ELECTRONEGATIVITY THEORY

by

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PART I

PREFACE

Chemists have long been interested in the electronic effects which influence the structural characteristics, stabilities, and reactivities of molecules. In principle, these electronic effects can be directly calculated by solving the Schrodinger wave equation for the stationary states of the molecules concerned. Since exact solutions of the wave equation cannot be obtained as yet for any but the smallest molecules, the main interest in modern quantum chemistry lies in the development of methods by which approximate, but realistic, wave functions and eigenvalues can be calculated for isolated molecules. Both wave-mechanical principles and chemical "intuition" are used in the development of the simpler approximate methods.

In this thesis, the use of the chemists' concept of ELECTRONEGATIVITY in approximate quantum-chemical techniques is explored, and electronegativity-based methods are used to estimate the distribution of electron density in the ground states of isolated molecules. In the procedures to be discussed, the one-electron wave functions of a molecule are expanded as a linear combination of atomic orbitals, and the electron distributions are discussed in terms of the "electron density" (or "charge density") associated with orbitals centred on the atoms. Since it will be assumed that the total electron density in a molecule can be "assigned" to the various atomic orbitals, the electron density of an atom can be obtained by a summation over the charge densities of its atomic orbitals. In some instances, it is simpler to express the electron density of an atom in terms of its "net" or "partial" charge; that is, the electron density of an atom in a molecule relative to the electron density for the isolated, neutral atom. For non-conjugated molecules, the electron densities in the chemical bonds are discussed by the "ionic character" or "polarity" of a bond; these terms denote the extent of electron density transfer from one atom to the other in the bond.

Part I of this thesis is concerned with the calculation of charge distributions in saturated molecules by "electronegativity equalization" methods. In Part II, the concept of electronegativity is applied to some standard quantum-chemical methods which deal with conjugated pi electron networks.

PART I

THE PRINCIPLE OF ELECTRONEGATIVITY EQUALIZATION AND CHARGE DISTRIBUTIONS IN SATURATED MOLECULES

I. 1 HISTORICAL BACKGROUND

Atomic electronegativity is a concept familiar to most chemists. It was developed to systematize many empirical observations related to the electronic effects of atoms in molecules. Pauling provided the first general definition of the property of electronegativity, and described a practical procedure for its evaluation (1,2,3). He defined electronegativity as "the power of an atom in a molecule to attract electrons to itself" (3), and proposed that atomic electronegativities could be evaluated from the dissociation energies of chemical bonds (1,2,3). The energy of dissociation, D_{LM} of a purely covalent bond between two atoms, L and M, was postulated to be equal to the mean of the dissociation energies of the homonuclear diatomic molecules LL and MM. Although the arithmetic mean was originally used by Pauling, he found that it was sometimes necessary to use the geometric mean (with the alkali hydrides for example) in order to obtain realistic covalent dissociation energies (3). For each bond L-M, a quantity termed the "extra ionic resonance energy" Δ_{LM}, was defined as:

$$\Delta_{LM} = D_{LM} - \text{Mean} \quad (D_{LL}, \; D_{MM}) . \tag{1}$$

By analysing the variations in the calculated values of Δ_{LM} for a large number of bonds, it was established that the function $(\Delta_{LM})^{1/2}$ could be represented as the difference between terms characteristic of the two atoms L and M (3). These characteristic atom terms were assumed to be related to the electronegativities, X, of the atoms (3) by

$$(\Delta_{LM})^{1/2} = K \left| X_L - X_M \right| \tag{2}$$

where K is a constant.

Only the relative electronegativities of atoms can be calculated by this equation. Mulliken (4) was able to establish some theoretical justification for equation 2; his analysis will be discussed later in this thesis.

Shortly after Pauling proposed his scheme, Mulliken (5) developed an alternative definition of electronegativity. He considered the three structures, I, II, and III, included in the simple valence-bond wave function for a diatomic molecule LM:

$$\underset{\mathrm{I}}{L^{+}M^{-}} \qquad \underset{\mathrm{II}}{L-M} \qquad \underset{\mathrm{III}}{L^{-}M^{+}} \quad .$$

Mulliken argued that the two ionic structures, I and III, would have equal weights in the wave function containing I and III and the completely covalent structure II, only under the condition that:

$$I_L - A_M = I_M - A_L \tag{3}$$

that is

$$I_L + A_L = I_M + A_M \tag{4}$$

where I_L and I_M are the ionization potentials of the atoms L and M, and A_L and A_M are the corresponding electron affinities. Under such a condition, the structures I and III occur in the wave function with equal weight, and the net polarity of the L-M bond is zero. The electronegativities of the atoms L and M must, therefore, be identical in such situations. From this analysis, Mulliken suggested that the term $(I_L + A_L)$ is a measure of the electronegativity of atom L, and gave the following definition for electronegativity (5):

$$X_L = \frac{I_L + A_L}{2} \quad . \tag{5}$$

The 1/2 factor was included so that X_L represents the average binding energy of an electron in the vicinity of atom L. A more rigorous derivation of equation 5 was later presented by Mulliken (6) and by Moffitt (7). Since the ionization potential and electron affinity required in equation 5 are those associated with the atomic orbital forming the bond, "valence state" (5,6) energies must be used in calculating I_L and A_L. Since the valence-state ionization potentials and electron affinities are dependent on the nature of the atomic orbital considered, the term "orbital electronegativity of an atom" is used for the Mulliken electronegativities (8). An extensive set of Mulliken electronegativity values has been given by Skinner and Pritchard (9) and by Hinze and Jaffe (10,11,12). The latter authors established that the electronegativity of an atomic orbital is linearly dependent on its s hybridization character (10).

Many other definitions of electronegativity, and schemes by which electronegativity values can be computed, have been given. In some cases, these methods proceed by assigning a physical meaning to electronegativity and evaluating it on this basis, whereas other scales are constructed by establishing a correlation between some physical or chemical property of atoms or molecules and the Pauling or Mulliken electronegativity values. Many of these techniques have been discussed in a review by Pritchard and Skinner (13).

One electronegativity definition of the first type discussed above is that given by Sanderson (14,15). He defined the "stability ratio," S, of an atom in terms of its electron density, D, and the electron density $D^{\star}$ of the hypothetical inert gas element which is isoelectronic with the atom:

$$S = \frac{D}{D^{\star}} \quad . \tag{6}$$

The electron densities are calculated from Z, the number of electrons associated with the atom, and R, the covalent radius of the atom (15):

$$D = \frac{3\ Z}{4\ \pi\ R^3} \quad . \tag{7}$$

The stability ratios for neutral atoms were found to correlate with the Pauling electronegativities of the atoms (15):

$$X^{1/2} = 0.21\ S + 0.77 \quad . \tag{8}$$

The main use of stability ratio electronegativities has been in the calculation of approximate charge density distributions for molecules.

Other electronegativity scales have also been used to calculate electron distributions. Pauling established a correlation between the difference in electronegativity of the atoms L and M forming a single bond, and the ionic character, i_{LM}, of the bond which was assessed from the molecular dipole moment (3):

$$i_{LM} = 1 - \exp \left[- \frac{1}{4} (X_L - X_M)^2 \right] \quad . \tag{9}$$

Hannay and Smyth (16) improved the correlation fit for a series of diatomic molecules by using the formula

$$i_{LM} = 0.16 \left| X_L - X_M \right| + 0.035 \left| X_L - X_M \right|^2 \quad . \tag{10}$$

Several correlations of the ionic character of single bonds with the electronegativity difference of the atoms forming the bonds have been made by the use of nuclear quadrupole coupling constants for halide molecules. Gordy (17) assumed that the bonding orbitals used by the halogen atoms in forming single bonds were pure p, and established the relations

$$i_{LM} = 0.5 \left| X_L - X_M \right| \quad \text{for} \quad \left| X_L - X_M \right| < 2 \tag{11}$$

and

$$i_{LM} = 1.0 \qquad \text{for } |X_L - X_M| \geq 2 \quad . \tag{12}$$

Townes and Dailey (18) proposed slightly different relations to fit the same data. Wilmshurst (19), and Polansky and Derflinger (20), have derived the ionic character equation:

$$i_{LM} = \frac{|X_L - X_M|}{X_L + X_M} \quad . \tag{13}$$

Wilmshurst has used this expression to analyze quadrupole coupling constants (19).

Sanderson (15) developed an approach to the calculation of molecular charge density distributions by using his stability ratio definition of electronegativity. He noted that since the effective nuclear charge of an atom which acts upon the valence electrons decreases as the total charge density associated with the atom increases, the ability of the atom to attract electrons, its electronegativity, must also decrease in the same manner. The electronegativity of an atom is, therefore, a function of the amount of electronic charge density on the atom. Although the functional dependence of electronegativity on atomic charge had been noted previously (21), Sanderson was the first to fully exploit the idea in the calculation of charge distributions. He advanced the theory that charge transfer would occur between the atoms in a molecule until the electronegativities of all the atoms were identical; Sanderson called this the Principle of Electronegativity Equalization (15). The intermediate value of electronegativity for the atoms in molecules was calculated by taking the geometric mean of the stability ratios of the neutral atoms. By this technique, the partial charges of atoms in a large number of molecules were computed and correlated with many molecular properties (15).

The idea that atom electronegativities were direct functions of the atomic charges was extended by Pritchard and Sumner (22), and more fully by Iczkowski and Margrave (23). The latter authors decided that, since Pauling's verbal definition implied that electronegativity is a potential, the electronegativity function could be defined as the first derivative of the energy of an atom with respect to the atom charge density. Iczkowski and Margrave expressed the total energy, E_L, of an atom as a function of its <u>net</u> charge, Q_L:

$$E_L\ (Q_L) = a\ Q_L + b\ Q_L^{\ 2} + c\ Q_L^{\ 3} + \ldots \tag{14}$$

The electronegativity of the atom was then defined as

$$X_L\ (Q_L) = -\frac{d\ (E_L)}{d\ (Q_L)} = -\ (a + 2\ b\ Q_L + 3\ c\ Q_L^{\ 2} + \ldots)\ . \tag{15}$$

The parameters a, b, c, . . . were calculated by fitting the experimental ionization potentials, for removing the valence-shell electrons of the atom, to equation 14. The charge densities in a few simple molecules were calculated (23) by using this electronegativity function (equation 15) together with the Principle of Electronegativity Equalization.

Ferreira (24) discussed a similar scheme in which the electronegativity equalization concept was used. The electronegativity was assumed to be linearly dependent on the net charge of the atom. The parameters of the electronegativity function were evaluated from the screening constants for the atoms (24). Ferreira estimated the dipole moments, force constants and dissociation energies of several simple molecules by this technique (24).

Jorgensen (25,26) defined the Differential Ionization Energy, DI, as the first derivative of the energy of an atom, E_L, with respect to the net atomic charge, Q_L:

$$(DI)_L = \frac{d\,(E_L)}{d\,(Q_L)} = a_o + a_1 Q_L + a_2 Q_L^2 + \ldots \tag{16}$$

This function, resembling the electronegativity definition of Iczkowski and Margrave, was also used to estimate the charge transfer in some small molecules by means of the electronegativity equalization concept (26). It was noted that the ionic characters calculated by this procedure for bonds which are usually considered to be almost completely ionic were much smaller than expected. To overcome this deficiency, Jorgensen extended the definition of the differential ionization energy to include terms for the energy of attraction of oppositely-charged atoms (26).

Hinze, Whitehead and Jaffe (8) proposed an electronegativity function which is similar to that of Iczkowski and Margrave, but which emphasizes the atomic <u>orbital</u> nature of electronegativity. It was assumed that

1) the charge density associated with an atomic orbital can have both integral and non-integral values,

2) the energy of an atom can be expressed as a continuous and differentiable function of the charge density associated with any of its atomic orbitals, and

3) the variation in the energy, E_L, of an atom L with changes in the charge density, n_j, of one of its atomic orbitals, ϕ_j, can be adequately expressed by the use of a three term series in n_j :

$$E_L\,(n_j) = a_j + b_j n_j + c_j n_j^2 \,. \tag{17}$$

The constants a_j, b_j, and c_j for each atomic orbital were calculated using the three estimated valence-state energies (27), for n_j = 0, 1 and 2. The electronegativity of an atomic ORBITAL of an atom was then defined as the first derivative of the atom energy with respect to the charge density of that orbital (8):

$$X_j\ (n_j) = \frac{d\ (E_L)}{d\ (n_j)} = b_j + 2\ c_j\ n_j\ . \tag{18}$$

The parameters b_j and c_j for an atomic orbital are related to the ionization potential, I_j, of the orbital, and A_j, its electron affinity (8,28) by:

$$b_j = \frac{3\ I_j - A_j}{2} \tag{19}$$

and

$$c_j = \frac{A_j - I_j}{2}\ . \tag{20}$$

The orbital electronegativities of unoccupied, singly-occupied and doubly-occupied orbitals were then defined:

$$X_j\ (n_j = 0) = b_j = \frac{1}{2}\ (3\ I_j - A_j) \tag{21}$$

$$X_j\ (n_j = 1) = b_j + 2\ c_j = \frac{1}{2}\ (I_j + A_j) \tag{22}$$

and

$$X_j\ (n_j = 2) = b_j + 4\ c_j = \frac{1}{2}\ (3\ A_j - I_j)\ . \tag{23}$$

The electronegativity of a singly-occupied orbital, $\frac{1}{2}\ (I_j + A_j)$, is identical to the Mulliken definition, equation 5.

Hinze et al. (8) stated that their electronegativity definition was in the form of a POTENTIAL, and that since the potential seen by the electrons which form the bond between atomic orbitals ϕ_j and ϕ_k must be equal, then the electronegativities of these two orbitals must be identical in the bond:

$$X_j\ (n_j) = X_k\ (n_k)\ . \tag{24}$$

For a two-centre, two-electron bond in which each orbital initially contributes one electron, the condition of orbital electronegativity equalization is sufficient to determine the ionic character, i_{jk}, in the bond (8,28):

$$i_{jk} = \frac{X_k(1) - X_j(1)}{2(c_j + c_k)} \qquad (25)$$

where $$i_{jk} = n_j - 1 \quad . \qquad (26)$$

Since Hinze et al. were able to calculate I_j and A_j values for orbitals of atoms in which the other valence-shell atomic orbitals formed partially ionic bonds, the electronegativities of GROUPS of atoms could also be assessed. For example, the electronegativity of the methyl group, H_3C, was determined by first calculating the ionic characters of the C-H bonds by equation 25, then determining the ionization potential and electron affinity of the singly-occupied, non-bonding valence-shell orbital of the carbon atom, and hence the electronegativity of this orbital by equation 22. By this technique, the electronegativities of a large number of organic functional groups were determined (8). Huheey (29) has used an approximate form of the method of Hinze et al. to calculate electronegativity functions for 99 common inorganic and organic groups.

Attempts have been made to establish values for the effective electronegativities of groups from various types of experimental data for molecules (13). For example, Shoolery et al. (30,31) used the proton nuclear magnetic resonance chemical shift of the hydrogen atoms in the general type of molecule CH_3CH_2R to determine the electronegativities of groups R. By analyzing the infrared stretching frequencies of the carbonyl group in a number of molecules, Kagarise (32) attempted to find a relation between the effective electronegativity of a group and the electronegativities of the atoms which form the group. For a substituted methyl group, -CXYZ, he was able to show empirically that the relation

$$X_{-CXYZ} = \frac{1}{2} X_C + \frac{1}{6} (X_X + X_Y + X_Z) \qquad (27)$$

held quite well (32).

Whitehead and Jaffe (33) combined the group electronegativity formula of Kagarise with the electronegativity values of Hinze et al. (8,10), the ionic character expression of Gordy (equation 11) and some <u>nuclear quadrupole coupling constants</u> to calculate the charge distributions and halogen atom bonding orbital hybridizations in a number of group III, IV and V halides. The ionic character formula of Gordy was used since it was believed to approximate closely to equation 25. In these calculations, the hybridization of the central atoms in the halides was estimated using the experimental bond angles in these molecules (33). Gilson (34) repeated some of the calculations by estimating the carbon atom bonding orbital hybridizations from $^{13}C - {}^{1}H$ N.M.R. coupling constants rather than the bond angles.

The concept of electronegativity equalization in molecules has been discussed in terms of molecular orbital theory by Klopman (35,36). He noted that a molecule will achieve maximum stability when the potentials around each atom in each atomic orbital are equalized. Klopman defined this potential as the first derivative of the energy of a <u>molecule</u> with respect to the atomic orbital charge density. Hence for two orbitals ϕ_j and ϕ_k in a molecule,

$$\frac{\partial (E_{\text{molecule}})}{\partial (n_j^i)} = \frac{\partial (E_{\text{molecule}})}{\partial (n_k^i)} \qquad (28)$$

where n_j^i and n_k^i are the charge densities due to electron i in orbitals ϕ_j and ϕ_k (36). Such orbitals were called EQUIPOTENTIAL ORBITALS, and Klopman noted that equation 28 agrees with the principle of electronegativity equalization.

Klopman's use of the electronegativity equalization concept differs from that of Hinze et al.(8) in several ways. He has insisted (35,36) that the potential around each atom in each orbital must be calculated by using a function which represents the total molecular energy, whereas Hinze et al. defined this potential by reference to the energy function for the atom concerned(8). He also objected to Hinze, Whitehead and Jaffe's use of the same function relating atom energy with orbital charge density for situations in which the orbital is partially occupied by one electron, and for situations in which it is partially occupied by two electrons (35). Klopman developed alternative atom energy schemes, and incorporated these into a molecular orbital method based upon the concept of equipotential orbitals (35,36,37,38). In this method, the "neutral electronegativity" of an atomic orbital appears as a part of the diagonal elements of the Hamiltonian matrix (35,36,37).

Since 1963, the Hinze, Whitehead and Jaffe method of electronegativity equalization (8) has been used successfully by several workers to estimate group electronegativities and to establish correlations of these electronegativities with molecular properties (39,40,41). The function relating atom energy to orbital charge has also been used as a basis for empirical calculation schemes in which the molecular energy function includes atom energies, electrostatic attraction energies between partially charged atoms (42), and covalent bonding energies (43,44,45). Until now, however, there have been no attempts to assess the validity of the molecular charge density distributions which can be easily calculated using the Hinze, Whitehead and Jaffe method.

I. 2 THE THEORY OF ELECTRONEGATIVITY EQUALIZATION

I. 2. A INTRODUCTION

The wave function, Φ, for a molecular system is a solution of the Schrodinger equation,

$$\overset{o}{H}\,\Phi = -\frac{\hbar}{i}\frac{\partial\Phi}{\partial t} \qquad (29)$$

where $\overset{o}{H}$ is the HAMILTONIAN OPERATOR for the molecule, t represents time,

$\hbar = \frac{h}{2\pi}$ where h is Planck's constant, and

$$i = (-1)^{1/2} .$$

Since, in the systems to be considered the potential energy is not dependent upon time, Φ may be written as a product of two wave functions, one of which, Φ_C, is dependent upon the space co-ordinates, and the second of which, Φ_T, is dependent upon time (46):

$$\Phi = \Phi_C\ \Phi_T \quad . \qquad (30)$$

When this product is substituted for Φ in equation 29, the Schrodinger equation is separable into two wave equations (46). One such wave equation represents the behaviour of the molecular system with time. This relationship is not of primary interest in this study, and attention will be focused on the second wave equation, from which the molecular energy, ϵ, may be obtained:

$$\overset{o}{H}\,\Phi_C = \epsilon\ \Phi_C \quad . \qquad (31)$$

The Hamiltonian operator, $\overset{o}{H}$, may be expressed in terms of Laplacian operators, ∇^2_α and ∇^2_a, for the nuclei, α, and the electrons, a, of the molecule, and in terms of the potential energy, V. The potential energy of the molecule is given by the total Coulomb electrostatic interaction between all pairs of charged particles. In Cartesian co-ordinates, the Laplacian operator is defined by:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad . \qquad (32)$$

If M_α represents the mass of nucleus α, and m_o is the electron mass, then the Hamiltonian is

$$\overset{o}{H} = - \sum_{\alpha=1}^{\beta} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 - \sum_{a=1}^{b} \frac{h^2}{2\,m_o} \nabla_a^2 + V \quad . \qquad (33)$$

The summation from $\alpha = 1$ to $\alpha = \beta$ is over all the nuclei, and that from $a = 1$ to $a = b$ is over all the electrons.

When molecules are considered quantum-mechanically, the BORN-OPPENHEIMER APPROXIMATION is usually used to simplify the mathematical treatment of the wave equation (47). The time-independent wave equation is then solved first by assuming that the positions of the nuclei are fixed. Under this assumption, the electronic wave equation is (47):

$$\left[- \sum_{a=1}^{b} \frac{\hbar^2}{2m_o} \nabla_a^2 + V \right] \Psi_e = E\Psi_e \quad , \qquad (34)$$

Both the ELECTRONIC WAVE FUNCTION, Ψ_e, and the ELECTRONIC ENERGY, E, are dependent upon the positions of the nuclei. The wave equation for the nuclear motion is

$$\left[- \sum_{\alpha=1}^{\beta} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + E \right] \Psi_n = \mathcal{E}\,\Psi_n \quad . \qquad (35)$$

In this wave equation, Ψ_n describes the motion of the nuclei, and E is used as the potential energy function (47).

The essence of the Born-Oppenheimer approximation is that the energy $\mathcal{E}$ found by solving equation 35 is a good approximation to the energy $\mathcal{E}$ of the original Schrodinger equation, and that the product of the wave functions Ψ_e and Ψ_n is a good approximation to the actual wave function Φ_C:

$$\Phi_C \approx \Psi_e \Psi_n \quad . \tag{36}$$

The Born-Oppenheimer approximation works quite well for isolated molecular systems, since the nuclear motion is much slower than the motion of the electrons (47).

Since, for all but the smallest of molecules, it is extremely difficult to solve the wave equation exactly even when the simplifying Born-Oppenheimer approximation is used, approximate methods are usually employed to estimate Ψ_e and $\mathcal{E}$. One such approximate method is that of MOLECULAR ORBITALS. In this technique, a one-electron wave function, χ_i^a, called a MOLECULAR SPIN ORBITAL (MSO), is assigned to each electron a = 1, . . . b in the molecule (48). Each MSO, in turn, is the product of a space wave function, ψ_i^a, called a MOLECULAR ORBITAL (MO), and an electron spin wave function, η_i^a:

$$\chi_i^a = \psi_i^a(x,y,z)\ \eta_i^a(s) \tag{37}$$

where s denotes the spin co-ordinates of the electron.

The electronic wave function, Ψ_e, is an antisymmetrized product of the MSOs (48):

$$\Psi_e = \frac{1}{\sqrt{b\,!}} \begin{vmatrix} \chi_1^1 & \chi_2^1 & \cdot & \cdot & \cdot & \chi_N^1 \\ \chi_1^2 & \chi_2^2 & \cdot & \cdot & \cdot & \chi_N^2 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \chi_1^N & \cdot & \cdot & \cdot & \cdot & \chi_N^N \end{vmatrix} \tag{38}$$

where b is the number of electrons in the molecule. A linear combination of determinantal products is used to approximate Ψ_e. Each product represents a different configuration of occupied molecular orbitals in the molecule. The ground state of a diamagnetic molecule is usually well represented, however, by the single configuration in which the b electrons occupy the b molecular spin orbitals of greatest energetic stability (48). In this study, no interaction of this configuration with excited states is considered.

The molecular orbitals ψ_i are usually obtained by expanding ψ_i as a LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO) ϕ_u:

$$\psi_i = \sum_{u=1}^{v} c_{iu} \phi_u \tag{39}$$

where the coefficients, c_{iu}, are found by minimization of the electronic energy with respect to these coefficients. In general, the accuracy of the MOs increases as more members of the complete basis set of atomic orbitals are used, although in the simpler MO methods, only valence-shell and inner-shell atomic orbitals are considered in the expansion.

In all subsequent discussions, the usual practice of terming both "molecular spin orbitals" and "molecular orbitals" as, simply, "molecular orbitals" will be adopted.

I. 2. B MOLECULAR ORBITAL THEORY OF ELECTRONEGATIVITY EQUALIZATION

Klopman (36) has noted that the minimization of electronic energy in a molecule leads to the following condition for two atomic orbitals ϕ_u and ϕ_v:

$$\frac{\partial E}{\partial n_u^a} = \frac{\partial E}{\partial n_v^a} \quad . \tag{40}$$

In this equation, n_u^a represents the contribution of electron a to the total electronic charge density, n_u, associated with atomic orbital ϕ_u in the molecule. Klopman has suggested (36) that if the orbital electronegativities are identified with the terms $\frac{\partial E}{\partial n_u^a}$, then equation 40 is equivalent to the principle of electronegativity equalization. Unfortunately, it is difficult to formulate a general electronegativity function on this basis, since the relationship between the electronic energy and each orbital charge density is quite complicated.

In order to formulate an electronegativity function which is convenient for calculations, and which is derived from atomic properties, it is necessary to simplify the expression for the molecular energy. A convenient definition of electronegativity can be derived if it is possible to expand[☆] the molecular energy, E, of a molecule as a sum of terms which are characteristic of the component atoms of the molecule:

$$E = \sum_{L=1}^{M} E_L \, (n_u, \ldots \, n_v) \quad . \tag{41}$$

In this expansion, each term E_L is dependent upon the orbital charge densities

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[☆] This expansion is analyzed in Part I. 2. D.

