrac{1}{2}$.

The results are conveniently illustrated by simple diagrams of the type shown in fig. 1 for ethylene.
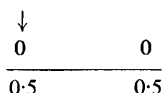

FIG. 1.— Correlation diagram for ethylene.

The figures above the line give the probability of there being another α-electron at the atom given that there is one at the position of the arrow. The figures below the line give the corresponding probabilities for a β-electron. The interaction between the α-electron and 0·5 β-electrons on the same atom gives rise to the term $\frac{1}{2}(11 \mid G \mid 11)$ in the energy expression (3.2) while its interaction with the σ-core of the other atom (screened by 0·5 β-electrons) gives $- \frac{1}{2}R_{12}^{-1}$.

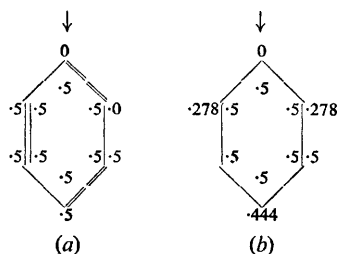Corresponding diagrams for benzene are given in fig. 2 (the β-probabilities being written inside the ring). The diagram for one of the Kekulé structures is shown in (a) (using three localized ethylene orbitals) and is to be compared with (b) derived from the molecular orbitals (3.3). Fig. 2(b) shows that if there is an α-electron at position 1, then according to the single· determinant wave function, there is a deficiency of α-electrons at the *ortho* and *para* positions. In the Kekulé structure, however, this same electron deficiency is concentrated at one of the *ortho* positions. The $\frac{1}{12} R_{12}^{-1}$ term in the expression for the resonance energy of benzene can be obtained by counting the interactions of α-electrons with all partially screened σ-cores in the two cases.

FIG. 2.—Correlation diagrams for benzene.

As a third example we may consider butadiene. The correlation diagrams based on the orbitals obtained by the Hückel procedure are shown in fig. 3. It is seen that part of the stabilization energy arises from the interaction of an α-electron in position 1 with an incompletely screened σ-core at position 4. The theory of § 3 predicts this *cis* isomer to be more stable because the 1 and 4 positions are then closer. This extra stability, however, may be more than offset by other factors such as repulsion between the hydrogen atoms.

FIG. 3.—Correlation diagrams for butadiene.

· The author is indebted to Dr. G. G. Hall and Prof. C. A. Coulson for valuable discussion and criticism.

APPENDIX.—Here we shall prove the results $P_{\mu\mu} = 1$ for the cyclic process of solving the self-consistent equations for alternants described in § 4. The proof follows an inductive method. Let $x_{i\mu}^{(n)}$ be the nth approximation to the self-consistent coefficients $x_{i\mu}$ (obtained after $(n-1)$ cycles), $E_i^{(n)}$ being the corresponding energy. $x_{i\mu}^{(0)}$ are the coefficients obtained by the Hückel procedure (i.e. solving (2.3) with $S_{\mu\nu} = \delta_{\mu\nu}$, all $F_{\mu\mu}$ identical, $F_{\mu\nu} = \beta$ if μ and ν are bonded and zero otherwise). Define

$$P_{\mu\nu}^{(n)} = 2 \sum_i \bar{x}_{i\mu}^{(n)} x_{i\nu}^{(n)}, \qquad (6\cdot1)$$

and let $F_{\mu\nu}^{(n)}$ be the corresponding matrix element calculated from (2·17) or (2·18). Divide the carbon centres into two classes (" starred " and " unstarred ") so that each starred atom is bonded to only unstarred atoms and vice versa. We can then establish the following theorem which is a generalization of that proved by Coulson and Rushbrooke.[1]

Theorem.—If $H_{\mu\nu} = 0$ unless $\mu = \nu$ or μ and ν are neighbouring atoms, then for even alternant hydrocarbons it follows that $P_{\lambda\sigma}^{(n)} = \delta_{\lambda\sigma}$ for all n if λ and σ are both starred or both unstarred.

Proof.—Assume the result for $n - 1$ as an inductive hypothesis. The coefficients $x_{i\mu}^{(n)}$ and the energy levels $E_i^{(n)}$ are then determined by the linear equations

$$[F_{\mu\mu}^{(n-1)} - E_i^{(n)}]x_{i\mu}^{(n)} + \sum_{\nu(\neq\mu)} F_{\mu\nu}^{(n-1)}x_{i\nu}^{(n)} = 0, \qquad (6.2)$$

where, from the inductive hypothesis and eqn. (2.17) and (2.18)

$$F_{\mu\nu}^{(n-1)} = \{U_{11} + \tfrac{1}{2}(11 \mid G \mid 11)\}\delta_{\mu\nu}, \qquad (6.3)$$

if μ and ν are both starred or both unstarred. It then follows from (6.2) that from the coefficients $x_{i\mu}^{(n)}$ of one orbital with energy $E_i^{(n)}$ the coefficients of another corresponding to an energy

$$2F_{\mu\mu}^{(n-1)} - E_i^{(n)}$$

can be obtained by changing the sign of the coefficients of the starred atomic orbitals. The molecular orbitals ψ_i can therefore be paired in this way, to each occupied orbital $\psi_1 \ldots \psi_N$ corresponding one of the unoccupied orbitals $\psi_{N+1}, \ldots \psi_{2N}$, $2N$ being the number of carbon centres. If i and j are orbitals corresponding in this way, it follows that, if μ and ν are both starred or both unstarred, then

$$\bar{x}_{i\mu}^{(n)}x_{i\nu}^{(n)} = \bar{x}_{j\mu}^{(n)}x_{j\nu}^{(n)} \qquad (6.4)$$

Hence
$$\sum_{i=N}^{N} \bar{x}_{i\mu}^{(n)}x_{i\nu}^{(n)} = \sum_{i=N+1}^{2N} \bar{x}_{i\mu}^{(n)}x_{i\nu}^{(n)}. \qquad (6.5)$$

But from the unitary property of the complex matrix $x_{i\mu}$

$$\sum_{i=1}^{2N} \bar{x}_{i\mu}^{(n)}\bar{x}_{i\nu}^{(n)} = \delta_{\mu\nu}. \qquad (6.6)$$

It follows immediately that $P_{\mu\nu}^{(n)} = \delta_{\mu\nu}$.

The proof for $n = 1$ follows identical lines, so the theorem is established. If convergence is assumed the same result must apply to the limiting self-consistent solution.

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