$n_u , \ldots n_v$ of only the atomic orbitals $\phi_u , \ldots \phi_v$ associated with the atom L. If the expansion in equation 41 can be made, it is possible to define an ORBITAL ELECTRONEGATIVITY function, X_u, for each atomic orbital ϕ_u:

$$X_u(n_u) = \left(\frac{\partial (E_L\ (n_u, \ldots n_v)\ )}{\partial\ (n_u)} \right)_{\ldots n_u} . \qquad (42)$$

The electronegativity equalization conditions which result, if the expansion in equation 41 and the definition of equation 42 are used in a molecular orbital method, have been discussed recently by Baird, Sichel, and Whitehead (49). These authors analyzed the electronegativity equalization conditions by using the variables n_{ui}, the contribution to the orbital charge density n_u from the molecular orbital ψ_i , and N_i , the total charge density associated with the molecular orbital ψ_i. Hence,

$$n_u = \sum_{i=1}^{i} n_{ui} \qquad \text{for each AO } \phi_u , \qquad (43)$$

and

$$N_i = \sum_{u=1}^{v} n_{ui} \qquad \text{for each MO } \psi_i , \qquad (44)$$

where it has been assumed in equation 44 that all of the charge density in a molecule has been completely divided between the atoms. The total molecular energy, E, may be minimized with respect to each n_{ui} (which is equivalent to minimization with respect to the coefficients of the atomic orbitals in the occupied molecular orbitals) subject to the restraints in equations 43 and 44 by defining a new function F:

$$F = E + \sum_{i=1}^{i} \left[\lambda_i\ (N_i - \sum_{u=1}^{v} n_{ui}) \right] , \qquad (45)$$

The parameters λ_i are undetermined Lagrangian multipliers. If F is minimized with respect to each n_{ui}, then for a given n_{ui} the following condition results:

$$0 = \left(\frac{\partial F}{\partial n_{ui}}\right)_{n_{vj \neq ui}} = \left(\frac{\partial E}{\partial n_{ui}}\right)_{n_{vj \neq ui}} - \lambda_i$$

$$= \left(\frac{\partial E}{\partial n_u}\right)_{n_{v \neq u}} \left(\frac{\partial n_u}{\partial n_{ui}}\right)_{n_{vj \neq ui}} - \lambda_i \quad . \tag{46}$$

From the expression for n_u in equation 43, then

$$\left(\frac{\partial n_u}{\partial n_{ui}}\right)_{n_{vj \neq ui}} = 1 \tag{47}$$

and from the expansion of E in terms of E_L in equation 41, and from equation 42, then

$$\left(\frac{\partial E}{\partial n_u}\right)_{n_{v \neq u}} = \left(\frac{\partial E_L}{\partial n_u}\right)_{n_{v \neq u}} = X_u \quad . \tag{48}$$

By substituting these two relations into equation 46, the energy minimization condition can be rewritten:

$$\left(\frac{\partial E_L}{\partial n_u}\right)_{n_{v \neq u}} = X_u = \lambda_i \quad . \tag{49}$$

The condition expressed in equation 49, that $X_u = \lambda_i$, applies to all atomic orbitals and to all molecular orbitals in the molecule. In general, therefore, the electronegativities of all the atomic orbitals must be identical. Modifications of this principle will be discussed in the material to be presented later.

In order to calculate molecular charge distributions by this principle of electronegativity equalization, it is necessary to specify the form of the energy functions, E_L, associated with each atom L, and thereby to specify the nature of the electronegativity functions of equation 42. As a first approximation, the terms E_L could be taken to be equal to the functions which express the energy of ISOLATED (non-bonded) atoms in their valence states as a function of the charge densities of their atomic orbitals. The orbital electronegativities to be equalized in the molecule are then the first derivatives of the isolated atom energies with respect to the orbital charge densities.

There are, however, several objections to the use of such a definition of electronegativity with the principle that all the orbital electronegativities in a molecule are equal;

i) it is impossible, in general, to achieve numerical equality of the electronegativities of all the occupied atomic orbitals in a molecule without violating the condition that each orbital charge density, n_u, should lie between the limits

$$0 \leqslant n_u \leqslant 2 \quad .$$

The origin of the difficulty is that the electronegativities of the inner-shell orbitals are extremely high, and it is impossible in most instances to find a molecular charge distribution in which the X_u for these orbitals are equal to those of the valence-shell orbitals;

ii) since the orbital electronegativity functions contain no interatomic terms, and since the electronegativities of all the atomic orbitals are constrained to be identical in the molecule, the molecular charge distribution generated in such schemes is completely independent of the nature of the bonding in the molecules. Chemically inequivalent atoms of the same atomic number in a molecule would be predicted to possess the same charge density characteristics, and all the atomic orbitals of an atom which are of the same principal and azimuthal quantum number would necessarily have the same charge density.

These difficulties may be overcome by placing certain limitations on the extent to which the orbital electronegativities are equalized in a molecule. Huheey (39) has used a scheme which effectively equalizes the electronegativities of only the atomic orbitals which are considered to be "bonding" in a molecule. Huheey's method overcomes the first difficulty (although in a rather arbitrary manner), but does not relieve the second difficulty.

One method by which electronegativity equalization conditions, compatible with the atom energy based electronegativity functions, may be obtained is through the concept of the localized chemical bond. In this concept, the electron density in a saturated molecule is assumed to be distributed between the atoms in such a way that a number of two-centre, two-electron bonds are formed, and the remainder of the electron density is assigned to one-centre molecular orbitals which are localized on the various atoms. Each bond is formed by the combination of two atomic orbitals, one orbital from each of a pair of atoms which are "neighbours" in the molecule. Each bonding atomic orbital, which may be one of the original s, p, d, . . . orbitals of the atoms, or hybrids thereof, is assumed to participate in only one occupied molecular orbital. The concept of the two-electron, two-centre chemical bond has been studied by molecular orbital theory, and has been found to be valid to a fair degree of approximation for various saturated molecules (50,51).

The localization of the molecular orbitals to give two-centre, two-electron chemical bonds may be illustrated by considering the ammonia molecule. If it is assumed that the nitrogen atom uses four valence-shell sp^3 (or tetrahedral, termed "te") hybrid orbitals for bonding, and the hydrogen atoms use 1s orbitals, the localization procedure leads to two one-centre, "lone pair" molecular orbitals (one for the inner shell electrons of N, and one corresponding to a doubly-occupied te atomic orbital of N) and three two-centre, two-electron bonds. Each two-centre N-H bond corresponds to a molecular orbital in which the 1s atomic orbital of one H atom, and one te orbital of the nitrogen, are paired together.

When the localized bond concept is combined with the electronegativity equalization theory given above, equations 43 and 44 are altered. If the atomic orbitals involved in these equations represent the hybrid atomic orbitals which participate in only one localized molecular orbital, then the summation in equation 41 over all the occupied MOs from ψ_i to ψ_j involves only one term, *that for the specific MO in which AO ϕ_u actually participates.* In addition, the sum over all the AOs used in equation 44 to calculate N_i is now restricted to either one or two hybrid AOs, since each localized molecular orbital extends over only one or two orbital centres.

The result of applying the localization approximations to the electronegativity equalization condition expressed in equation 49 is that, *for a given MO ψ_i, only the electronegativities of the one or two atomic orbitals which participate in this molecular orbital are required to be identical and equal to λ_i.* Since no atomic orbital is presumed to participate in more than occupied molecular orbital, the terms λ_i for different ψ_i need not be identical *according to equation 49.* The net effect of treating the molecular orbitals as being completely independent and localized is that a less general condition of electronegativity equalization is established. This "sub-condition" of the general principle of electronegativity equalization is actually the one which was used by Hinze, Whitehead, and Jaffe in their technique (8), and is the form employed for the charge density distributions reported in this study.

In general, the use of the "restricted" electronegativity equalization condition in schemes which use electronegativity functions based upon isolated atom energies is superior to the use of the general equalization principle for the following reasons:

i) numerical equalization of the electronegativities within each localized molecular orbital can generally be achieved,

ii) the chemical concept of the two-electron, two-centre bond is retained, as are the concepts of the inner-shell and lone-pair electrons, and

iii) since any localization of the molecular orbitals in LCAO-MO calculations is dependent on the interatomic energy terms, and since no interatomic energy terms are included in the bond electronegativity function used, the localization effects must be introduced before the calculations are made. The use of a "restricted" equalization procedure achieves this localization.

In summary, it appears that the approximation of localized chemical bonds must be made in approximate electronegativity equalization theories in order to partially compensate for some of the other approximations invoked.

I. 2. C THE CALCULATION OF MOLECULAR CHARGE DENSITY DISTRIBUTIONS BY THE ELECTRONEGATIVITY EQUALIZATION PRINCIPLE

One of the main objectives of this work is to establish the extent to which molecular charge density distributions calculated by the electronegativity equalization method of Hinze, Whitehead, and Jaffe are compatible with chemical evidence for inductive effects in saturated molecules. For this, it is necessary to establish the constraints on the orbital charge densities which result from electronegativity equalization conditions. Very general conditions for the molecular charge density can be established for any electronegativity equalization scheme in which the electronegativities of the atoms (or orbitals) are assumed to be linearly dependent upon the electronic charge of that atom (or orbital).

General Relationships

In order to establish molecular charge distributions using the electronegativity equalization principle, the nature of the functional dependence of electronegativity upon charge must be established. Such relationships will be termed BOND ELECTRONEGATIVITY functions (8). Most of the bond electronegativity functions which have been proposed to date can be expressed by the general relation

$$X_L = F_L + k\, G_L\, Q_L \tag{50}$$

where X_L is the electronegativity of the atom or orbital L, F_L and G_L are bond electronegativity function parameters for L, and Q_L is some measure of the electronic density of L. The term Q_L represents the NET charge of the atom or orbital L, or its total electronic density. When the magnitudes of the terms F_L, k and G_L are calculated, it is found that the electronegativity of L decreases as the electronic charge density of L increases.

By the principle of electronegativity oqualization, the X_L in the set L = 1, ... M are all required to be equal to the same value, X^{*}, in the molecule considered:

$$X^{*} \ (=X_L) = F_L + k\, G_L\, Q_L \qquad \text{for all } L = 1, \ldots M. \tag{51}$$

A general formula for X^{*} may be found by dividing each side of equation 51 by G_L, and then summing the terms on each side over all L = 1, ...M :

$$X^{*} \sum_{L=1}^{M} \left(\frac{1}{G_L}\right) = \sum_{L=1}^{M} \left(\frac{F_L}{G_L}\right) + k \sum_{L=1}^{M} Q_L \tag{52}$$

or,

$$X^{*} = \frac{\sum_{L=1}^{M} \left(\frac{F_L}{G_L}\right) + k \sum_{L=1}^{M} Q_L}{\sum_{L=1}^{M} \left(\frac{1}{G_L}\right)} . \tag{53}$$

Since the sum from L = 1 to L = M of the terms Q_L is always known, the summation $\sum_{L=1}^{M} Q_L$ may be replaced by its known value, Q :

$$X^{*} = \frac{\sum_{L=1}^{M} \left(\frac{F_L}{G_L}\right) + k\, Q}{\sum_{L=1}^{M} \left(\frac{1}{G_L}\right)} . \tag{54}$$

If each Q_L represents the net charge of L, and all the atoms (or orbitals) L in the molecule are included in the summation from 1 to M, then Q represents the *net* charge of the molecule. If each Q_L represents a total electron density, Q is the total electron density in the molecule.

Provided that the terms F_L and F_G have been evaluated for each L, X^{*} may be calculated for any molecule by equation 54. Once the magnitude of X^{*} is known, each Q_L may be calculated, since from equation 50,

$$Q_L = \frac{X^{*} - F_L}{k\ G_L} , \qquad (55)$$

In Sanderson's method of electronegativity equalization (15), the parameters F_L and G_L are related as:

$$G_L = (F_L)^{1/2} \qquad (56)$$

and for this case, the formulae in equations 54 and 55 for X^{*} and Q_L may be written more simply:

$$X^{*} = \frac{\sum\limits_{L=1}^{M} (F_L)^{1/2} + k\ Q}{\sum\limits_{L=1}^{M} \left(\frac{1}{F_L}\right)^{1/2}} \qquad (57)$$

$$Q_L = \left(\frac{1}{F_L}\right)^{1/2} \left(\frac{X^{*} - F_L}{k}\right) . \qquad (58)$$

Sanderson did not derive a general formula for X^{*} in his work, but assumed that the geometric mean of all the F_L in a molecule was a good approximation for X^{*} (15). The analysis which follows indicates that the expression for X^{*} in equation 57 does reduce to the geometric mean of the F_L when a diatomic molecule is considered, but does not reduce to geometric mean for larger systems:

For a diatomic molecule LM,

$$X^{\star} = \frac{(F_L)^{1/2} + (F_M)^{1/2}}{\left(\frac{1}{F_L}\right)^{1/2} + \left(\frac{1}{F_M}\right)^{1/2}}$$

$$\therefore \quad X^{\star} = \frac{(F_L)^{1/2} + (F_M)^{1/2}}{\dfrac{(F_L)^{1/2} + (F_M)^{1/2}}{(F_L\,F_M)^{1/2}}} \quad .$$

$\therefore$ $X^{\star} = (F_L\,F_M)^{1/2}$, the geometric mean of F_L and F_M. (59)

The use of the geometric mean, rather than equation 57, leads to only very small errors in the calculation of $X^{\star}$ for a molecule, since the geometric mean is usually a good approximation to the formula in equation 57.

In general, the expressions for $X^{\star}$ and Q_L in equations 54 and 55 are quite simple whenever the electronegativities of only two atoms or orbitals are equalized. For such cases,

$$X^{\star} = \frac{\dfrac{F_L}{G_L} + \dfrac{F_M}{G_M} + k\,Q}{\dfrac{1}{G_L} + \dfrac{1}{G_M}}$$

or,

$$X^{\star} = \frac{F_L\,G_M + F_M\,G_L + k\,Q\,G_L\,G_M}{G_L + G_M} \tag{60}$$

and,

$$Q_L = \frac{X^* - F_L}{k\ G_L} = \frac{\dfrac{F_L G_M + F_M G_L + k\ Q\ G_L G_M}{G_L + G_M} - F_L}{k\ G_L}$$

or,

$$Q_L = \frac{F_M - F_L + k\ Q\ G_M}{k(G_L + G_M)} \quad . \tag{61}$$

Two-Centre Bonds

One of the properties of interest, which can be derived from the charge distribution in a diatomic molecule, is the IONIC CHARACTER, i_{LM}, of the L-M bond. This quantity is defined as the net transfer of electron density between the atoms or atomic orbitals. In this study, i_{LM} will be defined as the gain in electron density of L relative to the electron density of L before bond formation, Q_L^o :

$$i_{LM} = Q_L - Q_L^o \quad . \tag{62}$$

In general, the terms Q_L, Q_M, Q_L^o , and Q_M^o are related to Q by the equations

$$Q = Q_L^o + Q_M^o = Q_L + Q_M \quad . \tag{63}$$

The electronegativities of L and M for $Q_L = Q_L^o$ and $Q_M = Q_M^o$ (that is before bond formation) will be denoted as X_L^o and X_M^o respectively.

If the expression for Q_L in equation 61 is substituted for Q_L in equation 62, an expression for i_{LM} in terms of the bond electronegativity function parameters may be determined as:

$$i_{LM} = \frac{F_M - F_L + k\ Q\ G_M - k\ G_L\ Q_L^o - k\ G_M\ Q_L^o}{k\ (G_L + G_M)} \quad . \tag{64}$$

Upon introducing the expression for Q in terms of Q_L^o and Q_M^o (equation 63), the ionic character may be related to the electronegativities of L and M before bond formation:

$$i_{LM} = \frac{F_M - F_L + k\ G_M\ Q_L^{\ o} + k\ G_M\ Q_M^o - k\ G_L\ Q_L^{\ o} - k\ G_M\ Q_L^{\ o}}{k\ (G_L + G_M)}$$

$$= \frac{(F_M + k\ G_M\ Q_L^o) - (F_L + k\ G_L\ Q_L^o)}{k\ (G_L + G_M)}$$

$$= \frac{X_M^o - X_L^o}{k\ (G_L + G_M)} \qquad (65)$$

since $X_L^o = F_L + k\ G_L\ Q_L^o$, (66)

and similarly for X_M^o. The ionic character of a two-centre bond is then proportional to the electronegativity difference of the two centres before bond formation, and is inversely proportional to the sum of the G parameters. Since this expression for i_{LM} is valid for a two-centre bond in any of the electronegativity equalization schemes which use a bond electronegativity function of the type defined by equation 50, electronegativity equalization methods are in agreement with the intuitive idea that ionic character is linked to the difference of electronegativities of the atoms, but are in disagreement with empirical schemes which usually assume that there is a unique curve relating i_{LM} to the electronegativity difference.

By intuitive reasoning, Wilmshurst (19) has derived an expression for i_{LM} which is similar in some respects to equation 65. His formula is expressed in terms of Pauling electronegativities, X^P :

$$i_{LM} = \frac{\left| X_M^P - X_L^P \right|}{X_L^P + X_M^P} \quad . \tag{67}$$

This same formula can be derived from equation 65 if the following bond electronegativity function is used:

$$X_L = X_L^P + X_L^P Q_L \quad . \tag{68}$$

This function requires the equality of all electronegativities at $Q_L = -1$.

If Hinze, Whitehead, and Jaffe's bond electronegativity function, $X_u\ (n_u)$, for an atomic orbital ϕ_u of charge density n_u is used in the ionic character expression, equation 65, then

$$i_{uv} = \frac{X_v^o - X_u^o}{2(c_u + c_v)} \tag{69}$$

since (8)

$$X_u\ (n_u) = b_u + 2c_u\, n_u \quad . \tag{70}$$

For a two-electron bond formed by atomic orbitals which initially have one electron, then

$$X_u^o = X_u\ (n_u = n_u^o = 1) = X_u\ (1) \tag{71}$$

and i_{uv} is given by the formula of Hinze et al. (8),

$$i_{uv} = \frac{X_v(1) - X_u(1)}{2(c_u + c_v)} \quad . \tag{72}$$

In addition to expressions for the equilibrated electronegativities and charge densities in a molecule, an equation for the extra ionic resonance energy can be derived from the principle of electronegativity equalization for a two-centre bond. If the bond electronegativity function in equation 50 is defined as the first derivative of the energy of the atom with respect to the charge parameter Q_L, then the atom energy function must be of the form

$$E_L(Q_L) = E_L(0) + F_L Q_L + \frac{1}{2} k G_L Q_L^2 \tag{73}$$

in which $E_L(0)$ represents the atom energy for $Q_L = 0$. Since no charge transfer between the atoms occurs in the homonuclear diatomics LL and MM, then the charge densities Q_L in LL and Q_M in MM are equal to Q_L^o and Q_M^o respectively. The electronic energies of these molecules is, according to equations 41 and 73,

$$E_{LL} = 2\left[E_L(0) + F_L Q_L^o + \frac{1}{2} k G_L (Q_L^o)^2\right] \tag{74}$$

and similarly for E_{MM}. The electronic energy of LM, on the other hand, is given by

$$E_{LM} = E_L(0) + E_M(0) + F_L Q_L + F_M Q_M + \frac{1}{2} k (G_L Q_L^2 + G_M Q_M^2) . \tag{75}$$

The EXTRA IONIC RESONANCE ENERGY, Δ_{LM}, is defined as

$$\Delta_{LM} = E_{LM} - \frac{1}{2}(E_{LL} + E_{MM}) . \tag{76}$$

Substituting the expressions for E_{LM}, E_{LL}, and E_{MM} given above into equation 76, then

$$\Delta_{LM} = F_L(Q_L - Q_L^o) + F_M(Q_M - Q_M^o) + \frac{1}{2} k \Big\{ G_L \left[Q_L^2 - (Q_L^o)^2\right] + G_M \left[Q_M^2 - (Q_M^o)^2\right] \Big\} . \tag{77}$$

By substituting the relations

$$Q_L^2 - (Q_L^o)^2 = (Q_L + Q_L^o)(Q_L - Q_L^o) \tag{78}$$

and

$$Q_L + Q_L^o = 2 Q_L^o + i_{LM} \tag{79}$$

$$Q_M + Q_M^o = 2\,Q_M^o - i_{LM} \tag{80}$$

together with the definition of i_{LM} in equation 62 into the expression for Δ_{LM} given above, then

$$\Delta_{LM} = i_{LM}\,(F_L + \frac{1}{2}\,k\,Q_L - F_M - \frac{1}{2}\,k\,Q_M) + \frac{k\,i_{LM}^2}{2}\,(G_L + G_M) \,. \tag{81}$$

The term Δ_{LM} may be written in terms of the electronegativities of L and M by substituting the ionic character equation 65 into equation 81,

$$\Delta_{LM} = \frac{-\,(X_M^o - X_L^o)^2}{2k\,(G_L + G_M)} \,. \tag{82}$$

The extra ionic resonance energy, Δ_{LM}, is predicted by the electronegativity equalization method to be proportional to the square of the difference in the electronegativities of L and M before bond formation, and inversely proportional to the sum of the G parameters for L and M. The expression for Δ_{LM} in equation 82 is similar to the relation developed by Pauling (3) who established empirically that Δ_{LM} is proportional to the square of the electronegativity difference between L and M. The electronegativity equalization relation for Δ_{LM} differs from the empirical one in that no unique relation between Δ_{LM} and the electronegativity difference exists, a similar situation to that found for the ionic character.

For the specific case of the Hinze-Whitehead-Jaffe bond orbital electronegativity function (equation 70), the extra ionic resonance energy equation 82 becomes

$$\Delta_{LM} = \frac{-\left[X_v(1) - X_u(1)\right]^2}{4(c_u + c_v)} \tag{83}$$

if the orbitals ϕ_u and ϕ_v are occupied in the valence-state of the free atom by one electron. Equation 83 has been derived previously by Hinze (27).

Bond Electronegativity Functions

As indicated by equation 55, the principle of electronegativity equalization leads to a unique condition for the molecular charge density distributions, when a bond electronegativity function of the type in equation 50 is used. In order to calculate charge distributions on the basis of equation 55, the electronegativity function parameters F_L and G_L must first be numerically evaluated. This evaluation may be achieved, for atomic orbital definitions of X_L, by considering the functional dependence of the atom energy upon the orbital charge densities, and using this dependence to derive the parameters on the basis of equation 42.

In the scheme proposed by Hinze, Whitehead, and Jaffe (8), the atom energy E_L is related to the electronic charge density n_u associated with atomic orbital ϕ_u by the relation

$$E_L\ (n_u \ldots n_v) = a_{Lu} + b_{Lu}\, n_u + c_{Lu}\, n_u^2 \quad . \tag{84}$$

The dependence of E_L upon the charge densities of the orbitals other than ϕ_u is included in the terms a_{Lu}, b_{Lu}, c_{Lu}. The parameters a_{Lu}, b_{Lu}, c_{Lu} are obtained by fitting equation 84 to the three energies, corresponding to $n_u = 0, 1,$ and 2, which were calculated by Hinze et al. for the valence state of the free atom. By defining the valence-state ionization potential, I_u, and electron affinity A_u, as

$$I_u = E_L\ (n_u = 1) - E_L\ (n_u = 0) \tag{85}$$

$$A_u = E_L\ (n_u = 2) - E_L\ (n_u = 1) \tag{86}$$

then,

$$b_{Lu} = \frac{1}{2}\ (3I_u - A_u) \tag{87}$$

$$c_{Lu} = \frac{1}{2}\ (A_u - I_u) \tag{88}$$

$$a_{Lu} = E_L\ (n_u = 0) \tag{89}$$

and

$$E_L(n_u) = E_L(n_u = 0) + \frac{1}{2}\,(3I_u - A_u)\ n_u + \frac{1}{2}\,(A_u - I_u)\ n_u^{\,2}\ . \tag{90}$$

The bond electronegativity function for orbital ϕ_u is then given by the expression

$$X_u = \frac{\partial(E_L\ (n_u, \ldots .n_v)\ )}{\partial\ (n_u)} = b_{Lu} + 2c_{Lu}\ n_u$$

$$\therefore\ X_u = 0.5\ \ (3I_u - A_u) + (A_u - I_u)\ n_u\ . \tag{91}$$

An alternative relationship between the atom energy and the valence-shell orbital charge densities has been derived by Klopman (35). In this method, the energy of an atom is specified by three parameters, B_{Lu}, A_L^{+}, and A_L^{-} defined as follows:

i) B_{Lu} represents the energy of attraction between an electron in a valence-shell atomic orbital ϕ_u and the "core" of the atom L, where this "core" represents the nucleus and completely filled inner shells of the atom;

ii) A_L^{+} represents the energy of repulsion of two valence-shell orbital electrons of atom L, provided the electrons have parallel spins, and

iii) A_L^{-} represents the repulsion energy of two valence-shell orbital electrons which have opposite spins.

The energy of the atom, relative to the energy of the core, is then given by (35)

$$E_L = \sum_{a=1}^{c} B_{Lu} + \frac{1}{2} \sum_{a=1}^{c} \sum_{b(\neq a)=1}^{c} A_L^{+} \delta_{ab} + \frac{1}{2} \sum_{a=1}^{c} \sum_{b(\neq a)=1}^{c} A_L^{-} (1 - \delta_{ab}) \qquad (92)$$

where $\delta_{ab} = 1$ if electrons a and b have parallel spins
and $\delta_{ab} = 0$ if electrons a and b have opposite spins.

The summations from a, b = 1 to c run over all the electrons in the valence-shell orbitals of the atom.

The atom energy expression of Klopman, equation 92, may be used to derive a relation between the energy of an atom and the charge density of one of its valence-shell orbitals, ϕ_u, when this orbital participates in a two-electron, two-centre chemical bond. If $B_{Lu}^{\star}$ is defined as the energy of interaction of an electron in orbital ϕ_u with the core plus the electrons in the other valence-shell orbitals of atom L, then the relationship between $E_L\,(n_u)$ and n_u becomes

$$E_L\,(n_u) = E_L\,(n_u = 0) + n_u B_{Lu}^{\star} + \frac{n_u^{2} A_L^{-}}{4} \qquad (93)$$

for an atomic orbital ϕ_u which participates in a two-electron, two-centre bond. Note that since the two electrons in the bond are necessarily of opposite spin, no term involving A_L^{+} is present in the expression. The coefficient, $\frac{n_u^{2}}{4}$, of the term A_L^{-} is the probability (according to molecular orbital theory) that both electrons in the bond occupy orbital ϕ_u simultaneously. The expression for E_L given in equation 93 is a continuous function of the charge density n_u, and may be differentiated with respect to n_u to yield a bond electronegativity function for orbital ϕ_u :

$$X_u = \frac{\partial(E_L(n_u))}{\partial(n_u)} = B_{Lu}^{\star} + \frac{n_u A_L^{-}}{2} . \qquad (94)$$

It should be noted that it is necessary to specify that orbital ϕ_u is in a condition of bonding before a continuous function between E_L and n_u can be written.

Klopman maintains that E_L cannot be differentiated with respect to n_u if E_L represents the energy of an atom L which is not bonded (35).

The parameters $B_{Lu}^{\star}$ and A_L^{-} of equations 93 and 94 may be evaluated from the known energies of an isolated, non-bonded atom L. For such an atom, the difference in atom energy between the states with one electron in ϕ_u, and that with zero electrons in this orbital is the ionization potential of the orbital, and is equal to $B_{Lu}^{\star}$:

$$B_{Lu}^{\star} = I_u . \qquad (95)$$

Since the energy of a doubly-occupied orbital ϕ_u is equal to the sum $E_L\ (n_u = 0) + I_u + A_u$, where A_u is the electron affinity, then

$$A_L^{-} = A_u - I_u . \qquad (96)$$

The expressions for the atom energy (equation 93) and the bond electronegativity of the orbital (equation 94) may be rewritten in terms of the ionization potential and electron affinity:

$$E_L\ (n_u) = E_L\ (n_u = 0) + n_u I_u + n_u^2 \frac{(A_u - I_u)}{4} \qquad (97)$$

and

$$X_u = \frac{I_u + n_u (A_u - I_u)}{2} . \qquad (98)$$

Since Klopman derived his atom energy scheme for use in molecular orbital theory, the expression in equation 98 for X_u will be termed the MOLECULAR ORBITAL (MO) BOND ELECTRONEGATIVITY FUNCTION.

The quantitative difference between the atom energy function and bond electronegativity function of Hinze, Whitehead, and Jaffé and that given above may be found by defining two new functions ΔE_L and ΔX_u :

$$\Delta E_L = E_L\,(\mathrm{HWJ}) - E_L(\mathrm{MO}) \tag{99}$$

$$\Delta X_u = X_u\,(\mathrm{HWJ}) - X_u(\mathrm{MO}) \tag{100}$$

where the subscript HWJ refers to the Hinze-Whitehead-Jaffe expressions, and MO refers to the expressions given in equations 97 and 98. Then from equations 90 and 97

$$\Delta E_L = 0.5 n_u\,(I_u - A_u)\,(1 - 0.5 n_u) \tag{101}$$

and from equations 91 and 98,

$$\Delta X_u = 0.5\,(I_u - A_u)\,(1 - n_u)\ . \tag{102}$$

Both terms, ΔE_L and ΔX_u, increase in magnitude as the difference between the ionization potential and the electron affinity increase. The energy difference is zero at the points $n_u = 0$ and $n_u = 2$, is maximum at $n_u = 1$, and is symmetric about $n_u = 1$. The electronegativity difference is zero at $n_u = 1$, where both bond electronegativity functions are equivalent to Mulliken's electronegativity formula (equation 5).

The physical significance of the differences between the HWJ and MO atom energy and electronegativity functions may be pointed up by considering the values of E_L for $n_u = 1$. For the MO definition, E_L at $n_u = 1$ is equal to $\left(3/4\ I_u + 1/4\ A_u\right)$ while for the HWJ definition it is simply I_u.

The MO energy at $n_u = 1$ is equivalent to that for two electrons each spending one-half the time in orbital ϕ_u, with no correlation between the motions of the electrons.[☆] The HWJ energy at $n_u = 1$, on the other hand, corresponds to the same situation but with a complete correlation of the electronic motion such that if the first electron occupies ϕ_u, the second electron must be present in the other bonding orbital, and vice-versa. The MO atom energy function underestimates inter-orbital electron correlation while the HWJ function overestimates this property, since the electronic motions are partially correlated (47).

In the calculation of the ionic characters of two-centre, two-electron chemical bonds, the formula given in equation 72 may be used with both the HWJ and MO bond electronegativity function. Since the $X_u(n_u = 1)$ of both definitions are identical, and since from equations 88 and 98 the c_u terms are related as

$$c_u \text{ (HWJ)} = 2\, c_u \text{ (MO)} \tag{103}$$

then the ionic characters are related:

$$i_{uv} \text{ (HWJ)} = \frac{1}{2}\, i_{uv} \text{ (MO)} . \tag{104}$$

The magnitudes of the ionic characters calculated by the HWJ and MO bond electronegativities are then quite different, but are always in a constant ratio of 1:2.

[☆] That is, no correlation of the motion between the two orbitals.

I. 2. D COMPARISON OF ELECTRONEGATIVITY EQUALIZATION WITH MOLECULAR ORBITAL METHODS

Various integrals involving the atomic orbitals ϕ_u, $\phi_v \ldots$ must be defined before the relationships for ionic character and ionic resonance energy obtained by the electronegativity equalization method can be compared to those obtained from semi-empirical LCAO-MO methods.

"Coulomb" Integrals α_u:

$$\alpha_u = \int \phi_u^{*} \overset{o}{H} \phi_u \, d\tau \tag{105}$$

"Resonance" Integrals β_{uv}:

$$\beta_{uv} = \int \phi_u^{*} \overset{o}{H} \phi_v \, d\tau \tag{106}$$

"Overlap" Integrals S_{uv}:

$$S_{uv} = \int \phi_u^{*} \phi_v \, d\tau \tag{107}$$

where the integrations $\int d\tau$ are over all space, and ϕ^{*} represents the complex conjugate of ϕ.

The first attempt to find a correspondence between the electronegativity concept of Pauling and the molecular orbital method was made by Mulliken in 1935 (4). By using a simple LCAO-MO scheme which did not neglect overlap integrals, but which did not treat electron repulsion explicitly, Mulliken found that the extra ionic resonance energy Δ_{uv} associated with a single bond between atomic orbitals ϕ_u and ϕ_v could be expressed in terms of the difference in Coulomb integrals between the atomic orbitals (4):

$$\Delta_{uv} = \frac{-(\alpha_u - \alpha_v)^2}{4\,Y_{uv}} + (\alpha_u - \alpha_v)^4 \frac{(1 - S_{uv}^2)}{64\,Y_{uv}^3} - \ldots \quad . \tag{108}$$

In this equation,

$$Y_{uv} = \beta_{uv} - \frac{S_{uv}}{2}(\alpha_u + \alpha_v) \ . \tag{109}$$

Mulliken also showed that the ionic character of the bond could be written in terms of the difference in Coulomb integrals:

$$i_{uv} = \frac{-(\alpha_v - \alpha_u)}{2\,Y_{uv}} + 0\,(\alpha_v - \alpha_u)^3 + \ldots . \quad . \tag{110}$$

From these relationships between Δ_{uv} and i_{uv} with $(\alpha_v - \alpha_u)$, Mulliken associated the Pauling electronegativity X^P with the Coulomb integral as follows:

$$X_u^P = -\frac{\alpha_u}{2\,(-Y_{uv})^{1/2}} \ . \tag{111}$$

In terms of an LCAO-MO scheme which does not explicitly include overlap integrals, Mulliken's relations for Δ_{uv} and i_{uv} may be written, for small differences between the Coulomb integrals, as

$$\Delta_{uv} = \frac{-(\alpha_v - \alpha_u)^2}{4\beta_{uv}} \ , \tag{112}$$

$$i_{uv} = \frac{\alpha_v - \alpha_u}{2\beta_{uv}} \ . \tag{113}$$

Similar relations can be derived from Klopman's (38) bonding energy expression, E_{uv}, for a single bond:

$$E_{uv} = \frac{(n_u - n_v)}{2}\,(B_u^{*} - B_v^{*}) + \frac{n_u^{2}}{4}\,(A_u^{-} + \Gamma_{uv}) + \frac{n_v^{2}}{4}\,(A_v^{-} + \Gamma_{uv})$$
$$+ 2\beta_{uv}\sqrt{n_u\, n_v} \quad . \qquad (114)$$

In this equation, the terms B_u^{*} and A_u^{-} correspond to B_{Lu}^{*} and A_L^{-} which have been discussed in the previous section, and β_{uv} is the resonance integral defined relative to the core Hamiltonian. The term Γ_{uv} represents the negative of the energy of repulsion between one electron in orbital ϕ_u and one in orbital ϕ_v (38).

Expressions relating the ionic character predicted by this scheme to the electronegativity difference can be derived by re-writing the equation for E_{uv} in terms of i_{uv}, the ionic character of the two-electron bond between ϕ_u and ϕ_v. If the ionic character is defined as

$$i_{uv} = n_u - 1 \qquad (115)$$

then

$$n_u = i_{uv} + 1 \qquad (116)$$

and

$$n_v = 1 - i_{uv} \quad . \qquad (117)$$

Substituting these definitions into equation 114, then

$$E_{uv} = i_{uv}\left(B_u^{*} - B_v^{*} + \frac{A_u^{-}}{2} - \frac{A_v^{-}}{2}\right) + i_{uv}^{2}\left(\frac{A_u^{-} + A_v^{-}}{4} + \frac{\Gamma_{uv}}{2}\right)$$
$$+ \left(\frac{A_u^{-} + A_v^{-}}{4} + \frac{\Gamma_{uv}}{2}\right) + 2\beta_{uv}\sqrt{1 - i_{uv}^{2}} \quad . \qquad (118)$$

An expression for i_{uv} may be obtained by minimizing E_{uv} with respect to i_{uv} :

$$\frac{d(E_{uv})}{d(i_{uv})} = 0 = \left(B_u^{*} - B_v^{*} + \frac{A_u^{-} - A_v^{-}}{2}\right) + i_{uv}\left(\frac{A_u^{-} + A_v^{-}}{2} + \Gamma_{uv}\right) - \frac{2\beta_{uv}\, i_{uv}}{\sqrt{1 - i_{uv}^{2}}} \, . \qquad (119)$$

Hence,

$$i_{uv} = \frac{\left(B_v^{*} + \frac{A_v^{-}}{2}\right) - \left(B_u^{*} + \frac{A_u^{-}}{2}\right)}{\frac{A_u^{-} + A_v^{-}}{2} + \Gamma_{uv} - \frac{2\beta_{uv}}{\sqrt{1 - i_{uv}^{2}}}} \, . \qquad (120)$$

As indicated by equation 94, the terms $\left(B_u^{*} + \frac{A_u^{-}}{2}\right)$ and $\left(B_v^{*} + \frac{A_v^{-}}{2}\right)$ correspond to $X_u(1)$ and $X_v(1)$ for the MO bond electronegativity function. The terms $\frac{A_u^{-}}{4}$, $\frac{A_v^{-}}{4}$ correspond to c_u, c_v of the MO bond electronegativity function. Hence, equation 120 may be re-written as:

$$i_{uv} = \frac{X_v(1) - X_u(1)}{2(c_u + c_v) + \left(\Gamma_{uv} - \frac{2\,\beta_{uv}}{\sqrt{1 - i_{uv}^{2}}}\right)} \, . \qquad (121)$$

This ionic character expression is very similar to that obtained when the bond electronegativity function is used with the principle of electronegativity equalization (equation 72). The i_{uv} equations differ only in the term $\left[\Gamma_{uv} - \frac{2\,\beta_{uv}}{\sqrt{1 - i_{uv}^{2}}}\right]$ present in the denominator of equation 121. For low values of i_{uv}, the term $\sqrt{1 - i_{uv}^{2}}$ differs very little from unity, so that to a good approximation, the two equations for i_{uv} differ by the term

$\left(\Gamma_{uv} - 2\,\beta_{uv} \right)$ when i_{uv} is low. Since the parameters Γ_{uv}, β_{uv} are both of opposite sign to the parameters c_u, c_v and since generally
(38)

$$\left| \Gamma_{uv} \right| > \left| \beta_{uv} \right| ,$$

the i_{uv} of Klopman's scheme will be greater in magnitude than those calculated by the MO bond electronegativity function and the equalization principle.

If Δ_{uv}, the extra ionic resonance energy, is defined as the <u>difference</u> in bonding energy between the cases where i_{uv} has the value given by equation 121 and where $i_{uv} = 0$, then an expression for Δ_{uv} in terms of the electronegativity difference may be derived from the expression for E_{uv} in equation 114:

$$\Delta_{uv} = i_{uv}\,(B_u^{\star} - B_v^{\star}) + \frac{(2i_{uv} + i_{uv}^{\;2})}{4}\,(A_u^- + \Gamma_{uv}) + \frac{(i_{uv}^{\;2} - 2i_{uv})}{4}\,(A_v^- + \Gamma_{uv}) + 2\,\beta_{uv}\left(\sqrt{1 - i_{uv}^{\;2}} - 1\right) \qquad (122)$$

or, by using $X(1)$ instead of the $(B^{\star} + \frac{A^-}{2})$ terms, then

$$\Delta_{uv} = i_{uv}\,(X_u(1) - X_v(1)) + \frac{i_{uv}^{\;2}}{4}\,(A_u^- + A_v^- + 2\,\Gamma_{uv}) + 2\,\beta_{uv}\left(\sqrt{1 - i_{uv}^{\;2}} - 1\right) . \qquad (123)$$

Substituting the i_{uv} expression of equation 121 into equation 123, then Δ_{uv} becomes

$$\Delta_{uv} = -\frac{\left(X_v(1) - X_u(1)\right)^2}{F_{uv}} + 2\,\beta_{uv}\left(\sqrt{1 - i_{uv}^{\;2}} - 1\right) \qquad (124)$$

where

$$\frac{1}{F_{uv}} = \frac{c_u + c_v + 0.5\,\Gamma_{uv} - (2\beta_{uv}/\sqrt{1 - i_{uv}^2})}{2(c_u + c_v) + \Gamma_{uv} - (2\beta_{uv}/\sqrt{1 - i_{uv}^2})} \quad . \tag{125}$$

The extra ionic resonance energy, Δ_{uv}, is then directly proportional to the square of the electronegativity difference when the ionic character is low, since in this case the terms $(\sqrt{1 - i_{uv}^2} - 1)$ is almost zero, and all the $\sqrt{1 - i_{uv}^2}$ factors in the parameter F_{uv} are approximately equal to 1.

From the above discussion, it can be concluded that both the electronegativity equalization method and simple LCAO-MO schemes lead to expressions for i_{uv} and Δ_{uv} of the form

$$i_{uv} = \frac{X_v(1) - X_u(1)}{f_1\ (u, v)} \quad , \tag{126}$$

$$\Delta_{uv} = -\frac{\left(X_v(1) - X_u(1)\right)^2}{f_2\ (u, v)} \tag{127}$$

for two-electron, two-centre bonds, where the functions $f_1\ (u, v)$ and $f_2\ (u, v)$ depend upon the nature of the orbitals ϕ_u and ϕ_v and, in the case of the equations from LCAO-MO theory, upon the nature of the bond formed by the orbitals. Ferreira has shown (44) that his semi-empirical technique for chemical bonds also leads to an ionic character equation which has the form of equation 126 above.

Extensions of the Bond Electronegativity Function

One approach that can be followed in attempting to extend the bond electronegativity function so as to account for the interatomic terms included in LCAO-MO treatments is to break the LCAO-MO expression for molecular energy into two parts, such that each part is an "atomic" term in that it is a function only of the charge density of the atomic orbital associated with it. If this is possible, then the improved bond electronegativity functions, together with the principle of electronegativity equalization, will lead to expressions for i_{uv} and Δ_{uv} which retain the general form of these in equations 126 and 127.

For the simple LCAO-MO method which does not consider overlap integrals or electron repulsions explicitly, the molecular energy E for a two-centre MO case may be written

$$E = 2c_u^2 \alpha_u + 2c_v^2 \alpha_v + 4c_u c_v \beta_{uv} \qquad (128)$$

where c_u and c_v are the coefficients of atomic orbitals ϕ_u and ϕ_v in the doubly-occupied bonding molecular orbital, and are related to the orbital charge densities n_u and n_v by

$$n_u = 2 c_u^2$$

and similarly for n_v. Hence E may be rewritten

$$E = n_u \alpha_u + n_v \alpha_v + 2\beta_{uv} \sqrt{n_u n_v} \quad . \qquad (129)$$

This relation for E may be divided into two symmetrical "atomic" parts, each part being dependent upon only one orbital charge density

$$E_u = n_u \alpha_u + \beta_{uv} \sqrt{n_u n_v}$$

$$= n_u \alpha_u + \beta_{uv} \sqrt{2n_u - n_u^2} \qquad (130)$$

and

$$E_v = n_v \alpha_v + \beta_{uv} \sqrt{2n_v - n_v^2} \qquad (131)$$

since the sum of n_u and n_v is two. A bond electronegativity function may be defined from "atomic" energy terms:

$$X_u = \frac{d\,(E_u)}{d\,(n_u)} = \alpha_u + \frac{\beta_{uv}\,(1 - n_u)}{\sqrt{2n_u - n_u^2}} \quad . \tag{132}$$

A bond electronegativity function can also be derived from Klopman's LCAO-MO method which includes electron repulsions explicitly. His molecular energy expression is (38)

$$E = n_u\,B_u^{*} + n_v\,B_v^{*} + \frac{n_u^2}{4}\,(A_u^- + \Gamma_{uv}) + \frac{n_v^2}{4}\,(A_v^- + \Gamma_{uv}) + 2\beta_{uv}\sqrt{n_u\,n_v} \tag{133}$$

from which the following "atomic" terms may be obtained:

$$E_u = n_u\,B_u^{*} + \frac{n_u^2}{4}\,(A_u^- + \Gamma_{uv}) + \beta_{uv}\sqrt{2n_u - n_u^2} \tag{134}$$

and

$$E_v = n_v\,B_v^{*} + \frac{n_v^2}{4}\,(A_v^- + \Gamma_{uv}) + \beta_{uv}\sqrt{2n_v - n_v^2} \quad . \tag{135}$$

The bond electronegativity function derived from these expressions is

$$X_u = \frac{d(E_u)}{d(n_u)} = B_u^{*} + \frac{n_u}{2}\,(A_u^- + \Gamma_{uv}) + \frac{\beta_{uv}\,(1 - n_u)}{\sqrt{2n_u - n_u^2}} \tag{136}$$

and similarly for X_v. Pritchard (52) has noted that, at the point of energy minimization in the LCAO-MO method which includes resonance integrals, the electronegativities are not equalized if the term β_{uv} is not present in the bond electronegativity definition.

It is possible, then, to include inter-atomic terms in the molecular energy expression for a diatomic molecule, and still be able to define a general bond electronegativity function. There are several difficulties in using such a function, however:

i) the calculation of the inter-atomic parameters β_{uv}, Γ_{uv} is a difficult matter at present,

ii) the bond electronegativity function becomes very complicated when polyatomic molecules are considered,

iii) the bond electronegativity function can no longer be defined from considerations of the energy of the isolated atom. In general, the functions Γ_{uv} and β_{uv} depend strongly upon both the nature of ϕ_u, and ϕ_v, and upon the u-v bond length, and

iv) the linear dependence of electronegativity upon orbital charge density is destroyed by the inclusion of the term involving β_{uv}.

Conclusions

The above analysis has indicated that the concept of electronegativity equalization can be preserved when inter-atomic energy terms are explicitly considered in a LCAO-MO scheme. This conclusion is general for many semi-empirical schemes, since other workers have indicated how it is possible to add various interatomic parameters to other bond electronegativity functions (26,42). In the present study, however, charge distributions will be calculated by using bond electronegativity functions which can be defined solely from the energy function of the isolated atoms, both for the reasons (i) to (iv) given above, and because one of the objects of this thesis is to determine the extent to which such isolated atom electronegativity functions are useful in predicting molecular charge distributions.

I. 3 ELECTRON DENSITY CALCULATIONS BY THE ELECTRONEGATIVITY EQUALIZATION METHOD

In Part I. 2 of this study, the theory of bond electronegativity functions and the Principle of Electronegativity Equalization have been outlined. In this section, Part I. 3, the bond electronegativity equalization method is applied to the calculation of electron densities in a large number of saturated molecules.

I. 3. A. ELECTRONEGATIVITY PARAMETERS AND THE METHOD OF CALCULATION

Bond Electronegativity Function Parameters

As discussed in the previous section, the parameters of the Hinze-Whitehead-Jaffe (HWJ) bond orbital electronegativity function can be evaluated from the valence-state ionization potential and electron affinity for the orbital. Hinze (27) has calculated valence-state energy data for four sets of hybrid atomic orbitals for the elements from Li to Ar:

i) sppp

where these atomic orbitals correspond to the valence-shell orbitals s, p_x, p_y, p_z .

ii) di di π π

where the digonal (di) hybrid orbitals are defined by

$$\phi_{di(1)} = \frac{1}{\sqrt{2}}\left(\phi_s + \phi_{p_x}\right)$$

$$\phi_{di(2)} = \frac{1}{\sqrt{2}}\left(\phi_s - \phi_{p_x}\right)$$

and the two π orbitals correspond to the original p_y, p_z orbitals.

iii) tr tr tr π

where the trigonal (tr) hybrids are

$$\phi_{tr(1)} = \frac{1}{\sqrt{3}}\phi_s + \sqrt{\frac{2}{3}}\phi_{p_x}$$

$$\phi_{tr(2)} = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_x} + \frac{1}{\sqrt{2}}\phi_{p_y}$$

$$\phi_{tr(3)} = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_x} - \frac{1}{\sqrt{2}}\phi_{p_y}$$

and $\phi_\pi = \phi_{p_z}$

iv) te te te te

where the tetrahedral (te) hybrids are

$$\phi_{te(1)} = \frac{1}{2}\left(\phi_s + \phi_{p_x} + \phi_{p_y} + \phi_{p_z}\right)$$

$$\phi_{te(2)} = \frac{1}{2}\left(\phi_s + \phi_{p_x} - \phi_{p_y} - \phi_{p_z}\right)$$

$$\phi_{te(3)} = \frac{1}{2}\left(\phi_s - \phi_{p_x} + \phi_{p_y} - \phi_{p_z}\right)$$

$$\phi_{te(4)} = \frac{1}{2}\left(\phi_s - \phi_{p_x} - \phi_{p_y} + \phi_{p_z}\right) .$$

When integral charge densities are assigned to these orbitals, the densities are denoted by superscripts—for example, $s^2\ p^2\ p^1\ p^1$. The four valence-shell orbitals of each atom will be denoted generally as ϕ_u, ϕ_v, ϕ_w, and ϕ_x.

The ionization potentials, I_u, and electron affinities, A_u, are available (53) for hybrid atomic orbitals, ϕ_u, of the types listed above for states with integral charge densities n_v, n_w, and n_x. Hence the HWJ bond electronegativity parameters, b_u and c_u, for such states can be evaluated:

$$X_u = b_u + 2c_u n_u \quad , \tag{137}$$

$$b_u = \frac{1}{2}(3I_u - A_u) \quad , \tag{138}$$

$$c_u = \frac{1}{2}(A_u - I_u) \quad . \tag{139}$$

The values of b_u and c_u for the atoms from H to Cl (except for the inert gases) and for Br and I are listed in Table I-I. The charge densities used in this table for the valence-shell orbitals are such that the atoms are electrically neutral when $n_u = 1$. The electronegativities of orbital ϕ_u have also been listed in Table I-I for $n_u = 0$, 1 and 2 (see equations 21, 22, and 23).

TABLE I-I: HWJ Electronegativity Function Parameters for Singly-Occupied Orbitals

Atom	Orb-ital	Valence State of Atom	I_u (e.v.)	A_u (e.v.)	b_u (e.v.)	c_u (e.v.)	$X_u(1)$ (e.v.)	$X_u(2)$ (e.v.)
H	s	s^1	13.60	0.75	20.02_5	-6.42_5	7.17_5	-5.67_5
Li	s	s^1	5.39	0.82	7.67_5	-2.28_5	3.10_5	-1.46_5
Be	s	s^1p^1	9.92	3.18	13.92	-3.37	6.55	-0.19
	p	s^1p^1	5.96	0.11	8.88_5	-2.92_5	3.03_5	-2.81_5
	di	di^1di^1	8.58	0.99	12.37_5	-3.79_5	4.78_5	-2.80_5
B	p	s^2p^1	8.30	-0.50	12.70	-4.40	3.90	-4.90
	s^*	$s^1p^1p^1$	14.91	5.70	19.51_5	-4.60_5	10.30_5	1.09_5
	p^*	$s^1p^1p^1$	8.42	0.32	12.47	-4.05	4.37	-3.73
	tr	$tr^1tr^1tr^1$	11.29	1.38	16.24_5	-4.95_5	6.33_5	-3.57_5
	te	$te^1te^1te^1$	10.43	1.53	14.88	-4.45	5.98	-2.92
C	p	$s^2p^1p^1$	10.93	-0.44	16.61_5	-5.68_5	5.24_5	-6.12_5
	s^*	$s^1p^1p^1p^1$	21.01	8.91	27.06	-6.05	14.96	2.86
	p^*	$s^1p^1p^1p^1$	11.27	0.34	16.73_5	-5.46_5	5.80_5	-5.12_5
	di	$di^1di^1\pi^1\pi^1$	17.42	3.34	24.46	-7.04	10.38	-3.70
	π	$di^1di^1\pi^1\pi^1$	11.19	0.10	16.73_5	-5.54_5	5.64_5	-5.44_5
	tr	$tr^1tr^1tr^1\pi^1$	15.62	1.95	22.45_5	-6.83_5	8.78_5	-4.88_5
	π	$tr^1tr^1tr^1\pi^1$	11.16	0.03	16.72_5	-5.56_5	5.59_5	-5.53_5

TABLE I-I continued

Atom	Orbital	Valence State of Atom	I_u (e.v.)	A_u (e.v.)	b_u (e.v.)	c_u (e.v.)	$X_u(1)$ (e.v.)	$X_u(2)$ (e.v.)
	te	$te^1te^1te^1te^1$	14.61	1.34	21.24_5	-6.63_5	7.97_5	-5.29_5
N	p	$s^2p^2p^1$	14.05	1.31	20.42	-6.37	7.68	-5.06
	$p^{\star}$	$s^2p^1p^1p^1$	13.94	0.78	20.52	-6.58	7.36	-5.80
	tr	$tr^2tr^1tr^1\pi^1$	20.60	5.14	28.33	-7.73	12.87	-2.59
	π	$tr^2tr^1tr^1\pi^1$	14.12	1.78	20.29	-6.17	7.95	-4.39
N	$tr^{\star}$	$tr^1tr^1tr^1\pi^2$	19.72	4.92	27.12	-7.40	12.32	-2.48
	te	$te^2te^1te^1te^1$	18.93	4.15	26.32	-7.39	11.54	-3.24
O	p	$s^2p^2p^1p^1$	17.28	2.01	24.91_5	-7.63_5	9.64_5	-5.62_5
	tr	$tr^2tr^2tr^1\pi^1$	26.65	7.49	36.23	-9.58	17.07	-2.09
	π	$tr^2tr^2tr^1\pi^1$	17.70	2.47	25.31_5	-7.61_5	10.08_5	-5.14_5
	$tr^{\star}$	$tr^2tr^1tr^1\pi^2$	26.14	7.32	35.55	-9.41	16.73	-2.09
	te	$te^2te^2te^1te^1$	24.39	6.11	33.53	-9.14	15.25	-3.03
F	p	$s^2p^2p^2p^1$	20.86	3.50	29.54	-8.68	12.18	-5.18
Na	s	s^1	5.14	0.47	7.47_5	-2.33_5	2.80_5	-1.86_5
Mg	s	s^1p^1	8.95	2.80	12.02_5	-3.07_5	5.87_5	-0.27_5
	p	s^1p^1	4.52	0.06	6.75	-2.23	2.29	-2.17
	di	di^1di^1	7.10	1.08	10.11	-3.01	4.09	-1.93
Al	p	s^2p^1	5.98	-0.08	9.01	-3.03	2.95	-3.11
	$s^{\star}$	$s^1p^1p^1$	12.27	4.92	15.94_5	-3.67_5	8.59_5	1.24_5

TABLE I-I continued

Atom	Orbital	Valence State of Atom	I_u (e.v.)	A_u (e.v.)	b_u (e.v.)	c_u (e.v.)	$X_u(1)$ (e.v.)	$X_u(2)$ (e.v.)
	p^*	$s^1p^1p^1$	6.47	1.37	9.02	-2.55	3.92	-1.18
	tr	$tr^1tr^1tr^1$	8.83	2.11	12.19	-3.36	5.47	-1.25
	te	$te^1te^1te^1$	8.17	2.58	10.96_5	-2.79_5	5.37_5	-0.21_5
Si	p	$s^2p^1p^1$	7.67	0.87	11.07	-3.40	4.27	-2.53
	s^*	$s^1p^1p^1p^1$	17.31	6.94	22.49_5	-5.18_5	12.12_5	1.75_5
	p^*	$s^1p^1p^1p^1$	9.19	2.82	12.37_5	-3.18_5	6.00_5	-0.36_5
	di	$di^1di^1\pi^1\pi^1$	14.06	4.07	19.05_5	-4.99_5	9.06_5	-0.92_5
	π	$di^1di^1\pi^1\pi^1$	9.18	2.20	12.67	-3.49	5.69	-1.29
	tr	$tr^1tr^1tr^1\pi^1$	12.61	3.20	17.31_5	-4.70_5	7.90_5	-1.50_5
	π	$tr^1tr^1tr^1\pi^1$	9.17	2.00	12.75_5	-3.58_5	5.58_5	-1.58_5
	te	$te^1te^1te^1te^1$	11.82	2.78	16.34	-4.52	7.30	-1.74
P	p	$s^2p^2p^1$	10.78	1.22	15.56	-4.78	6.00	-3.56
	p^*	$s^2p^1p^1p^1$	10.73	1.39	15.40	-4.67	6.06	-3.28
	tr	$tr^2tr^1tr^1\pi^1$	15.59	3.74	21.51_5	-5.92_5	9.66_5	-2.18_5
	π	$tr^2tr^1tr^1\pi^1$	11.64	1.80	16.56	-4.92	6.72	-3.12
	tr^*	$tr^1tr^1tr^1\pi^2$	15.18	3.76	20.89	-5.71	9.47	-1.95
	te	$te^2te^1te^1te^1$	14.57	3.24	20.23_5	-5.66_5	8.90_5	-2.42_5
S	p	$s^2p^2p^1p^1$	12.39	2.38	17.39_5	-5.00_5	7.38_5	-2.62_5
	tr	$tr^2tr^2tr^1\pi^1$	16.33	5.43	21.78	-5.45	10.88	-0.02

TABLE I-I continued

Atom	Orbital	Valence State of Atom	I_u (e.v.)	A_u (e.v.)	b_u (e.v.)	c_u (e.v.)	$X_u(1)$ (e.v.)	$X_u(2)$ (e.v.)
	π	$tr^2tr^2tr^1\pi^1$	12.70	2.76	17.67	-4.97	7.73	-2.21
	tr^{*}	$tr^2tr^1tr^1\pi^2$	16.27	5.49	21.66	-5.39	10.88	0.10
	te	$te^2te^2te^1te^1$	15.50	4.77	20.86_5	-5.36_5	10.13_5	-0.59_5
Cl	p	$s^2p^2p^2p^1$	15.08	3.73	20.75_5	-5.67_5	9.40_5	-1.94_5
Br	p	$s^2p^2p^2p^1$	13.10	3.70	17.80	-4.70	8.40	-1.00
I	p	$s^2p^2p^2p^1$	12.67	3.52	17.24_5	-4.57_5	8.09_5	-1.05_5

Notes:

a) I_u and A_u data from Table 14 of reference 27.

b) All parameters and electronegativities are for the Hinze-Whitehead-Jaffe function.

Several trends are evident in the data listed in Table I-I:

i) Since $I_u > A_u$ in all cases, the parameters b_u are all positive, and the parameters c_u are all negative.

ii) All the electronegativities for $n_u = 0$ and for $n_u = 1$ are positive, and in most cases the electronegativities for $n_u = 2$ are negative.

iii) The parameter b_u and the electronegativities generally increase as the ratio of s to p character of the orbital ϕ_u increases for a given atom. The values of c_u are much less dependent upon the s/p ratio than are b_u and the electronegativities. These trends are illustrated in Figure I-1 for carbon.

iv) For an orbital ϕ_u of given hybrid character, the absolute values of b_u and c_u, and of the electronegativities, generally increase from left to right in each row of the periodic table.

In the "molecular orbital" bond electronegativity function discussed previously, b_u and c_u are related to I_u and A_u by:

$$b_u = I_u \quad , \tag{140}$$

$$c_u = \frac{1}{4}(A_u - I_u) \quad . \tag{141}$$

The values of b_u in this case are the I_u listed in Table I-I, and the c_u for this function are equal to one-half of the c_u listed for the HWJ function.

Since the bond electronegativity parameters are readily evaluated, the ionic character of bonds formed by atoms, with valence states corresponding to those listed in Table I-I, may be calculated by the electronegativity equalization principle. In polyatomic molecules, however, the bonds formed by the orbitals ϕ_v, ϕ_w, ϕ_x can be polar. For such cases, the b_u and c_u calculated for neutral atoms cannot be used, and it is necessary to evaluate

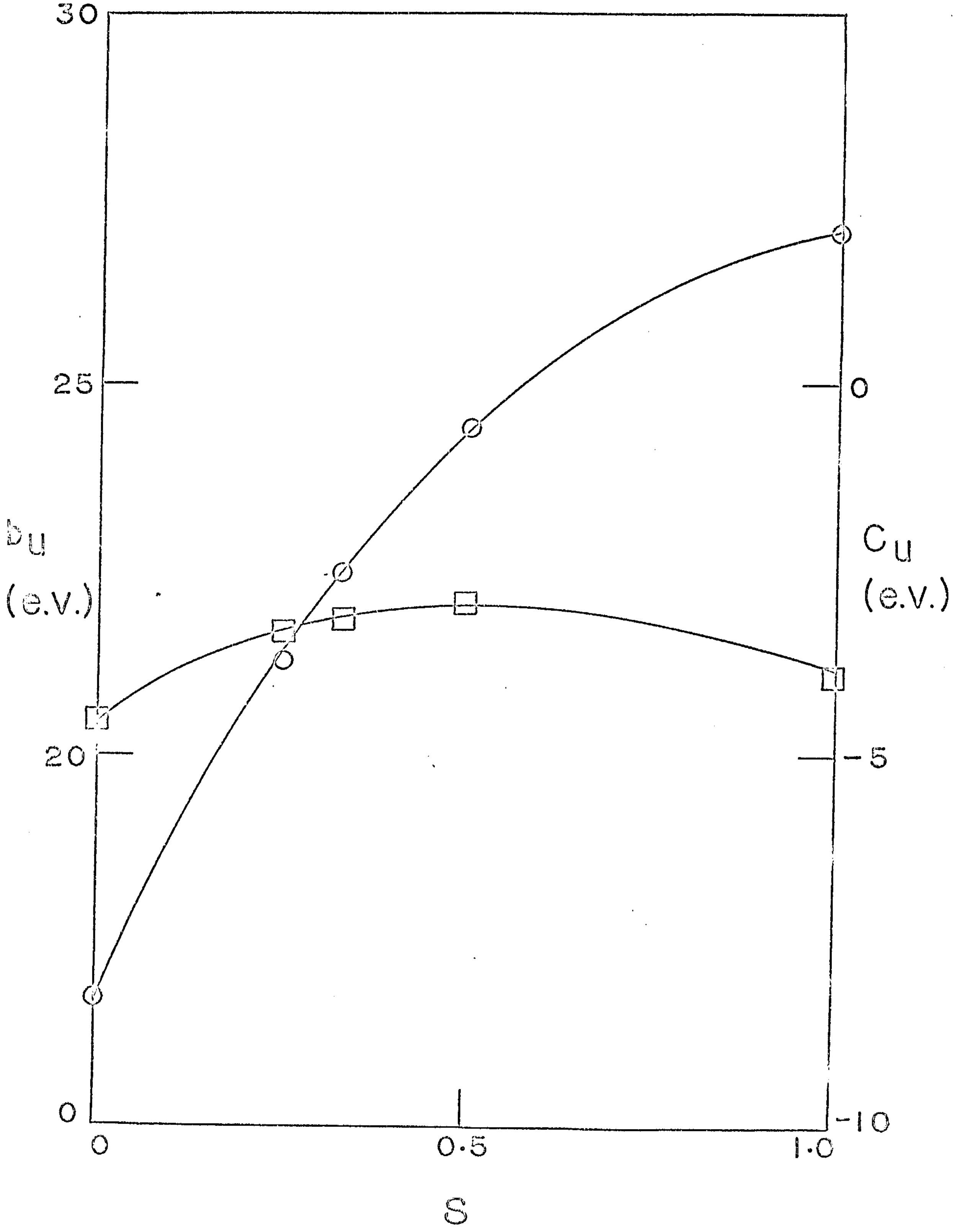
Figure I-1:

DEPENDENCE OF BOND ELECTRONEGATIVITY FUNCTION PARAMETERS ON s-p CHARACTER OF CARBON BONDING ORBITAL

Notes: ○ represents b_u

☐ represents c_u

s represents s character of s-p hybrid orbital


30
25
20
0
b_u
(e.v.)
C_u
(e.v.)
0
-5
-10
0
0·5
1·0
S

b_u and c_u as functions of the orbital charge densities n_v, n_w, and n_x. Hinze, Whitehead and Jaffe (8) developed a scheme whereby I_u and A_u can be calculated for non-integral values of n_v, n_w, and n_x. In their scheme, a large number of curves were drawn which connect the points at which the valence-state atom energy is known; that is, for integral n_u, n_v, n_w, and n_x. The energies of states with non-integral orbital charge densities were obtained by extrapolation of these curves to the points of interest. Unfortunately, the extrapolation procedure is quite complicated when n_u, n_v, n_w, and n_x vary independently. Even for the simple case of carbon in the te valence state, about twenty extrapolated curves are required to obtain the valence-state energy data for electronegativity equalization calculations (Figure 4, reference 8).

To simplify the graphical extrapolation procedure, an approximate method of determining I_u and A_u as a function of the charge densities n_v, n_w, and n_x has been developed in the present study. The basis of this approximation is that, for three orbitals ϕ_v, ϕ_w, and ϕ_x of the same hybrid character, both I_u and A_u are mainly dependent on the sum, T, of the charge densities of the other three orbitals

$$T = n_v + n_w + n_x \tag{142}$$

and only slightly dependent upon the manner in which the total charge density is divided among the orbitals. Both I_u and A_u can therefore be explicitly expressed in terms of T, and the need for the graphical extrapolation procedure is eliminated. The functional dependence of both I_u and A_u on T can be expressed as a three-term series in T:

$$I_u = \alpha_u + \beta_u T + \gamma_u T^2 \tag{143}$$

$$A_u = \delta_u + \epsilon_u T + \zeta_u T^2 \quad . \tag{144}$$

If the scheme discussed above is to be used in place of the graphical extrapolation procedure, two requirements must be met:

i) The values of I_u and A_u must be dependent upon the <u>sum</u> of the charge densities n_v, n_w, and n_x, but must be virtually independent of the individual values of each charge density.

ii) The variation of I_u and A_u with T must be given accurately by a three-term series in T, at least in the range of T which is to be used in the calculations. The degree to which requirements (i) and (ii) are met can be illustrated by the example of the (te te te te) valence state of carbon.

The ionization potentials and electron affinities for the tetrahedral orbitals of carbon have been calculated from the valence-state energy data (53) for all possible integral values of n_v, n_w, and n_x, and are listed in Table I-II. From the data for the three values of T(T = 2,3,4) for which more than one inequivalent combination of n_v, n_w, and n_x is possible, it can be concluded that the dependence of both I_u and A_u on the manner in which the T electrons are split up among the three orbitals is small (0.2 to 0.9 e.v.), compared to the changes of 5 to 12 e.v. in I_u and A_u which occur when T is altered by one electron. Since similar results are obtained for other atoms, requirement (i) above is met to a good degree of approximation. In general, however, requirement (i) is met only when the orbitals whose charge densities are included in T are of the <u>same</u> hybrid character.

The second requirement can be discussed by considering the plots of I_u and A_u against T given by the full curves in Figures I-2 and I-3 respectively.

TABLE I-II: Ionization Potentials and Electron Affinities for Carbon (tetetete)

Value of T	Orbital Charge Densities			I_u (e.v.)	A_u (e.v.)
	te_v	te_w	te_x		
0	0	0	0	58.47	36.70
1	0	0	1	41.64	22.67
2	0	1	1	26.70	11.38
2	0	0	2	27.62	12.18
3	1	1	1	14.61	1.34
3	0	1	2	15.41	1.60
4	1	1	2	4.57	-4.36
4	0	2	2	4.83	-3.68
5	1	2	2	-1.39	-4.77
6	2	2	2	-2.49	-3.51

Note:

a) Data from Table 18 of reference 27.

Figure I-2:

DEPENDENCE OF IONIZATION POTENTIAL ON CHARGE DENSITY T
FOR A CARBON te ORBITAL

Note: The charge density T, in electrons, represents the sum of the charges of the other three valence-shell orbitals.

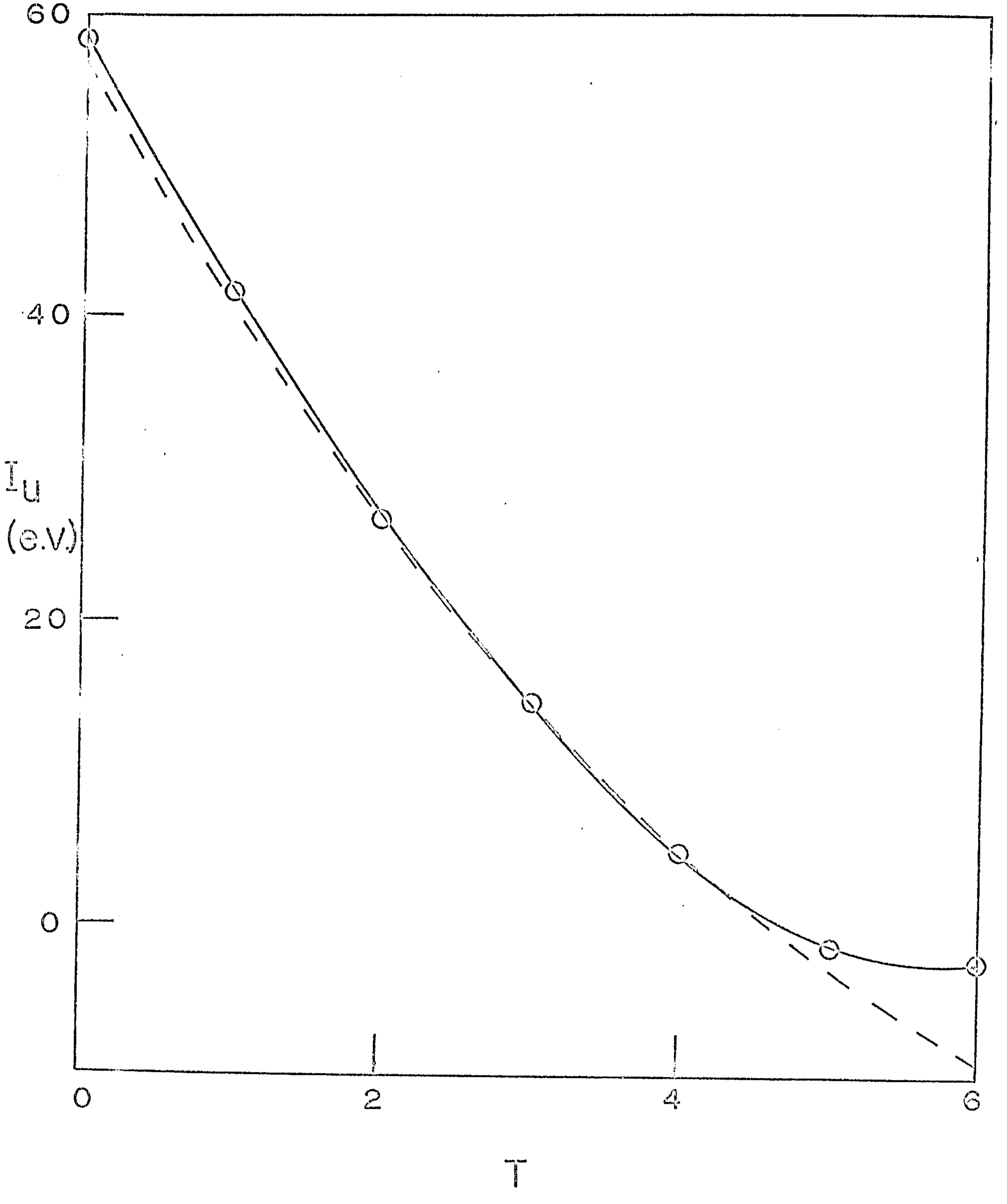
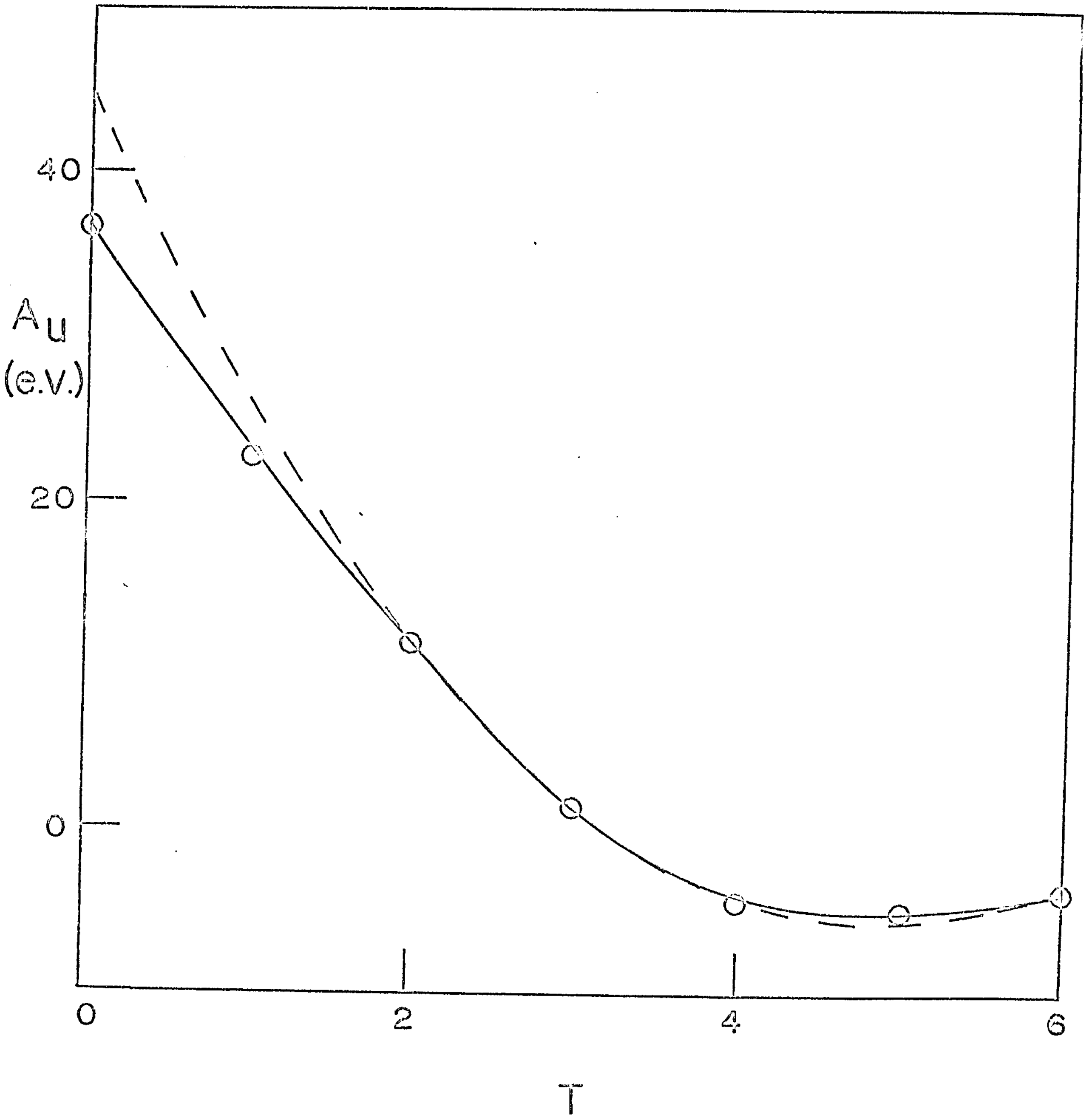

60
40
20
0
I_u (e.V.)
0
2
4
6
T

Figure I-3:

DEPENDENCE OF ELECTRON AFFINITY ON CHARGE DENSITY T

FOR A CARBON te ORBITAL


40
20
0
A_u
(e.v.)
0
2
4
6
T

These graphs have been constructed by using the I_u and A_u data in Table I-II. For T = 2,3, and 4, the I_u and A_u were chosen for the configuration in which the charge density is spread most evenly among the three orbitals, since this represents a more realistic distribution of the electron density which is encountered in the molecules to be considered. The dashed lines in Figures I-2 and I-3 illustrate the dependence of I_u and A_u on T which is predicted by the use of equations 143 and 144, when the parameters α_u, β_u, . . . ζ_u are evaluated by using I_u and A_u for T = 2, 3, and 4. The curves based on equations 143 and 144 fit the empirical variations of I_u and A_u with T very well between T = 2 and T = 4. The fit is less exact outside of this region. Similar results are obtained for other atoms and valence states. Requirement (ii) is met, therefore, provided that the parameters α_u, β_u, . . . ζ_u are evaluated for the range of T which is to be used in the electronegativity equalization calculations.

The parameters α_u to ζ_u of equations 143 and 144 have been calculated for the valence states and atoms of interest by use of the valence-state atom energy data (53), and are given in Table I-III. In several of the atomic valence states listed in this table, the charge densities summed in T are restricted to one or two orbitals of the set ϕ_v, ϕ_w, and ϕ_x in order that the charge density calculations can be simplified. The electron densities of orbitals which are <u>not</u> used in the summation are indicated by superscripts in the valence state listings.

All the parameters β_u and ϵ_u listed in Table I-III are negative, and in general $|\beta_u| >> |\gamma_u|$ and $|\epsilon_u| >> |\zeta_u|$. Hence both I_u and A_u decrease as T increases. This variation in the ionization potential and

TABLE I-III: Parameters for Ionization Potential and Electron Affinity Equations

Atom	Valence State of Atom	Orbital	Atomic Orbitals Included in T	Ionization Potential Parameters in e.v.			Electron Affinity Parameters in e.v.		
				α_u	β_u	γ_u	δ_u	ϵ_u	ζ_u
C	$te_u te_v te_w te_x$	te_u	$te_v te_w te_x$	57.067	-17.240	1.029	44.465	-20.879_5	2.168_5
C	$tr_u tr_v tr_w \pi_x^1$	tr_u	$tr_v tr_w$	40.853	-14.386_5	0.885_5	26.049	-16.226	2.089
C	$tr_u tr_v tr_w \pi_x^0$	tr_u	$tr_v tr_w$	60.373	-19.081	1.482	37.478	-15.125_5	1.151_5
C	$\pi_u tr_v tr_w tr_x$	π_u	$tr_v tr_w tr_x$	56.622	-19.109_5	1.318_5	45.392	-22.155_5	2.344_5
C	$di_u di_v \pi_w^1 \pi_x^1$	di_u	di_v	28.153	-11.282	0.554	12.965	-11.455_5	1.835_5
C	$\pi_u \pi_v^1 di_w di_x$	π_u	$di_w di_x$	38.481	-16.107	1.230	26.161	-17.724	2.348
N	$p_u p_v p_w s_x^2$	p_u	$p_v p_w$	48.229	-21.101	1.977	29.017	-19.920_5	2.901_5
N	$te_u te_v te_w te_x^2$	te_u	$te_v te_w$	53.752	-22.073_5	2.329_5	29.853	-17.699_5	2.424_5
N	$te_u te_v te_w te_x$	te_u	$te_v te_w te_x$	100.057	-28.169_5	1.971_5	70.500	-25.395	2.202
O	$p_u p_v p_w^2 s_x^2$	p_u	p_v	34.284	-18.906_5	1.900_5	15.207	-14.868_5	1.663_5
O	$te_u te_v te_w^2 te_x^2$	te_u	te_v	40.798	-17.451_5	1.044_5	20.427	-16.362_5	2.044_5
Si	$te_u te_v te_w te_x$	te_u	$te_v te_w te_x$	32.822	-6.778_5	-0.074_5	26.566	-8.872_5	0.314_5

TABLE I-III continued

Atom	Valence State of Atom	Orbital	Atomic Orbitals Included in T	Ionization Potential Parameters in e.v.			Electron Affinity Parameters in e.v.		
				α_u	β_u	γ_u	δ_u	ϵ_u	ζ_u
S	$p_u p_v p_w^2 s_x^2$	p_u	p_v	23.052	-11.661_5	1.002_5	11.033	-8.581_5	-0.072_5
S	$te_u te_v te_w^2 te_x^2$	te_u	te_v	29.248	-16.154	2.403	13.715	-8.826	-0.119

Note:

a) Based on data from Table 18 of reference 27.

electron affinity as the total charge density of the atom increases is due to the decrease in the effective nuclear charge experienced by electrons in orbital ϕ_u as the number of valence-shell electrons increases.

Shortly after the method described above was published in the literature (54), Cusachs and Reynolds (55) described a similar scheme which relates I_u and A_u to the total charge density of the atom. These authors attempted to fit I_u and A_u to the atom charge density by a number of different polynomials, and concluded that a three term series such as that used in the present study was sufficient to accurately represent the dependence of I_u and A_u on T.

Calculation Method for Polyatomic Molecules

The ionic character associated with a two-electron, two-centre bond can be calculated, according to the HWJ electronegativity equalization method, by the equation:

$$i_{ur} = \frac{X_r(1) - X_u(1)}{2(c_u + c_r)} \quad . \tag{145}$$

The parameters X(1) and c are determined from the ionization potential and electron affinity by equations 22 and 139 for the pair of atomic orbitals ϕ_r and ϕ_u which are singly-occupied in the valence state of the free atoms. If, however, ϕ_r and ϕ_u are atomic orbitals in a polyatomic molecule, I_u and A_u cannot be evaluated until the ionic characters of all the other bonds in the molecule are known. These other ionic characters, however, cannot be determined until i_{ur} has been evaluated.

Under these circumstances, the charge density distribution in a molecule must be determined by the SELF-CONSISTENT FIELD (SCF) procedure, a technique which is often used in molecular orbital problems. In the SCF method of determining the ionic characters in a polyatomic molecule, an initial value for the polarity of each bond is calculated by assuming that the ionic character of all the other bonds is zero. In the second set of calculations, the ionic character of each bond is calculated by assuming that the ionic character of each _other_ bond in the molecule is equal to that determined in the first set of calculations. The process is continued until the assumption, that the ionic character of each bond is identical to that found in the previous set of calculations, is correct. These ionic characters are then consistent with each other, and the charge distribution in the molecule is self-consistent.

The iterative technique of the SCF calculation can be illustrated by the example of the water molecule. Assuming that the oxygen atom is tetrahedrally hybridized, the ionic characters of each O-H bond may first be calculated by assuming the other O-H bond to have zero ionic character, whence $i_{OH} = 25.9\%$, the oxygen atom being negatively charged. The ionic character of the first O-H bond is then recalculated by assuming that the ionic character of the other O-H bond is 25.9%. The calculations are continued until the ionic character of the first O-H bond is equal to that obtained in the previous step in the calculation. The self-consistent i_{OH} is 18.3%; that is, if the second O-H bond is assumed to have $i_{OH} = 18.3\%$, the ionic character of the first bond will also be 18.3%.

Since i) a large number of molecules are to be considered,

ii) each molecule has, on the average, about five different bonds, and

iii) the number of iterative calculations required to achieve a self-consistent field is fairly large,

a computer programme was devised to do the computations for a given molecule, once certain information regarding the bonding in the molecule is available.

The main steps in the computer programme, which is written in Fortran IV language for the McGill IBM 7044 computer, are discussed below. Further details of the programme are discussed in Appendix I.

The steps in the computer programme are as follows:

i) Data giving the code number, atomic number, atomic orbital numbers, and initial charge density of the valence-state atomic orbitals, for each chemically inequivalent atom in the molecule, is punched on IBM cards and read in to the computer.

ii) Parameters α_u through ζ_u are defined for the bonding orbitals of each atom. The assignment of parameters is based on the atomic number assigned to the atom.

iii) The ionic character of each two-centre bond in the molecule is calculated, the required ionization potential and electron affinity for each orbital being calculated using charge densities of the previous iteration.

iv) The orbital charge densities, calculated from the ionic characters in (iii), are checked for self-consistency against the corresponding densities of the previous iteration.

v) If the orbital charge densities are found to be self-consistent, these densities are printed out by the computer, and the next molecule is then considered. If the orbital charge densities are not self-consistent, the programme returns to step (iii), and continues to execute steps (iii), (iv), and (v) until self-consistent charge densities are obtained. The orbital charge densities are assumed to be self-consistent when each is within ±0.000002 electron of the orbital electron density calculated in the previous iteration.

A typical set of results printed out for a molecule is given in Appendix I. All the orbital charge density distributions for polyatomic molecules discussed in the present study have been generated by the programme described above. The computer programme has been devised so that the following atoms and valence states may be considered: H(s), C(tetetete), C(trtrtrπ), C(didi$\pi\pi$), N(sppp), N(tetetete), O(sppp), O(tetetete), Si(tetetete), S(sppp), S(tetetete).

The $\alpha_u \longrightarrow \zeta_u$ parameters used in the calculations are those listed in Table I-III. The charge density distributions calculated in this manner will be termed "B.E.E.method" results (Bond Electronegativity Equalization Method).

I. 3. B. THE IONIC CHARACTERS OF SINGLE BONDS

The ionic character of single bonds between atomic orbitals ϕ_u and ϕ_v can be calculated for diatomic molecules directly by use of the bond electronegativity function parameters (Table I-I) and the ionic character equation:

$$i_{uv} = \frac{X_v(1) - X_u(1)}{2(c_u + c_v)} , \tag{146}$$

The ionic characters of the bonds in a common set of diatomic molecules have been calculated in this manner, and are listed in matrix form in Table I-IV. The halogen atoms considered are assumed to employ pure p orbitals in these bonds, whereas the alkali atoms and hydrogen are considered to use s orbitals. The sign convention used in Table I-IV is that the ionic character of the bond between atoms L and M in the diatomic molecule LM is positive if the bond polarity is $L^{\delta+} M^{\delta-}$, and is negative if the polarity is $L^{\delta-} M^{\delta+}$.

The ionic characters listed in Table I-IV were calculated by use of the Hinze-Whitehead-Jaffe bond electronegativity function. The corresponding ionic characters calculated by the molecular orbital bond electronegativity function are exactly twice those listed. For both bond electronegativity schemes, all the ionic characters considered are less than 100%.

The chemical bond between the atoms in an alkali halide molecule is usually considered to be almost completely ionic (3, 56). The ionic characters listed in Table I-IV for these molecules are larger than for any other molecules considered in the present study. The ionic characters for these molecules lie between 36 and 43 per cent, whereas the molecular orbital bond electronegativity function ionic characters range from 73 to 85 per cent. The

TABLE I-IV: Ionic Characters of Some Diatomic Molecules L-M

	Ionic Character (in Per Cent)					
Atom M Atom L	H	Li	F	Cl	Br	I
H	0.0	-23.4	16.6	9.2	5.5	4.2
Li	23.4	0.0	41.4	39.6	37.9	36.4
Na	24.9	3.3	42.6	41.2	39.8	38.3
F	-16.6	-41.4	0.0	-9.7	-14.1	-15.4
Cl	-9.2	-39.6	9.7	0.0	-4.8	-6.4
Br	-5.5	-37.9	14.1	4.8	0.0	-1.6
I	-4.2	-36.4	15.4	6.4	1.6	0.0

Notes:

a) Ionic characters in this and all subsequent tables were calculated by the HWJ electronegativity function.

b) $i_{LM} > 0$ for $M^{\delta-}$. Ionic characters in this and in subsequent tables are reported in per cent.

c) The H, Li, and Na atomic bonding orbitals are s-type; the halogen bonding orbitals are p-type.

corresponding range of bond polarities calculated by Pauling's method for this series of molecules is 43 to 91 per cent (3). The ionic characters of the lithium and sodium halides considered by Klopman and Ferreira by their semi-empirical methods generally clustered at about 84 per cent (38, 44).

The ionic characters calculated by all the methods mentioned above predict that the ionic characters of the alkali-halogen bonds formed by a given alkali atom decrease in the order of decreasing halogen atom electronegativity:

$$F > Cl > Br > I \quad .$$

The sodium-halogen bonds are slightly more ionic than the corresponding lithium-halogen bonds.

The ionic characters of LiH and NaH (in the sense $H^{\delta-}$) of 23.4% and 24.9% respectively, are lower than those of the alkali halides, and are much closer to those predicted by Pauling's method (26 and 30%), than to the results obtained from the M.O. bond electronegativity function (47 and 50%), or from Klopman's method (58.9 and 59.6%).

The ionic characters of the four hydrogen halides, HF, HCl, HBr, and HI, are in the sense $H^{\delta+}$, as expected from the trend in electronegativity of the atoms. The bond polarities listed for HF (16.6%), HCl (9.2%), and HBr (5.5%), are substantially smaller than those calculated by Pauling's, Klopman's and Ferreira's methods. The M.O. electronegativity function ionic characters for these systems lie about midway between the two extremes. The bond electronegativity methods predict a <u>lower</u> ionic character in hydrogen fluoride than in lithium hydride, whereas the schemes of Klopman and Pauling predict the reverse. It is interesting to note that Bader and Henneker (57) have established, on the basis of a detailed study of the Hartree-Fock wave functions, that the HF bond is less ionic than that of LiH.

The ionic characters of the hydrogen halides and alkali halides would be greater than those listed if any s orbital character were attributed to the halogen atom bonding orbitals. It is difficult to establish the hybridization of the bonding orbitals in diatomic molecules, since no bond angle data is available.

The remaining molecules listed in Table I-IV are the inter-halogen compounds FCl, FBr, FI, ClBr, ClI and BrI. The order of decreasing bond polarity is

$$\mathrm{FI} > \mathrm{FBr} > \mathrm{FCl} > \mathrm{ClI} > \mathrm{ClBr} > \mathrm{BrI}$$

This order is in complete agreement with that established by Ferreira's calculations, and is in disagreement with that predicted by Pauling's and Klopman's methods only in the relative ordering of ClBr and BrI. In all cases, the halogen atom of higher atomic number forms the positive end of the bond. Although little agreement exists between any of the calculation methods regarding the size of the ionic characters in these bonds, the molecular orbital electronegativity function bond polarities are fairly close to those calculated by Pauling's scheme for FCl, FBr, and FI, whereas the HWJ electronegativity function results for the remaining three molecules in the series are close to Pauling's results.

As discussed previously, the ionic characters of bonds in polyatomic molecules must be calculated by a self-consistent field procedure. When the bonds in such molecules are not very ionic, it is possible to estimate the approximate polarity of each bond by assuming that all the other bonds in the molecule are completely covalent. The ionic character of such bonds, which are isolated from the polarity effects of the neighbouring bonds, can be simply calculated by the method used for diatomic molecules. Such data will be referred to as being for "isolated bonds."

Although the ionic character of a large number of such "isolated bonds" may be easily calculated by means of the ionic character equation and the electronegativity parameters in Table I-I, the present discussion will be restricted to the bonds of most interest in organic chemistry; that is, the single bonds formed by carbon in its digonal, trigonal and tetrahedral valence states, and by the hydrogen atom, with the atoms of the first and second periods, and with the halogen atoms bromine and iodine. The ionic characters of such bonds have been calculated by the HWJ method, and are listed in matrix form in Table I-V. The sign convention used in Table I-V is the same as that for Table I-IV. The atoms involved in each sigma bond are listed with a subscript denoting the valence state of Table I-I which has been used in the calculations.

Four different types of orbitals corresponding to the atoms M are considered in Table I-V, with the orbital electronegativities X(1) increasing from left to right in the table:

$$X_{C_{di}}(1) > X_{C_{tr}}(1) > X_{C_{te}}(1) > X_H(1)$$

In all the bonds L-M, the charge density associated with a given atom L decreases from left to right in the table, since $X_M(1)$ increases in this direction. For example, the ionic character of the bonds formed by N_{te} are all polar in the sense $N^{\delta-}$, and the ionicity of these bonds decreases from 15.8% in N_{te}-H, to 4.0% in N_{te}-C_{di}.

The increase in $X_M(1)$ from hydrogen to C_{di} is responsible for the change in the sign of the ionic character in several rows of Table I-V.

TABLE I-V: "Isolated" Bond Ionic Characters

	Ionic Character (in Per Cent) of Bonds L-M			
Atom M Atom L	H_s	C_{te}	C_{tr}	C_{di}
H_s	0.0	3.1	6.1	11.9
Li_s	23.4	27.3	31.1	39.0
Be_{di}	11.7	15.3	18.8	25.8
B_{tr}	3.7	7.1	10.4	16.9
C_{di}	-11.9	-8.8	-5.8	0.0
C_{tr}	-6.1	-3.0	0.0	5.8
C_{te}	-3.1	0.0	3.0	8.8
$N_p^{\star}$	-0.7	2.3	5.3	11.1
N_{tr}	-20.1	-17.0	-14.0	-8.4
$N_{tr}^{\star}$	-18.6	-15.5	-12.4	-6.7
N_{te}	-15.8	-12.7	-9.7	-4.0
O_p	-8.8	-5.9	-3.0	2.5
O_{tr}	-30.9	-28.0	-25.2	-20.1
$O_{tr}^{\star}$	-30.2	-27.3	-24.4	-19.3
O_{te}	-25.9	-23.1	-20.2	-15.1
F_p	-16.6	-13.7	-10.9	-5.7
Na_s	24.9	28.8	32.6	40.4
Mg_{di}	16.4	20.1	23.8	31.3
Al_{tr}	8.7	12.5	16.3	23.6
Si_{te}	-0.6	3.0	6.5	13.3

TABLE I-V continued

	Ionic Character (in Per Cent) of Bonds L-M			
Atom M Atom L	H_s	C_{te}	C_{tr}	C_{di}
$P_p^{\star}$	5.0	8.5	11.4	18.4
P_{te}	-7.2	-3.8	-0.5	5.8
S_p	-0.9	2.5	5.9	12.4
S_{tr}	-15.6	-12.0	-8.5	-2.0
$S_{tr}^{\star}$	-15.7	-12.1	-8.6	-2.0
S_{te}	-12.6	-9.0	-5.5	1.0
Cl_p	-9.2	-5.8	-2.5	3.8
Br_p	-5.5	-1.9	1.7	8.4
I_p	-4.2	-0.5	3.0	9.8

Note:

a) Valence states of the atoms correspond to those listed in Table I-I.

The atoms L are listed down the table in order of increasing atomic number within each period, and are listed therefore in the approximate order of increasing electronegativity within each period. The bonds formed by hydrogen and the Group 1, 2, and 3 atoms (and $P_p^{\star}$) are all polar in the sense $H^{\delta-}$, whereas the rest of the hydrogen bonds have $H^{\delta+}$. Since the value of $X_{C_{te}}(1)$ is slightly greater than $X_H(1)$, all the atoms forming hydrogen bonds with $H^{\delta-}$ form C_{te} bonds with $C_{te}^{\delta-}$. In addition, there are several atoms ($N_p^{\star}$, Si_{te}, S_p) which form the negative end of their bonds with hydrogen, but form the positive end of their bonds to C_{te}, since the electronegativities of these three atoms lie between those of H and C_{te}. Similar trends occur in the bonds formed by C_{tr} and C_{di}.

On the basis of both empirical studies of inductive effects in organic molecules (58), and semi-empirical quantum chemistry calculations (3, 38), it is usually supposed that the single bonds formed by C_{te} and H with nitrogen, oxygen, fluorine, chlorine, and bromine are polar in the sense $C_{te}^{\delta+}$ and $H^{\delta+}$. These observations are confirmed by the results in Table I-V for such bonds. The only exception lies in the calculated results for the $N_p^{\star}$ - C_{te} bond, in which there is a small charge transfer of 2.3% of an electron from the nitrogen to the carbon. The bonds C-N, C-O, N-H and O-H will be considered further in the analysis of self-consistent field electronegativity equalization calculations on hydrocarbon derivatives (Part I. 3. D).

According to Pauling's electronegativity scheme, C-S and C-I bonds are expected to have zero ionic character. The data in Table I-V indicate that, according to the electronegativity equalization method, these bonds possess small ionic characters in the sense $C^{\delta-}S^{\delta+}$ and $C^{\delta+}I^{\delta-}$ if pure p orbitals are used by sulphur and iodine in bonding to te hybridized carbon atoms. Self-consistent field electronegativity calculations on the molecule CH_3SH indicate that the $C_{te}^{\delta-}$ $S_p^{\delta+}$ polarity is retained in thioalcohols, but the ionic character of the bond is reduced from 2.5% to about 1.3%. Both the "isolated" S_p-H bond, and that in CH_3SH, have $H^{\delta+}$, with the ionic character in the isolated S-H bond, 0.9%, increasing to 1.4% in CH_3SH.

In Pauling's electronegativity scheme, silicon-hydrogen bonds are expected to have 3% ionic character in the direction $H^{\delta-}$. The isolated bond ionic character listed for a Si_{te}-H bond is -0.6%, and is in the opposite sense to that predicted by Pauling. SCF electronegativity calculations on the molecule SiH_4 indicate that the Si-H bond polarity is smaller than that of the isolated bond, decreasing from 0.6% to 0.3%. The electronegativity equalization results agree with Pauling's scheme regarding the direction of the charge transfer in the Si_{te}-C_{te} bond, with $C_{te}^{\delta-}$. The ionic character for this bond as predicted by the Pauling, "isolated" bond, and SCF electronegativity methods are 12, 3.0, and 0.5% respectively.

Since it is difficult to determine the ionic character of a bond experimentally, attempts to establish the validity of the electronegativity equalization method by comparing isolated bond polarities with empirical observations are limited. Much more experimental data is available concerning the transmission of inductive effects within a molecule, relative acidities and basicities of different series of molecules, the changes in the polarity of a given bond in different molecular environments, and the inductive stabilization of ions, etc. than is known about the absolute magnitudes of the polarities of different chemical bonds.

For this reason, the charge distributions in a large series of organic molecules have been computed by the self-consistent field bond electronegativity equalization method. These charge distributions will be listed and discussed in the next sections. All the SCF electronegativity equalization calculations to be discussed have been generated by using the HWJ method. This method, rather than the molecular orbital bond electronegativity function, was used because:

i) For bonds of low ionic character, such as those to be considered, the analysis given above has not been able to show which of the two calculation methods is superior.

ii) The ionic characters of the two methods will parallel each other, since the isolated bond ionic characters differ by a factor of two in all cases.

iii) The HWJ scheme has been used by several workers in previous inductive effect studies, whereas the molecular orbital version has not yet been employed. It is one of the main purposes of this work to establish the validity of the HWJ method in chemical systems.

The charge distributions in various hydrocarbon molecules and their ions are reported in the next section, and the inductive effects in substituted alkanes are discussed in the section following it. Correlations of the calculated atom charge densities with nuclear magnetic resonance chemical shifts, and some conclusions concerning the electronegativity equalization method are discussed in later sections.

I. 3. C CHARGE DISTRIBUTIONS IN HYDROCARBONS AND HYDROCARBON IONS

The ionic characters listed in Table I-V for carbon-hydrogen and carbon-carbon bonds are consistent with the electronegativity order

$$X_{C_{di}}(1) > X_{C_{tr}}(1) > X_{C_{te}}(1) > X_H(1) \quad .$$

All the C-C and C-H bond polarities are small, but definite and regular variations in these quantities are found for different molecules when self-consistent field charge densities are established by the B.E.E. method. These variations are discussed and analyzed in this section of the thesis.

Charge Distributions in Neutral Alkane Molecules

Many common organic molecules are derivatives of the series of saturated hydrocarbons termed the alkanes. In both branched and unbranched alkane chains, and in many alkane derivatives, the H-C-H, C-C-H, and C-C-C bond angles are very close to tetrahedral (109.5°), and the carbon atoms in such molecules are usually assumed to use four valence-shell tetrahedral (te) orbitals for bonding. Due to the lack of precise information concerning deviations from tetrahedral bond angles in the alkanes, the B.E.E. method calculations reported herein have been accomplished by assuming that each bonding orbital of carbon in the alkanes and alkane derivatives is exactly te in character. All the hydrogen atoms are assumed to use 1s atomic orbitals for bonding.

The charge distributions calculated by the bond electronegativity equalization method for the neutral n-alkanes CH_4 through $C_{10}H_{22}$, and for some branched alkanes, are listed in Tables I-VI through I-IX. The numbering scheme used in these tables has the bonds associated with the terminal methyl groups in the n-alkanes denoted as C_1, those associated with the adjoining methylene group as C_2, and similarly along the chain.

The C-H bond ionic characters in these alkanes range from 1.4% to 2.3% (Table I-VI), all in the sense $C^{\delta-} H^{\delta+}$. The C-H bond polarity is generally lower than that calculated for an isolated C_{te}-H bond (3.1%), since the electronegativity of each carbon te hybrid orbital is lowered by the increase in the total electronic charge density of the other carbon orbitals. Thus the average net positive charge on each hydrogen atom is approximately +0.02 electron, rather than +0.03 electron predicted by the isolated bond data.

Although the calculated C-H bond polarities in the n-alkanes are very small, definite variations in i_{CH} are found when chemically inequivalent C-H bonds in the same molecule, or in different alkane molecules, are compared. In each n-alkane, the C-H bond ionic characters increase as the number of carbon atoms between the one considered, and that at the end of the molecule, increases (Table I-VI). For example, the C-H bond polarities in n-decane (m = 10 in the table) increase in the order 1.90, 2.15, 2.23, 2.25, and 2.25% toward the "centre" of the molecule. Within each n-alkane, the difference in i_{CH} between successive atoms along the chain decreases toward the centre of the molecule.

A comparison of the i_{CH} between different n-alkanes for a given position (e.g. C_1) shows that the C-H bond polarity generally increases as the length of the chain increases, the magnitude of this increase between successive n-alkanes decreasing as the chain length increases (Table I-VI). Since an increase in the chain length by one unit is equivalent to replacing a terminal hydrogen atom by a methyl group, and since by this replacement all the C-H

TABLE I-VI: Carbon-Hydrogen Bond Ionic Characters in the n-Alkanes C_mH_{2m+2}

Value of m	i_{C_1H}	i_{C_2H}	i_{C_3H}	i_{C_4H}	i_{C_5H}
1	1.478				
2	1.786				
3	1.868	2.048			
4	1.892	2.123			
5	1.899	2.144	2.196		
6	1.901	2.151	2.218		
7	1.901	2.152	2.224	2.239	
8	1.902	2.153	2.226	2.245	
9	1.901	2.153	2.226	2.247	2.251
10	1.902	2.153	2.226	2.248	2.253

Note:

a) In this and subsequent tables, all $i_{CH} > 0$ for $H^{\delta+}$, and i_{CH} is reported as a percentage.

bond ionic characters in the molecule are increased, the methyl group effectively <u>WITHDRAWS</u> electron density relative to hydrogen in the n-alkanes. This withdrawal of charge density occurs because, for this series of molecules, $X_{CH_3}(1) > X_H(1)$. Thus, for H and CH_3 bonded to a methyl group,

$$X_H(1) = 7.175 \text{ e.v.} \quad \text{whereas} \quad X_{CH_3}(1) = 7.473 \text{ e.v.}$$

The electronegativity of a methyl group is also greater than that of hydrogen in the branched alkanes, including the methylated methane series, $(CH_3)_{4-m}\,CH_m$. A decrease in m by one unit is equivalent to replacing one hydrogen atom in the CH_m unit by a methyl group, and leads to an increase in the net positive charge on the hydrogen atoms of the central carbon atom (Table I-VII). There is also a smaller corresponding increase in the net positive charge of the H atoms of the methyl groups.

A study of the self-consistent field electronegativities in the neutral alkanes considered indicates that, in general:

$$X_{\text{tertiary}}\ {}_{C}(1) > X_{\text{secondary}}\ {}_{C}(1) > X_{\text{primary}}\ {}_{C}(1) > X_H(1)\ .$$

The ionic characters of C-H bonds for tertiary carbon atoms are then greater than those for hydrogen atoms bonded to secondary carbon atoms, which in turn are greater than i_{CH} for hydrogen atoms on a primary carbon atom. This trend in i_{CH} for the alkanes is identical to that established in earlier electronegativity equalization calculations by Ferreira (59).

For the "isolated" carbon-carbon bond formed by two tetrahedrally-hybridized carbon atomic orbitals, $i_{CC} = 0$. Since the carbon atoms in the n-alkanes are not all equivalent, the ionic characters of the C-C bonds are usually non-zero. The calculated range of i_{CC} for these molecules is 0.0 to 0.6% (Table I-VIII). Within an n-alkane, i_{CC} decreases gradually toward the

TABLE I-VII: Charge Distributions and Chemical Shifts in Some Branched Alkanes

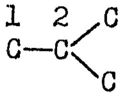
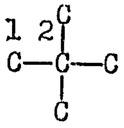
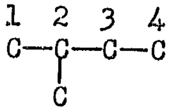
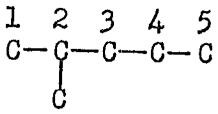
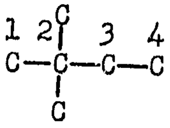
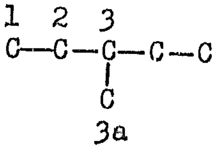
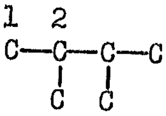
Alkane	Position	i_{CH} %	^{1}H N.M.R. Chemical Shift in p.p.m.	Carbon Atom Net Charge in Electrons	^{13}C N.M.R. Chemical Shift in p.p.m.
Methane	1	1.478	6.95$^{(b)}$	−0.05912	130.8
Ethane	1	1.786	6.32$^{(b)}$	−0.05358	122.8
Propane	1	1.868	6.27	−0.05210	113.10
1 2 C—C—C	2	2.048	5.84	−0.04887	112.62
Isobutane	1	1.940	6.27	−0.05083	104.35
	2	2.274	5.43	−0.04483	103.52
Neopentane	1	2.001	6.25	−0.04971	97.23
	2	—	—	−0.04130	100.8
2-Methylbutane	1	1.961	6.28	−0.05044	106.67
	2	2.342	5.8	−0.04361	98.80
	3	2.187	6.00	−0.04638	96.88
	4	1.912	6.29	−0.05132	117.18
2-Methylpentane	1	1.967	6.29	−0.05033	106.17
	2	2.362	5.8	−0.04325	100.9
	3	2.260	6.0	−0.04508	86.9
	4	2.163	6.0	−0.04681	108.0
	5	1.905	6.30	−0.05145	114.57

TABLE I-VII continued

Alkane	Position	i_{CH} %	^{1}H N.M.R. Chemical Shift in p.p.m.	Carbon Atom Net Charge in Electrons	^{13}C N.M.R. Chemical Shift in p.p.m.
2,2-Dimethylbutane	1	2.021	6.32	-0.04936	99.77
	2	—	—	-0.04019	98.26
	3	2.243	5.93	-0.04538	92.02
	4	1.930	6.33	-0.05100	120.03
3-Methylpentane	1	1.918	6.29	-0.05120	117.43
	2	2.207	6.0	-0.04603	99.4
	3	2.409	5.8	-0.04240	92.0
	3a	1.982	6.29	-0.05006	110.10
2,3-Dimethylbutane	1	1.979	6.32	-0.05011	109.35
	2	2.400	5.8	-0.04255	94.6

Notes:

a) All N.M.R. chemical shifts are relative to benzene. Unless otherwise indicated, all N.M.R. data is from reference 80.

b) Calculated from N.M.R. data in reference 84.

TABLE I-VIII: Carbon-Carbon Bond Ionic Characters in the n-Alkanes C_mH_{2m+2}

Value of m	$i_{C_1C_2}$ %	$i_{C_2C_3}$ %	$i_{C_3C_4}$ %	$i_{C_4C_5}$ %
2	0.000			
3	0.396			
4	0.508	0.000		
5	0.541	0.114		
6	0.550	0.148	0.000	
7	0.553	0.158	0.033	
8	0.554	0.160	0.043	0.000
9	0.554	0.161	0.046	0.010
10	0.554	0.161	0.047	0.013

Note:

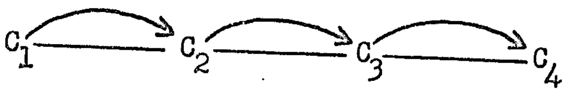
a) In each C-C bond, $i_{CC} > 0$ if the carbon atom nearest the centre of the chain is the negative end of the C-C bond.

centre of the chain, as does the difference in i_{CC} between successive carbon atoms. The negative (δ^-) end of each carbon-carbon bond is the carbon atom nearest the middle of the chain. The trends noted above may be illustrated using n-hexane (m = 6) as an example. Here, the terminal carbon-carbon bond (C_1-C_2) has $i_{CC} = 0.55\%$ (C_2 is δ^-); the i_{CC} of the C_2-C_3 bond is 0.15% (C_3 is δ^-); the i_{CC} of the C_3-C_4 bond is 0.00%. The changes between successive bonds are 0.40% for the C_1-C_2 and C_2-C_3 pair, and 0.15% for the C_2-C_3 and C_3-C_4 pair.

Replacing a terminal hydrogen atom by a methyl group in an n-alkane extends the hydrocarbon chain by one unit, and this change is expected to withdraw electron density toward the point of substitution, since $X_{CH_3}(1) > X_H(1)$ in the alkanes. This is confirmed by the i_{CC} results listed in Table I-VIII, and it may be illustrated by the following example. The charge transfer directions for the C-C bonds in propane are

.

If the terminal H atom is replaced by CH_3, electron density is withdrawn toward the point of substitution, and electron density shifts illustrated below are superimposed on those shown above:



,

The two effects are in the same direction for the C_1-C_2 bond, and $i_{C_1-C_2}$ increases from propane to n-butane (Table I-VIII). The effects are opposed for the C_2-C_3 bond, and exactly cancel each other. In the C_3-H bond, which is converted to C_3-C_4 in n-butane, the change due to the second effect is not sufficient to overcome the first, since C_3 forms the negative end of the

C_3-C_4 bond.

The ionic characters of the C-H and C-C bonds in the n-alkanes can be combined to give the net charge for each carbon atom (Table I-IX). According to the electronegativity equalization calculations, all the carbon atoms in the n-alkanes bear small net NEGATIVE charges of the order of -0.05 electron. The net negative charge of a carbon atom at a given position (e.g. C_1) decreases as the chain length increases, since the methyl group which is added to lengthen the chain withdraws electron density relative to the hydrogen atom which is replaced. In an n-alkane molecule, the carbon atom net charges decrease as the chain centre is approached, in contrast to the changes in C-H bond polarity. Although the contribution to the electron density of each carbon atom from each C-H bond increases as the chain centre is approached, this trend is opposed by the larger changes in C-C bond polarities in the same sequence. The change in carbon atom net charge between successive atoms decreases toward the middle of the hydrocarbon chain (Table I-IX).

The carbon atom net negative charges for some branched alkanes, including the methylated methanes series $(CH_3)_{4-m}\ CH_m$, are listed in Table I-VII. In the methylated methanes, the central carbon atom charges decrease when m is decreased by one unit. Similar, but smaller, charge density changes are found for the carbon atoms of the methyl group.

It is interesting to compare the n-alkane charge distributions which are calculated by the B.E.E. method with those determined by molecular orbital methods. Sandorfy (60) developed three approximate LCAO-MO techniques for treating the bonds in saturated hydrocarbons:

i) In his "C" approximation, only the carbon-carbon bonds are considered. The carbon atoms in neutral n-alkanes are found to have zero net charge

TABLE I-IX: Carbon Atom Net Charges in the Alkanes C_mH_{2m+2}

Value of m	Net Charge (in Electrons) of the Carbon Atoms				
	C_1	C_2	C_3	C_4	C_5
1	-0.05912				
2	-.05358				
3	-.05210	-0.04887			
4	-.05168	-.04754			
5	-.05156	-.04715	-0.04622		
6	-.05152	-.04703	-.04583		
7	-.05151	-.04700	-.04572	-0.04545	
8	-.05151	-.04699	-.04569	-.04534	
9	-.05150	-.04699	-.04568	-.04530	-0.04522
10	-.05151	-.04699	-.04567	-.04529	-.04519

in this approximation.

ii) In the "CH" approximation, each te hybrid orbital of carbon is considered explicitly if it is bonded to another carbon orbital, whereas each bond between a carbon te orbital and a hydrogen atom is treated by considering it as a group orbital. Sandorfy calculated the charge distributions for propane, n-butane, n-pentane, and 2-methylbutane by this approximation (60). The total charge associated with each C – H bond was found to be slightly less than 2 electrons, and that associated with each C-C bond slightly more than 2 electrons. The terminal C-C bonds were slightly polar, with the carbon atom nearest the molecular centre being the negative end of the bond, in agreement with the B.E.E. results. The other C-C bonds in propane, n-butane and n-pentane were found to have zero net polarity (60).

iii) In the "H" approximation, all the valence-shell orbitals of the carbon and hydrogen atoms are considered explicitly in a molecular orbital method that does not neglect overlap integrals. The "local" charges calculated by Sandorfy using this approximation were such that each C-H bond is polar in the sense $C^{\delta-}$ $H^{\delta+}$, the central C-H bonds being more polar than the terminal C-H bonds. The C-C bond in propane was found to be polar with the central atom being the negative end of the bond. It is remarkable that these propane molecule charge density trends, which were calculated by an MO method which does not treat electron repulsions explicitly but which does allow for delocalization of the molecular orbitals, agree so well with those found by using the B.E.E. method, which treats intra-atomic electron repulsions but makes no allowance for any delocalization effects.

Hoffmann(61) has devised an "Extended Huckel Theory"(EHT) Method for sigma and pi electron systems. The EHT method charge density results for saturated hydrocarbons agree with those of the present study in the following respects:

i) All the carbon atoms in the n-alkanes possess partial NEGATIVE charges.

ii) Within each n-alkane molecule, the TERMINAL carbon atom has the largest negative charge.

iii) The carbon atom in methane is the most negatively charged of all the carbon atoms in the n-alkanes.

iv) The electronic density of the central carbon atom in the methylated methanes series decreases as the number of methyl groups increases.

The charge density distributions in the alkanes calculated by the EHT method disagree with the B.E.E. method results in the following respects:

i) The magnitude of the carbon atom partial negative charges calculated by EHT are about four to ten times as large as the corresponding B.E.E. method net charges.

ii) There is little correspondence between the trends in carbon charge within each molecule calculated by the two methods, except for that noted in (ii) above.

Pople, Santry and Segal (62) have also developed an approximate LCAO-MO method for saturated molecules. This technique includes electron repulsions explicitly, and should therefore represent an improvement over the methods of Sandorfy and Hoffmann. Pople and Segal (63) recently applied the "CNDO" version of the technique of Pople et al.(62) to a variety of saturated methane and ethane derivatives including the two parent hydrocarbons themselves. The magnitude of the hydrogen atom net charges calculated by the CNDO method (about +0.034 electron) are about twice as large as those from B.E.E. method (about +0.017 electron), and the direction of the change in the hydrogen charge from methane to ethane predicted by the two methods disagree. Both methods predict the same sign for the net charges of the carbon atoms in these molecules, and the same direction of change in the C net charge from methane to ethane.

It will be interesting to compare the trends in C and H atom net charges calculated by the B.E.E. method with those from the CNDO procedure when more results from the latter method are available.

Sigma Bonds in Unsaturated Hydrocarbons

Since the electronegativity of a singly-occupied s-p hybrid atomic orbital of carbon increases linearly with the s character of the orbital (27), then

$$X_{\text{digonal }C}^{(1)} > X_{\text{trigonal }C}^{(1)} > X_{\text{tetrahedral }C}^{(1)} .$$

Hence the polarities of C-H bonds in which the hydrogen atoms are bonded to unsaturated carbon atoms are usually greater than those of saturated C-H bonds, and the $C_{di}-C_{te}$ and $C_{tr}-C_{te}$ bonds are much more polar than the C-C bonds in the alkanes. For example, the "isolated" bond polarities for $C_{di}-C_{te}$ and $C_{tr}-C_{te}$ are 8.8 % and 3.0% respectively compared to 0.0% for $C_{te}-C_{te}$, and the isolated $C_{di}-H$ and $C_{tr}-H$ bond ionic characters are 11.9% and 6.1% compared to 3.1% for $C_{te}-H$. The direction of charge transfer in these bonds is toward the orbital of the more electronegative carbon atom.

The charge distributions for several unsaturated hydrocarbons have been calculated by the B.E.E. method and are listed in Table I-X. Since the $H-C_{tr}-H$, $C_{te}-C_{tr}-H$ and $C_{tr}-C_{tr}-C_{te}$ bond angles in the alkenes considered are close to 120° (64), pure tr hybrid orbitals have been assumed for the sigma orbitals of the unsaturated carbon atoms in these molecules. The $H-C_{di}-C_{di}$ and $C_{te}-C_{di}-C_{di}$ bond angles are close to 180° (64), and pure di hybridization has been assumed for the sigma-bonded orbitals of the unsaturated carbon atoms in the alkynes. In all the unsaturated neutral molecules considered, the p_{π} orbital charge densities are equal to one electron due to the molecular symmetry.

The $C_{tr}-H$ bond polarities in the ethylenes and benzenes range from 4.5% to 6.1% according to the B.E.E. method calculations, whereas the ionic character of the $C_{di}-H$ bond in acetylene is 11.92% (Table I-X). The order of C-H bond polarities for the "isolated" bond is then unaltered when self-consistent field calculations are used:

TABLE I-X: Charge Density Data for Some Unsaturated Hydrocarbons

Molecule	i_{CH} of $H{-}C_{tr}$ Bond in %	i_{CC} of $C_{tr}{-}C_{te}$ Bond in %	i_{CH} of $H{-}C_{te}$ Bonds in %	Unsaturated Carbon Atom Net Charge in Electrons
$H_2C{=}CH_2$	4.520	—	—	−0.09041
$CH_3CH{=}CHCH_3$	4.604	4.277	2.678	−0.08881
$(CH_3)_2C{=}C(CH_3)_2$	—	4.377	2.699	−0.08754
(c)(b) $CH_3CH_2CH{=}CHCH_2CH_3$	4.688	4.032	2.883 (b) 2.132 (c)	−0.08721
Benzene	6.081	—	—	−0.06081
Hexamethylbenzene	—	6.306	3.102	−0.06306

Molecule	i_{CH} of $H{-}C_{di}$ Bond in %	i_{CC} of $C_{di}{-}C_{te}$ Bond in %	i_{CH} of $H{-}C_{te}$ Bonds in %	Unsaturated Carbon Atom Net Charge in Electrons
$HC{\equiv}CH$	11.920	—	—	−0.11920
$CH_3C{\equiv}CCH_3$	—	13.779	4.665	−0.13779
(c)(b) $CH_3CH_2C{\equiv}CCH_2CH_3$	—	13.731	4.715 (b) 2.710 (c)	−0.13731

Notes: a) The $H{-}C_{tr}$, $H{-}C_{di}$, $C_{te}{-}C_{tr}$, $C_{te}{-}C_{di}$ bonds are polar in the sense that the unsaturated carbon atom forms the negative end of the bond. The $C_{te}{-}H$ bonds are all polar in the sense $C^{\delta-}\ H^{\delta+}$.

b) "Methylene" unit C-H bond.

c) "Methyl" unit C-H bond.

$$ {}^{i}C_{di}\text{-}H > {}^{i}C_{tr}\text{-}H > {}^{i}C_{te}\text{-}H \quad . $$

The C-H bond ionic characters increase in the sequence ethane, ethylene, acetylene, in agreement with the experimental order of hydrogen atom acidity (65). The partial charges on hydrogen in these three molecules (+0.018, +0.045, and +0.119 respectively) are in good agreement with those calculated by the CNDO method (+0.033, +0.046, +0.107 respectively) (63).

The relative inductive effects of CH_3 and H in the mono-alkenes is similar to that found for the alkanes, since replacement of H in $H_2C = CH_2$ by CH_3 groups decreases the negative charge of the unsaturated carbon atoms and increases the C_{tr}-H bond polarity (Table I-X). Methyl groups are, however, electron releasing relative to hydrogen in the benzenes and acetylenes, since the calculated net charges of the unsaturated carbon atoms in hexamethylbenzene and dimethylacetylene are greater than those in benzene and acetylene respectively (Table I-X). The reversal of inductive effects of alkyl groups and hydrogen atoms in these molecules will be analyzed later.

The C_{di}-C_{te} and C_{tr}-C_{te} bond ionic characters in the substituted ethylenes, benzenes and acetylenes are listed in Table I-X. As expected from the isolated bond polarities, these C-C bonds are more ionic than saturated C-C bonds, and C_{te} forms the positive end in each case. The effect of the unsaturated atoms is transmitted to the C_{te}-H bonds, which are more ionic in the sense $H^{\delta+}$ than those of the alkanes.

Variations in the Electronegativities of Groups

In electronegativity equalization calculations, the ionic character of a bond between orbitals ϕ_u and ϕ_v is determined by the DIFFERENCE between $X_u(1)$ and $X_v(1)$, and by the SUM of the parameters c_u and c_v. For an alkyl group, $X_u(1)$ and c_u are a function of T, the total electronic charge of the other valence-shell orbitals of the same atom as ϕ_u. From the data in Table I-III for C_{te} orbitals and from the definitions of $X_u(1)$ and c_u in equations 137 and 139, the dependence of $X_u(1)$ and c_u on T may be obtained for a te orbital of carbon:

$$X_u(1) = 50.766 - 19.060\,T + 1.599\,T^2 \quad , \qquad (147)$$

$$c_u(1) = -6.301 - 1.820\,T + 0.570\,T^2 \quad . \qquad (148)$$

The rate of change of $X_u(1)$ and $c_u(1)$ with T for a "neutral" carbon atom (i.e. T = 3) can be established by differentiation of the functions above with respect to T at T = 3:

$$\left(\frac{d\ X_u(1)}{d\ T}\right)_{T=3} = -9.47 \quad , \qquad (149)$$

$$\left(\frac{d\ c_u}{d\ T}\right)_{T=3} = +1.60 \quad . \qquad (150)$$

The net effect of the variation of $X_u(1)$ and c_u with T is that the electronic charge density, n_u, of orbital ϕ_u will <u>decrease</u> as the total charge density, T, in the other orbitals of the same atom increases. Since this effect is due mainly to the dependence of $X_u(1)$ on T, the inductive effects of groups can be analyzed by considering their $X_u(1)$ values.

Consider the group R_3C- which is bonded to an identical group $-CR_3$. Since the groups are identical, $i_{CC} = 0$, and n_u, the electronic density of the bonding orbital of R_3C-, is one. If R_3C- is bonded to a group $-CR'_3$ of

HIGHER electronegativity, then $n_u < 1$. The electronegativity of the central C toward the groups R in this case is then lower than in $R_3C{-}CR_3$, and electron density shifts will occur in each R-C bond toward the central C. This charge transfer will increase T, and hence $X_u(1)$ will be decreased (see equation 149). If $-CR_3'$ has a LOWER electronegativity than R_3C-, $n_u > 1$ and electron density is shifted away from the central C of R_3C toward each R. These electron density changes decrease T, and increase $X_u(1)$.

Thus the electronegativity $X_u(1)$ of a group is dependent upon the nature of the radical or atom to which it is bonded:

i) $X_u(1)$ increases as n_u increases ,

ii) $X_u(1)$ decreases as the electronegativity, $X_v(1)$, of the group to which it is bonded increases.

These effects are graphically illustrated for alkyl groups in Figures I-4 and I-5.

The electronegativities $X_u(1)$ for the groups $-CH_3$ and $-CH(CH_3)_2$, and for the hydrogen atom, are plotted against n_u in Figure I-4. Since H is a monovalent atom, its electronegativity $X_u(1)$ is invariant with respect to n_u.

The curve for $-CH_2CH_3$ would lie between that of $-CH_3$ and that of $-CH(CH_3)_2$, and the curve for $-C(CH_3)_3$ would lie to the side of $-CH(CH_3)_2$ opposite to that of $-CH_3$ if there were sufficient space in Figure I-4 to plot $X_u(1)$ versus n_u for these two groups.

For small n_u, then

$$X_H(1) \gg X_{-CH_3}(1) > X_{-CH_2Me}(1) > X_{-CHMe_2}(1) > X_{-CMe_3}(1) .$$

If these groups are bonded to highly electronegative radicals or atoms, then

Figure I-4:

VARIATION OF $X_u(1)$ WITH n_u

Notes: Curve A represents the group $-CH_3$.

Curve B represents the group $-CH(CH_3)_2$.

Curve H represents Hydrogen.

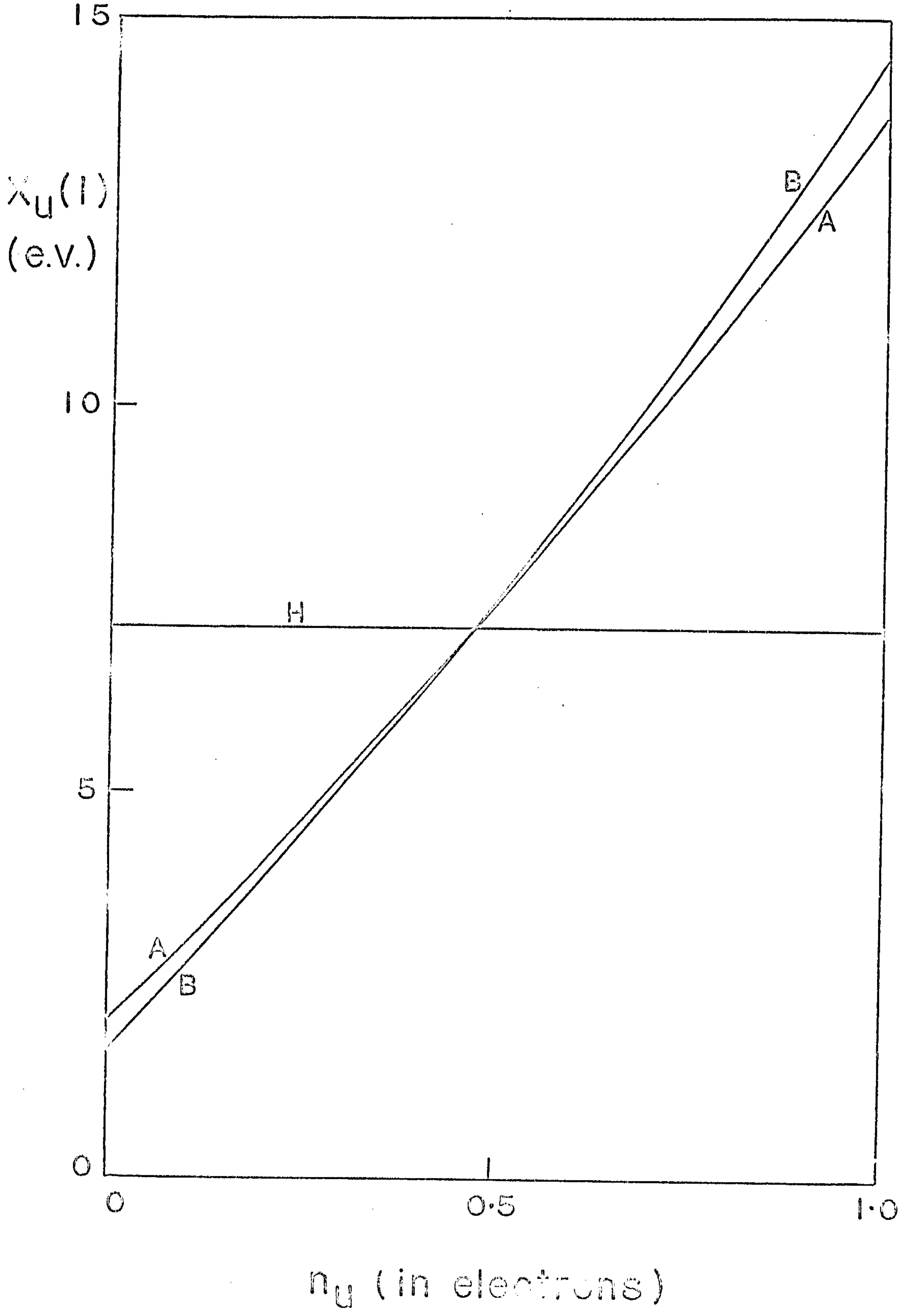

15
10
5
0
$X_u(I)$
(e.v.)
B
A
H
A
B
0
0·5
1·0
n_u (in electrons)

Figure I-5:

VARIATION OF $X_u(1)$ WITH $X_R(1)$ FOR MOLECULES R-H AND R-CH_3

Legend for groups R:

a) $- CH_2^-$

b) $- CHMe^-$

c) $- CH_2CH_2^-$

d) $- H$

e) $- CH = CHMe$

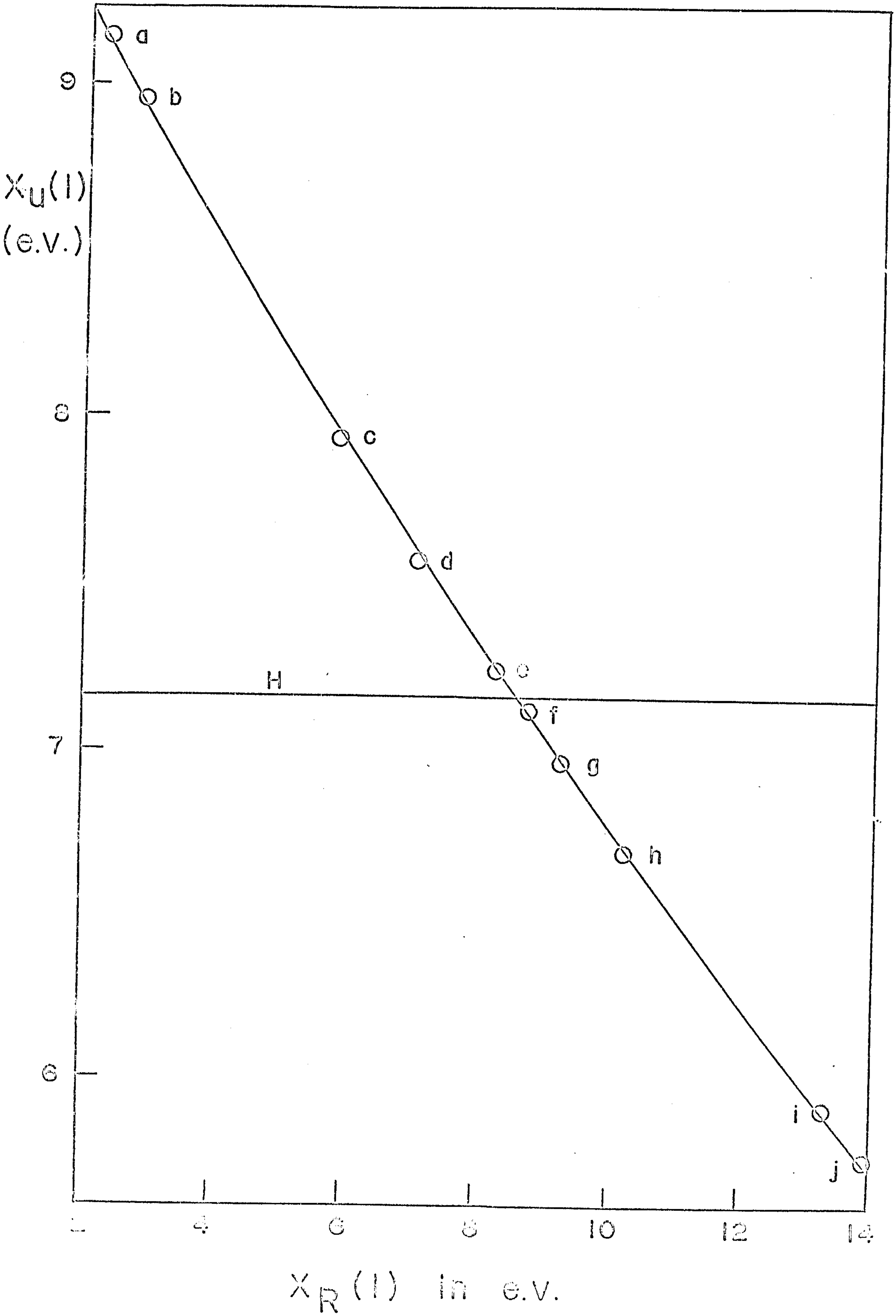
f) $- C_6Me_5$

g) $- CH_2CH_2^+$

h) $- C \equiv CMe$

i) $- CHMe^+$

j) $- CH_2^+$


9
8
7
6
Xu(1)
(e.v.)
a
b
c
d
e
f
g
h
i
j
H
4
6
8
10
12
14
XR(1) in e.V.

$n_u < 1$ and the normal order of inductive effects for hydrogen atoms and alkyl groups is obtained. However, for $n_u \gg 1$, the electronegativity order above is exactly reversed, and substitution of a hydrogen atom by a methyl group results in a withdrawal of electron density from the rest of the molecule.

The electronegativities of the methyl group and of the hydrogen atom are plotted against the electronegativity, $X_R(1)$, of the group R in Figure I-5 for a series of molecules R-H and R-CH_3. When the self-consistent field $X_R(1)$ is low, then $X_{CH_3}(1) > X_H(1)$, whereas for high values of $X_R(1)$, $X_H(1) > X_{CH_3}(1)$. When R corresponds to the group $-CH = CHCH_3$ (Figure I-5, point e), then $X_{CH_3}(1)$ is slightly larger than $X_H(1)$ but the reverse is true when R corresponds to the benzene ring (Figure I-5, point f). Hence, the $C_{te}-C_{tr}$ bond polarity in $CH_3-CH = CH-CH_3$ is smaller than the $H-C_{tr}$ bond polarity in $CH_2 = CH_2$, but the reverse is true in the molecules $C_6(CH_3)_5$ and C_6H_6.

The electronegativity equalization method, then, predicts that the relative inductive effects of groups of atoms are dependent upon the nature of the atom or group to which they are bonded. Huheey (39) has also arrived at this conclusion by analyzing the variations in group electronegativity which were calculated by a different electronegativity equalization method.

Transmission of Inductive Effects Through Carbon-Carbon Bonds

In saturated molecules, inductive effects produced by the substitution of one atom or group by another are usually considered to be attenuated along the chain. The inductive effect is considered to be transmitted from the point of substitution to different atoms in the molecule by two mechanisms (58):

i) Transmission through the localized bonds.

ii) Transmission directly through space between non-bonded atoms ("field" effects).

Since non-bonded interactions are neglected in the B.E.E. method, only effect (ii) is analyzed in this study.

The transmission of inductive effects through carbon-carbon bonds in hydrocarbon chains and rings can be studied by considering the changes in electronic density in the atomic orbitals of these systems when an artificial, standard perturbation of electron density is made in one orbital. The standard perturbation used is a change in electron density of one atomic orbital of carbon from 1 electron to 0 electrons. The carbon atom so perturbed is denoted by C_1, and the carbon atoms directly bonded to C_1 are denoted C_2, etc. The CHANGE in the total electron density at each hydrogen and carbon atom can be obtained from the B.E.E. method atom charges calculated for the molecule BEFORE and AFTER the perturbation at C_1 is made. For an atom at position m, a quantity Δ_m can be defined:

$$\Delta_m \equiv \frac{\text{Change in electron density at m due to perturbation}}{\text{Electron density at m before perturbation}} \quad . \qquad (151)$$

For example, the inductive effects in CH_3 are compared by calculating the C and H atom charges when the non-bonded carbon te orbital has an electron density of 1.0 and 0.0. The hydrogen atom total charge densities are 0.9821 and 0.7689 respectively, and the change in charge density is 0.2132 electron. Then the term Δ_1^H equals 0.2132/0.9821 or $\Delta_1^H = 0.217$. (The H superscript denotes that the atom concerned is hydrogen.)

The values of Δ_1^H for the hydrogen atoms in alkane chains with length one to five carbon atoms are listed in Table I-XI. The perturbation is made in a te orbital of the terminal carbon atom in these molecules. In each chain, Δ_m^H decreases as m increases, since the inductive effect is attenuated along the chain. For a given position along the chain (e.g. m = 2), Δ_m^H decreases slightly with increasing chain length.

The transmission of inductive effects from one carbon atom to the next in a chain can be studied by defining k, the TRANSMISSION COEFFICIENT of the inductive effect, by:

$$k^H_{(m-1,m)} = \frac{\Delta^H_m}{\Delta^H_{(m-1)}} \quad . \tag{152}$$

Transmission coefficients for the hydrocarbon chains are listed in Table I-XI. When m is a methylene unit ($-CH_2-$), $k^H = 0.300 \pm 0.007$, and when m is a terminal methyl group, $k^H = 0.320 \pm 0.008$. These average transmission coefficients agree well with those (0.29, 0.34 respectively) found by Smith and Eyring by means of an empirical calculation based upon dipole moment variations (66). In both methods, k is found to be almost independent of the magnitude of the inductive effect at C_{m-1}.

Quantities Δ_m^C and k^C may be defined from the changes in carbon atom charges for the hydrocarbon chains. For each molecule listed in Table I-XI, the transmission coefficients k^C are identical within ±0.01 to the

TABLE I-XI: Transmission of Inductive Effects in Hydrocarbon Chains and Rings

Hydrocarbon Chain Length (or Molecule Name)	Δ_1^H	Δ_2^H	Δ_3^H	Δ_4^H	Δ_5^H	k_{12}	k_{23}	k_{34}	k_{45}
1	.217								
2	.194	.064				$.32_8$			
3	.192	.059	.017			$.30_6$	$.31_6$		
4	.192	$.058_5$	.017	.005		$.30_5$	$.29_5$	$.31_4$	
5	.192	$.058_5$	.017	.005	.002	$.30_4$	$.29_4$	$.29_4$	$.31_3$
Cyclohexane	.173	.053	.017	.009		$.30_4$	$.31_6$	$.53_8$	
Benzene	—	.079	.028	.016		—	$.35_2$	$.58_3$	

Note:

a) See the text for definitions of Δ and of k.

corresponding k^H. Since the inductive effect parameters for hydrogen and carbon are so similar, the data for carbon has not been listed.

Inductive effect data is given in Table I-XI for two monocyclic rings, cyclohexane and benzene. The coefficients k_{34}^H and k_{34}^C for cyclohexane are substantially higher than the transmission coefficients in the hydrocarbon chains since two bonded pathways, one "clockwise" and the other "anti-clockwise," exist by which inductive effects can be transmitted between two carbon atoms in the ring. If the inductive effect is assumed to be transmitted independently in both directions according to a transmission coefficient K, the sum of the independent contributions at each carbon atom in cyclohexane will be $\Delta_1(K + K^5)$ at C_2, $\Delta_1(K^2 + K^4)$ at C_3, and $\Delta_1(K^3 + K^3)$ at C_4. Hence $k_{12} = K(1 + K^4)$, $k_{23} = K\left(\frac{1 + K^2}{1 + K^4}\right)$ and $k_{34} = K\left(\frac{2}{1 + K^2}\right)$.

If the value of K is taken to be 0.3 (i.e. that found in the hydrocarbon chains), then $k_{12} = 0.30$, $k_{23} = 0.32$ and $k_{34} = 0.55$, in good agreement with the coefficients listed for cyclohexane in Table I-XI. Thus the B.E.E. method predicts that inductive effects are transmitted independently in both directions in monocyclic rings.

If the transmission coefficients listed for benzene in Table I-XI are considered in the same manner as those for cyclohexane, then it is found that $K = 0.34$ for $C_{tr}-C_{tr}$ bonds, compared to $K = 0.30$ for $C_{te}-C_{te}$ bonds. If no electron density changes occur in the pi electron systems, then, unsaturated C-C bonds are predicted to be more efficient in transmitting inductive effects than are saturated bonds.

The transmission coefficients discussed above for saturated C-C bonds (0.30 to 0.32) are in good agreement with the experimental value of 0.36 established by Branch and Calvin (67) from a study of the relative acidities of substituted carboxylic acids. In addition, the relative transmission coefficients for $C_{te}-C_{te}$ and $C_{tr}-C_{tr}$ bonds are in the same order as that found by Bowden (68) from a statistical analysis of some reactivity data for aromatic systems.

Inductive Stabilization of Hydrocarbon Ions

It has been established experimentally (58) that the stability of carbonium ions produced from saturated hydrocarbons is greatly influenced by the "nature" of the central carbon atom:

$$C^{+}_{tertiary} > C^{+}_{secondary} > C^{+}_{primary} \;.$$

Carbonium ions are stabilized by delocalization of the unit positive charge from the central atom. Thus when the central carbon atom uses tr hybrid orbitals to form three coplanar sigma bonds in the ion, the positive charge associated with the unoccupied p_{π} atomic orbital can be delocalized from the central carbon by two mechanisms:

i) Hyperconjugation: The unoccupied p_{π} orbital of the central atom enters into a delocalized molecular orbital with occupied atomic orbitals (or group orbitals) of the surrounding groups.

ii) Inductive Stabilization: The polarity of the sigma bonds of the central carbon increase in the sense $\overset{\delta-}{C}_{tr}$, since the electronegativity of the positively charged carbon atom is large.

Only the second effect is considered in this study, due to difficulties in applying the B.E.E. method to multicentre bonds.

The first set of hydrocarbon ions considered are $(R_1R_2R_3C_{tr})^+$, where R_1, R_2, and R_3 are alkyl groups or hydrogen atoms, and C_{tr} is a trigonally-hybridized carbon atom having zero electron density in its p_{π} orbital. The parameters in Table I-III for the C(tr tr tr π^0) valence state were used in the calculations for the central carbon atom.

The net partial charges of the central carbon atom and of the hydrogen atoms bonded to it are listed in Table I-XII for a series of

TABLE I-XII: Net Charges of Atoms in Carbonium Ions and Carbanions

R_1	R_2	R_3	Net C_{tr} Charge in $(R_1R_2R_3C_{tr})^+$	Net H Atom Charge in $(R_1R_2R_3C_{tr})^+$	Extended Huckel Method (a) Net C_{tr} Charge in $(R_1R_2R_3C_{te})^+$	Net C_{te} Charge in $(R_1R_2R_3C_{te})^+$	Net C_{te} Charge in $(R_1R_2R_3C_{te})^-$
H	H	H	+0.2348	+0.2551	+0.609	+0.3068	-0.4335
H	H	Me	+0.1985	+0.2351	+0.571	+0.2752	-0.3897
H	Me	Me	+0.1690	+0.2191	+0.611	+0.2504	-0.3544
Me	Me	Me	+0.1444	—	+0.692	+0.2303	-0.3251
Et	Et	Et	+0.1413	—	—	+0.2279	-0.3143

Notes:

a) From reference 69.

b) Me denotes a methyl group, and Et denotes an ethyl group.

carbonium ions $(R_1R_2R_3C_{tr})^+$. The positive charges on these carbon and hydrogen atoms decrease as the hydrogen atoms in CH_3^+ are replaced by methyl groups. The methyl group is a more efficient electron donor to the central carbon than is hydrogen because the electronegativity of the central carbon is very large, and therefore $X_H(1) > X_{CH_3}(1)$ (see Figure I-5).

The partial positive charges of the central carbon atoms in these carbonium ions were calculated by Hoffmann (69) using his Extended Huckel Theory Method. These charges have been listed in Table I-XII for comparison with the B.E.E. method results. Since electron repulsions are not considered explicitly in the EHT method, most of the delocalization of the positive charge from the central carbon atom occurs by the hyperconjugation mechanism in these calculations. The net positive charges of the central carbon atom calculated by the B.E.E. method are substantially smaller than those obtained by the EHT method.

Since it is energetically favorable to delocalize the positive charge from the central carbon atom, the trend of the partial charges correlates with the experimental stability order if the partial positive charges on the central carbons decrease in the order

$$\text{primary} > \text{secondary} > \text{tertiary} \quad .$$

By reference to Table I-XII, it can be concluded that the B.E.E. method charges do correlate with the experimental order of stability, but that the EHT charges do not correlate.

The partial charges of the central carbon atoms in the ions $(R_1R_2R_3C_{te})^+$ and $(R_1R_2R_3C_{te})^-$ have also been calculated by the B.E.E. method, and are listed in Table I-XII. The unit positive or negative charge in these carbonium ions and carbanions was localized in a te hybrid orbital of the central carbon atom.

The B.E.E. method charges for the carbonium ions indicate that more extensive delocalization of the positive charge is obtained when the central carbon atom uses tr hybrids in the sigma bonds than when te hybridization is employed. The greater delocalization of positive charge in $(R_1R_2R_3C_{tr})^+$ compared to $(R_1R_2R_3C_{te})^+$ represents one factor which favors a planar geometry for the central carbon sigma bonds in carbonium ions. The Extended Huckel Method positive charges for the central carbon atoms are <u>greater</u> for planar geometries than for tetrahedral geometries (69).

Since the electronegativity of the sigma bond orbitals of the C_{te} carbon are quite low in the carbanions $(R_1R_2R_3C_{te})^-$, then $X_{CH_3}(1) > X_H(1)$ (see Figure I-5), and the replacement of the hydrogen atoms in $(CH_3)^-$ by methyl groups results in a DECREASE in the partial negative charge of the central carbon atom (Table I-XII). In both carbonium ions and carbanions, then, substitution of hydrogen atoms directly bonded to the central carbon leads to a reduction in the net partial charge (either positive or negative) of the central atom. A much smaller reduction in the net charge is predicted to occur when a hydrogen atom in one of the methyl groups is replaced by an alkyl group. For example, the decrease in the positive charge of the central carbon from $(H_3C_{tr})^+$ to $(Me_3C_{tr})^+$ is 0.090 electron, compared to a change of 0.003 electron in going from $(Me_3C_{tr})^+$ to $(Et_3C_{tr})^+$ (Table I-XII).

I. 3. D. CHARGE DISTRIBUTIONS IN SUBSTITUTED ALKANES

The inductive effects predicted by the B.E.E. method for saturated derivatives of alkanes are well illustrated by the charge distributions for aliphatic amines, alcohols, and ethers. Electron densities for such molecules are reported in this section. The alkyl halides form another set of hydrocarbon derivatives which can be analyzed by the B.E.E. method. In these molecules, the hybridization of the halogen atom bonding orbitals cannot be assessed from bond angles. An alternative technique for establishing chlorine and bromine atom hybridizations has been developed (49). This technique, which employs nuclear quadrupole resonance spectra, has been applied to a series of organic and inorganic halides by Kaplansky and Whitehead (70).

The electronegativities of the bonding orbitals of nitrogen and oxygen atoms are markedly dependent on the s-p hybridization of the orbitals. The ionic characters of the bonds formed by nitrogen and oxygen, and the size of the inductive effects produced by the presence of these atoms in a molecule, are therefore dependent on the choice of valence states for nitrogen and oxygen.

The hybrid character of the three bonding orbitals of trivalent, saturated nitrogen atoms is usually considered to lie between tetrahedral (te) and pure p. Since the H-N-H bond angle in ammonia and in methylamine is approximately 106° (64), and since the C-N-H and C-N-C bond angles in saturated amines are approximately 111° (64), the hybrid character of the bonding orbitals of nitrogen in these molecules should be close to tetrahedral, if it is assumed that these orbitals are directed at the bonded carbon and hydrogen atoms.

Similarly, the bond angles in the water molecule, and in saturated alcohols and ethers, indicate that the hybrid character of the bonding orbitals of the oxygen atom in such molecules lies between te and p (56, 64).

The electron density distributions in some simple saturated amines, alcohols, and ethers have been calculated by the B.E.E. method for both te and p bonding orbitals of nitrogen and oxygen, and are listed in Tables I-XIII to I-XXVI. These results will be discussed by considering the effect of alkyl substitution on the polarities of the bonds formed by nitrogen and oxygen, and by considering the inductive effects produced by substituting nitrogen and oxygen atoms into alkane molecules.

THE POLARITY OF THE BONDS FORMED BY NITROGEN AND OXYGEN

N_{te}-H and C-N_{te} Bonds

The ionic character of an "isolated" N_{te}-H bond is 15.8%, in the sense $H^{\delta+}$. The N-H bond polarity calculated by the self-consistent field B.E.E. method is 9.36%, and is lower than that for the isolated bond due to the presence of three polar bonds at nitrogen. If the hydrogen atoms in NH_3 are substituted by alkyl groups, the ionic characters of the remaining N-H bonds are reduced slightly, since alkyl groups bonded to N_{te} are electron-releasing relative to hydrogen. The effects of the different alkyl groups on the N_{te}-H bond are not large, however, since the range of N_{te}-H bond polarities in the amines is only 8.6 to 9.2% (Table I-XIII).

The electron-releasing character of alkyl groups bonded to tetrahedrally hybridized nitrogen atoms is also illustrated by the trends in the C-N bond polarities and the nitrogen atom net charges listed in Table I-XIII. The ionic character of the C-N_{te} bond in CH_3NH_2 of 10.82% (in the sense $C^{\delta+}$) is lower than that of 12.7% for an isolated C-N_{te} bond, and is further reduced as the hydrogen atoms bonded to nitrogen are replaced by alkyl groups. Similarly, the net charge on the nitrogen atom in NH_3 of -0.281 electrons is increased to -0.290 ± 0.009 electrons in the amines listed in Table I-XIII.

Since the amino group, $-NH_2$, is electron withdrawing relative to hydrogen, the polarities of the N_{te}-H and C-N_{te} bonds are increased when more than one amino group is present in the molecule.

Although alkyl groups are predicted to be electron-releasing relative to hydrogen when they are substituted for hydrogen atoms <u>bonded to nitrogen</u>,

TABLE I-XIII: Electron Distribution About Nitrogen (te Bonding Orbitals) in Some Amines

Molecule	i_{NH} %	i_{CN} %	Net Charge of N Atom in Electrons
NH_3	9.36	—	-0.2809
CH_3NH_2	8.99	10.82	-0.2881
$(CH_3)_2NH$	8.69	10.36	-0.2941
$(CH_3)_3N$	—	9.98	-0.2993
$CH_3CH_2NH_2$	9.03	10.70	-0.2875
$(CH_3CH_2)_2NH$	8.75	10.27	-0.2929
$(CH_3)_2CHNH_2$	9.05	10.59	-0.2870
$(CH_3)_3CNH_2$	9.08	10.50	-0.2865
$((CH_3)_3C)_2NH$	8.85	10.13	-0.2910
$CH_3CH_2CH_2NH_2$	9.05	10.62	-0.2871
Average (amines)	8.9±0.3	10.4±0.5	-0.290±0.009
"Isolated" Bond	15.80	12.71	—
$NH_2CH_2NH_2$	9.77	7.77	-0.2730
$NH_2CH_2CH_2NH_2$	9.26	9.78	-0.2829
$NH_2CH_2CH_2CH_2NH_2$	9.12	10.35	-0.2857

TABLE I-XIII continued

Notes:

a) The sign conventions used for the ionic characters reported in Tables I-XIII to I-XXVIII are discussed in the text.

b) Note that the "averages" given in the tables are for amines, alcohols, and ethers with only one functional nitrogen or oxygen heteroatom. The range of values for the quantities are given after the averages.

c) Since the charge density changes, from molecule to molecule, around nitrogen and oxygen are larger than those around carbon, the charge data for nitrogen and oxygen in all tables is given to one decimal place less than that for carbon.

they are found to be electron-withdrawing when substituted for hydrogen atoms bonded to carbon in the amines. For example, if one of the hydrogen atoms in the methyl group of CH_3NH_2 is replaced by another methyl group to give $CH_3CH_2NH_2$, the N_{te}-H bond polarity increases, and both the C-N_{te} bond polarity and the net negative charge on the nitrogen atom decrease (Table I-XIII).

N_p-H and C-N_p Bonds

The polarities of the N-H and C-N bonds calculated by assuming pure p bonding orbitals on nitrogen are listed in Table I-XIV for the amines. Since the electronegativity of a nitrogen atom p orbital is greater than that of hydrogen but is less than that of a te orbital of carbon, the polarities of these bonds are in the sense $N^{\delta-}-H^{\delta+}$ and $C^{\delta-}-N^{\delta+}$. The N-H bond ionic characters in the amines, 1.3 ± 0.7%, are larger than that of 0.71% for the isolated bond. The C-N_p bond polarity varies over a larger range, from -0.27% to -2.73%.

Since the electronegativity of a p orbital of nitrogen is only slightly less than that of a te carbon orbital, then $X_{alkyl}(1) > X_H(1)$, and alkyl groups are found to be electron-withdrawing relative to hydrogen in the amines. For example, the replacement of either type of hydrogen atom in CH_3NH_2 by a methyl group leads to a decrease in the electron density of the nitrogen atom. The calculated inductive effects of alkyl groups in amines are, therefore, very dependent on the nature of the hybridization which is assumed for the bonding orbitals of the nitrogen atom.

TABLE I-XIV: Electron Distribution About Nitrogen (p Bonding Orbitals) in Some Amines

Molecule	i_{NH} %	i_{CN} %	Net Charge of N Atom in Electrons
NH_3	0.39	—	-0.0116
CH_3NH_2	0.96	-1.57	-0.0035
$(CH_3)_2NH$	1.41	-0.85	+0.0029
$(CH_3)_3N$	—	-0.27	+0.0081
$CH_3CH_2NH_2$	1.09	-2.01	-0.0016
$(CH_3CH_2)_2NH$	1.63	-1.12	+0.0061
$(CH_3)_2CHNH_2$	1.20	-2.40	-0.0001
$(CH_3)_3CNH_2$	1.30	-2.73	+0.0013
$((CH_3)_3C)_2NH$	1.98	-1.54	+0.0111
$CH_3CH_2CH_2NH_2$	1.12	-2.13	-0.0011
Average (amines)	1.3±0.7	-1.6±1.3	+0.003±0.008
"Isolated" Bond	0.71	-1.13	—
$NH_2CH_2NH_2$	0.95	-1.54	-0.0036
$NH_2CH_2CH_2NH_2$	1.08	-1.99	-0.0017
$NH_2CH_2CH_2CH_2NH_2$	1.12	-2.13	-0.0012

Base Strength of Amines

The basic strength of saturated amines in aqueous solution is affected by the electronic structure of these molecules (71). For an amine R_3N, in which R_3 represents three different atoms or groups of atoms, the base strength is measured by the simplified equilibrium constant, K_b, of the reaction

$$R_3N + H_2O \rightleftharpoons (R_3NH)^+ + OH^-$$

$$K_b = \frac{\left[(R_3NH)^+\right]\left[OH^-\right]}{\left[R_3N\right]} \quad . \tag{153}$$

The constant K_b is usually expressed in terms of pK_b:

$$pK_b = -\log_{10}(K_b) \quad . \tag{154}$$

Brown et al. (71) have noted that the base strength of amines is increased by a large amount of electron density at the nitrogen atom, and is decreased by bulky groups bonded to nitrogen which sterically interfere with each other.

The pK_b values for a number of simple amines are listed in Table I-XV. The amines are classified in the table according to the number of carbon atoms bonded to nitrogen,[*] and within each group the amines are listed in order of increasing base strength. Charge density data for the free and protonated amines is also listed in Table I-XV. The electron densities in the free amines were calculated for the ($te^2tetete$) valence state of nitrogen, while those for the protonated amines were generated from the ($tetetete$) nitrogen valence state (Table I-III).

Within each of the three series of amines listed in Table I-XV,

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[*] NH_3 and $HONH_2$ are also included in the "primary" amine classification.

TABLE I-XV: Correlation Between Basicity and Electron Density of Some Amines

Amine	pK_b at 25°C (a)	i_{NH} in Protonated Amine(%)	Δi_{NH}	Net Charge of N in Free Base (in electrons)	Net Charge of N in Protonated Amine (in electrons)	Change in Net Charge of N (in electrons)
Primary						
$HONH_2$	7.49	28.95	14.08	−0.1754	+0.0902	0.2656
NH_3	4.14	24.70	15.34	−0.2809	+0.0119	0.2928
$NH_2CH_2CH_2NH_2$	3.89	23.32	13.56	−0.2729	−0.0139	0.2590
$CH_3CH_2CH_2NH_2$	2.99	23.14	14.09	−0.2871	−0.0173	0.2698
CH_3NH_2	2.88	23.20	14.21	−0.2881	−0.0161	0.2720
$CH_3CH_2NH_2$	2.77	23.13	14.11	−0.2875	−0.0175	0.2700
Secondary						
$(CH_3)_2NH$	2.99	21.93	13.34	−0.2942	−0.0402	0.2540
$(CH_3CH_2CH_2)_2NH$	2.70	21.83	13.04	−0.2922	−0.0420	0.2502
$(CH_3CH_2)_2NH$	2.60	21.81	13.06	−0.2929	−0.0423	0.2506
Tertiary						
$(CH_3)_3N$	4.28	20.83	—	−0.2993	−0.0610	0.2383
$(CH_3CH_2CH_2)_3N$	3.35	20.71	—	−0.2965	−0.0632	0.2333
$(CH_3CH_2)_3N$	3.25	20.69	—	−0.2975	−0.0637	0.2338

TABLE I-XV continued

Notes:

a) The pK_b are the statistically-corrected values given in Table 16-4 of F. E. Condon and H. Meislich "Introduction to Organic Chemistry" Holt, Rinehart and Winston. New York. 1960.

b) $\Delta i_{NH} = i_{NH}$ (protonated amine) - i_{NH} (free amine)

c) Change in net charge on N = Net charge in free base - Net charge in protonated amine.

both the N-H bond polarity, and the N atom charge, in the protonated amines correlate with the pK_b. The base strength increases as the positive charge of N and H decreases. Since these correlations are superior to those using the free amine charges, the basicity of an amine is probably determined primarily by the properties of the protonated form. The correlation of pK_b with N-H bond polarity in the protonated amines is illustrated in Figure I-6. The existence of different correlation lines (A, B, C) for the different N atom types is probably a steric effect.

O_{te}-H and C-O_{te} Bonds

The electron density distributions of the O-H and C-O bonds of some simple, saturated alcohols and ethers, in which the oxygen atom is assumed to use te hybrid orbitals for bonding, are given in Table I-XVI. Since the electronegativity of oxygen te orbitals is high, the O-H and C-O bonds are quite polar in the sense $O^{\delta-}$, and the net negative charges of the oxygen atoms are quite large. The ionic characters of the O-H bonds in alcohols, about 16.6%, are slightly lower than that of 18.3% in water, and are substantially less than that (25.9%) predicted for an isolated O-H bond. The C-O bond polarities in the alcohols of 22.5 ± 0.2% differ only slightly from that of 23.06% predicted for an isolated C-O_{te} bond. The polarities (20.5 ± 0.1%) of the C-O bonds in the ethers are somewhat lower than those in the alcohols. The net negative charge of the oxygen atoms in the ethers is about 0.02 electron greater than that in the alcohols (Table I-XVI).

The B.E.E. method charge distributions listed in Table I-XVI for

Figure I-6:

CORRELATION OF BASIC STRENGTHS OF AMINES WITH N-H BOND POLARITY IN THE PROTONATED AMINES

Notes: Curve A represents "primary" N atoms.

Curve B represents "secondary" N atoms.

Curve C represents "tertiary" N atoms.

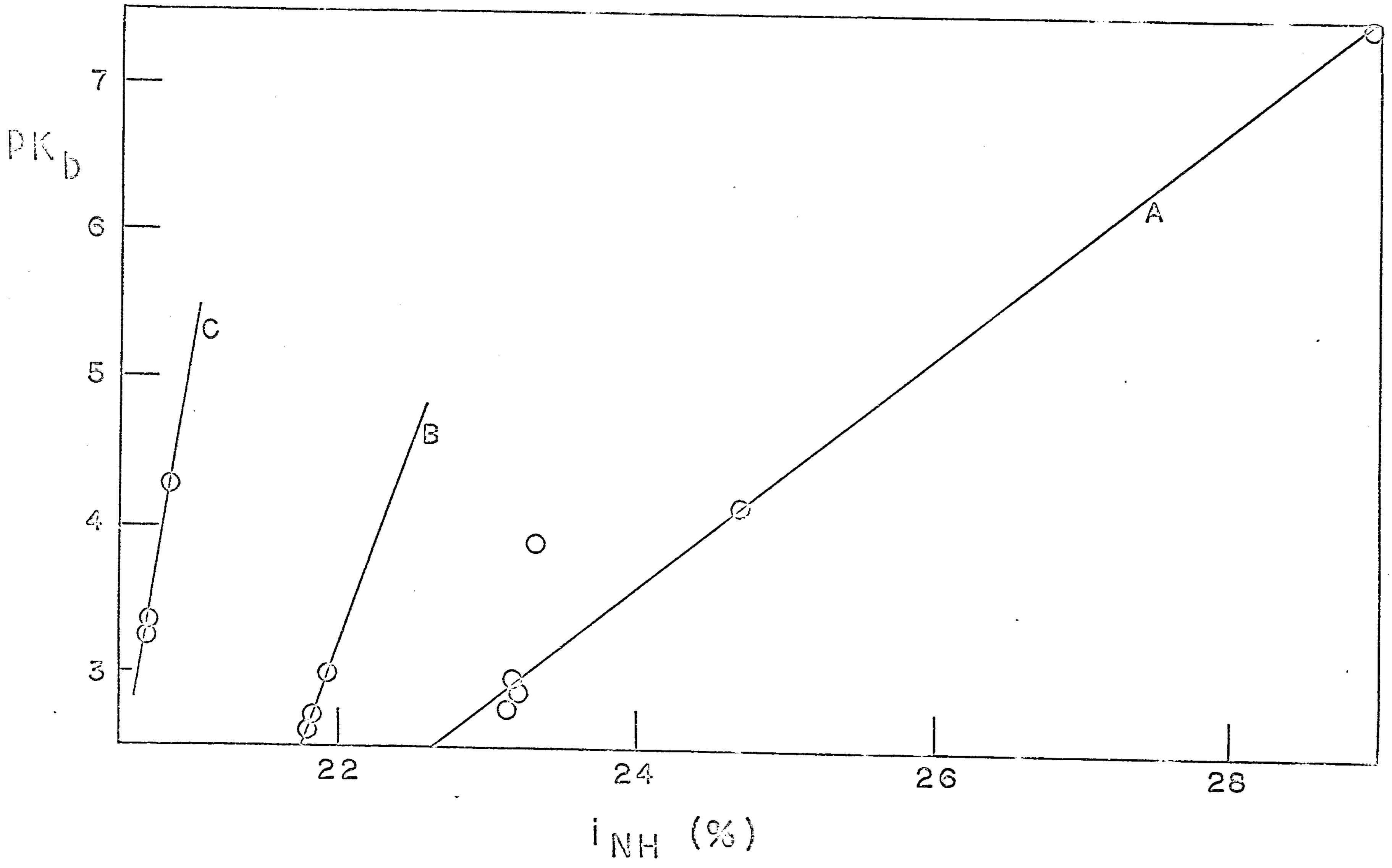

pKb
7
6
5
4
3
22
24
26
28
A
B
C
i_{NH} (%)

TABLE I-XVI: Electron Distribution About Oxygen (te Bonding Orbitals) in Some Alcohols and Ethers

Molecule	i_{OH} %	i_{CO} %	Net Charge of O Atom in Electrons
H_2O	18.32	---	-0.3665
CH_3OH	16.64	22.40	-0.3904
$(CH_3)_2O$	---	20.44	-0.4088
CH_3CH_2OH	16.60	22.51	-0.3910
$(CH_3CH_2)_2O$	---	20.48	-0.4095
$(CH_3)_2CHOH$	16.56	22.60	-0.3916
$(CH_3)_3COH$	16.53	22.68	-0.3920
$((CH_3)_3C)_2O$	---	20.53	-0.4106
$CH_3CH_2CH_2OH$	16.62	22.45	-0.3907
Average (alcohols)	16.6±0.1	22.5±0.2	-0.391±0.001
Average (ethers)	---	20.5±0.1	-0.410±0.002
"Isolated" Bond	25.94	23.06	---
$CH_2(OH)_2$	18.83	17.09	-0.3593
CH_2OHCH_2OH	17.24	20.94	-0.3818
$CH_2OHCH_2CH_2OH$	16.81	21.99	-0.3880

molecules with tetrahedrally-hybridized oxygen atoms indicate that alkyl groups are more effective electron-releasing agents than is hydrogen when the alkyl group replaces a hydrogen atom bonded to either the oxygen atom or to a carbon atom directly bonded to oxygen; replacement of a hydrogen atom bonded to any other type of carbon atom leads to a withdrawal of electron density.

O_p-H and C-O_p Bonds

Electron distributions for the O-H and C-O bonds in alcohols and ethers, in which the oxygen atom bonding orbitals are assumed to be pure p, are listed in Table I-XVII. Since the polarity of all the C-O and O-H bonds listed is in the sense $O^{\delta-}$, the oxygen atoms carry a net negative charge. The average O_p-H bond polarity of 6.0 ± 0.2% is lower than that of the isolated bond (8.78%), whereas the C-O_p bond ionic characters of 6.0 ± 0.4% are very close to that (5.85%) calculated for an isolated C-O_p bond. The clear differentiation between the polarities of the O-H (and C-O) bond in alcohols and in ethers, established for te hybridization of the oxygen, is not found in the electron distributions for O_p-H and C-O_p bonds. The relative inductive effects of alkyl groups and hydrogen atoms in alcohols and ethers in which p orbitals are used for bonding on oxygen are the same as those found for amines with tetrahedral nitrogen, since methyl groups are electron-releasing only when they substitute hydrogen atoms bonded to the oxygen atoms (Table I-XVII).

Summary of Inductive Effects

The inductive effects of alkyl groups relative to hydrogen predicted

TABLE I-XVII: Electron Distribution About Oxygen (p Bonding Orbitals) in Some Alcohols and Ethers

Molecule	i_{OH} %	i_{CO} %	Net Charge of O Atom in Electrons
H_2O	5.99	--	-0.1199
CH_3OH	5.87	6.25	-0.1212
$(CH_3)_2O$	—	6.11	-0.1222
CH_3CH_2OH	5.98	6.03	-0.1200
$(CH_3CH_2)_2O$	—	6.01	-0.1202
$(CH_3)_2CHOH$	6.07	5.84	-0.1190
$(CH_3)_3COH$	6.14	5.67	-0.1181
$((CH_3)_3C)_2O$	—	5.85	-0.1170
$CH_3CH_2CH_2OH$	6.02	5.94	-0.1196
Average (alcohols, ethers)	6.0±0.2	6.0±0.4	-0.120±0.003
"Isolated" Bond	8.78	5.85	--
$CH_2(OH)_2$	6.76	4.33	-0.1109
CH_2OHCH_2OH	6.24	5.45	-0.1169
$CH_2OHCH_2CH_2OH$	6.10	5.77	-0.1186

by the B.E.E. method calculations for hydrocarbons and their derivatives are summarized in Table I-XVII. In this table, "R" denotes that alkyl groups release electron density when substituted for a hydrogen atom bonded to the atom indicated, whereas "W" represents a withdrawal of electron density when the substitution is made. The predicted inductive effects in nitrogen and oxygen derivatives are in some conflict with experimental data, since alkyl groups are usually considered to be more effective electron-releasing agents than hydrogen when substituted at any point in a saturated alkane derivative containing an atom of greater electronegativity than carbon (58). This topic is discussed further in Part I. 4.

TABLE I-XVIII: Predicted Inductive Effects of Alkyl Groups Relative to Hydrogen in Hydrocarbon Derivatives

Nature of Heteroatom	Point of Substitution(a) At Heteroatom	 At Carbon Atom Bonded to Heteroatom	 At other Carbon Atoms
C_{te}	W	W	W
C_{tr}	R, W(b)	W	W
C_{di}	R	–	W
N_{te}	R	W	W
N_{p}	W	W	W
O_{te}	R	R	W
O_{p}	R	W	W

Notes:

(a) As explained in text.

(b) R for C_{tr} in benzenes, W for C_{tr} in ethylenes.

CARBON-HYDROGEN AND CARBON-CARBON BONDS IN AMINES, ALCOHOLS AND ETHERS

The presence of a nitrogen or oxygen atom in a chain of carbon atoms produces changes in the C-H and C-C bond polarities. These inductive effects are best discussed by considering both the C and H atom charge density distributions in substituted alkane derivatives, and the CHANGES in the charge distributions of the alkanes which occur when one carbon atom is replaced by a nitrogen or oxygen atom.

C-H Bonds

The ionic characters of the carbon-hydrogen bonds in the amines, alcohols and ethers previously discussed are listed in Tables I-XIX to I-XXII. A quantity Δi_{CH} is also listed in these tables for every C-H bond, and is defined as the INCREASE in i_{CH} in the alkane derivative over that in the corresponding alkane which is formed by replacing each nitrogen or oxygen atom in the molecule by a saturated carbon atom. It should be noted that only the C, N and O atom frameworks of the molecules are listed in these and subsequent tables, and that the atom numbering scheme differs from that used for hydrocarbons and hydrocarbon ions.

The polarity of all the C-H bonds listed in Tables I-XIX to I-XXII are in the sense $C^{\delta-} H^{\delta+}$. Since the electronegativity of the te orbitals of nitrogen, and of both te and p orbitals of oxygen, are greater than the electronegativity of the carbon atoms which they replace, the C-H bond ionic characters listed in Tables I-XIX, I-XXI, and I-XXII are larger than those in the alkanes (i.e. $\Delta i_{CH} > 0$ here). The electronegativity of a nitrogen atom p orbital is less than that of carbon, and the Δi_{CH} in Table I-XX

TABLE I-XIX: Carbon-Hydrogen Bond Ionic Characters in Some Amines (te Hybridization for Nitrogen)

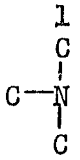
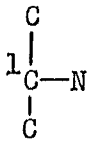
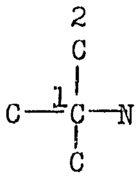
Molecular Framework	i_{C_1H} %	i_{C_2H} %	i_{C_3H} %	Δi_{C_1H}	Δi_{C_2H}	Δi_{C_3H}
$\overset{1}{\mathrm{C}}$—N	4.046			2.260		
$\overset{2}{\mathrm{C}}$—$\overset{1}{\mathrm{C}}$—N	4.142	2.529		2.094	0.661	
$\overset{1}{\mathrm{C}}$—N—C	3.950			2.082		
$\overset{3}{\mathrm{C}}$—$\overset{2}{\mathrm{C}}$—$\overset{1}{\mathrm{C}}$—N	4.204	2.734	2.085	2.081	0.611	0.193
$\overset{2}{\mathrm{C}}$—$\overset{1}{\mathrm{C}}$—N—C—C	4.061	2.503		1.917	0.604	
	3.869			1.929		
	4.223	2.555		1.949	0.615	
	—	2.577		—	0.576	
N—$\overset{1}{\mathrm{C}}$—N	6.369			4.321		
N—$\overset{1}{\mathrm{C}}$—C—N	4.841			2.718		
N—$\overset{1}{\mathrm{C}}$—$\overset{2}{\mathrm{C}}$—C—N	4.410	3.416		2.266	1.220	

TABLE I-XIX continued

Note:

a) In this and in subsequent tables

$$\Delta i_{CH} = i_{CH} \text{ (in amine or alcohol)} - i_{CH} \text{ (in alkane)} .$$

TABLE I-XX: Carbon-Hydrogen Bond Ionic Characters in Amines (p Hybridization for Nitrogen)

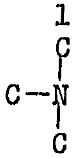
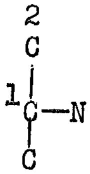
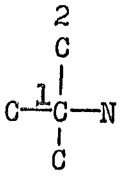
Molecular Framework	i_{C_1H} %	i_{C_2H} %	i_{C_3H} %	Δi_{C_1H}	Δi_{C_2H}	Δi_{C_3H}
$\overset{1}{C}$—N	1.459			−0.327		
$\overset{2}{C}$—$\overset{1}{C}$—N	1.743	1.773		−0.305	−0.095	
$\overset{1}{C}$—N—C	1.608			−0.260		
$\overset{3}{C}$—$\overset{2}{C}$—$\overset{1}{C}$—N	1.819	2.034	1.864	−0.304	−0.089	−0.028
$\overset{2}{C}$—$\overset{1}{C}$—N—C—C	1.912	1.825		−0.232	−0.074	
	1.730			−0.210		
	1.988	1.850		−0.286	−0.090	
	—	1.917		—	−0.084	
N—$\overset{1}{C}$—N	1.444			−0.604		
N—$\overset{1}{C}$—C—N	1.731			−0.392		
N—$\overset{1}{C}$—$\overset{2}{C}$—C—N	1.815	2.019		−0.329	−0.177	

TABLE I-XXI: Carbon-Hydrogen Bond Ionic Characters in Some Alcohols and Ethers (te Hybridization for Oxygen)

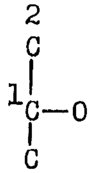
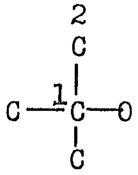
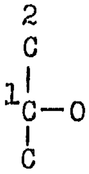
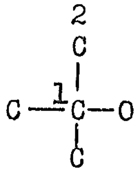
Molecular Framework	i_{C_1H} %	i_{C_2H} %	i_{C_3H} %	Δi_{C_1H}	Δi_{C_2H}	Δi_{C_3H}
$\overset{1}{C}-O$	6.474			4.688		
$\overset{2}{C}-\overset{1}{C}-O$	6.375	3.237		4.327	1.369	
$\overset{1}{C}-O-C$	6.062			4.194		
$\overset{3}{C}-\overset{2}{C}-\overset{1}{C}-O$	6.423	3.390	2.291	4.300	1.267	0.399
$\overset{2}{C}-\overset{1}{C}-O-C-C$	5.991	3.115		3.847	1.216	
 $\underset{\underset{C}{\vert}}{\overset{\overset{\overset{2}{C}}{\vert}}{{}^{1}C}}-O$	6.291	3.210		4.017	1.270	
 $C-\underset{\underset{C}{\vert}}{\overset{\overset{\overset{2}{C}}{\vert}}{{}^{1}C}}-O$	—	3.188		—	1.187	
$O-C-O$	11.366			9.318		
$O-\overset{1}{C}-C-O$	7.811			5.688		
$O-\overset{1}{C}-\overset{2}{C}-C-O$	6.844	4.731		4.700	2.535	

TABLE I-XXII: Carbon-Hydrogen Bond Ionic Characters in Alcohols and Ethers (p Hybridization for Oxygen)

	i_{C_1H} %	i_{C_2H} %	i_{C_3H} %	Δi_{C_1H}	Δi_{C_2H}	Δi_{C_3H}
$\overset{1}{C}-O$	3.091			1.305		
$\overset{2}{C}-\overset{1}{C}-O$	3.260	2.250		1.212	0.382	
$\overset{1}{C}-O-C$	3.062			1.194		
$\overset{3}{C}-\overset{2}{C}-\overset{1}{C}-O$	3.328	2.477	2.003	1.205	0.354	0.111
$\overset{2}{C}-\overset{1}{C}-O-C-C$	3.256	2.249		1.112	0.350	
 $\begin{array}{c}2\\C\\|\\{}^{1}C\\|\\C\end{array}\!-O$	3.405	2.296		1.131	0.356	
 $C-\begin{array}{c}2\\C\\|\\\overset{1}{C}\\|\\C\end{array}\!-O$	—	2.336		—	0.335	
$O-\overset{1}{C}-O$	4.545			2.497		
$O-\overset{1}{C}-C-O$	3.696			1.573		
$O-\overset{1}{C}-\overset{2}{C}-C-O$	3.456	2.902		1.312	0.706	

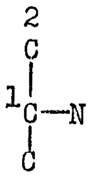
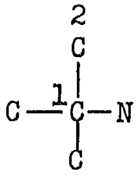
are negative. The Δi_{CH} within each molecule decrease rapidly as the number of C-C bonds between the N or O atom and the C-H bond of interest increases. The transmission coefficients for the inductive effect are similar to those established for hydrocarbon chains in Part I. 3. C. For the amines, alcohols, and ethers in which te hybridization is used for the bonding orbitals of the nitrogen and oxygen atoms, the Δi_{CH} values for the amines (Table I-XIX) are approximately one-half of the corresponding Δi_{CH} in the alcohols and ethers (Table I-XXI). The B.E.E. method predicts, then, that the inductive effect produced by O_{te} is twice as great as that of N_{te}.

Since, in each of Tables I-XIX to I-XXII, the Δi_{CH} for a given position (e.g. C_1) are almost independent of the structure of the molecule containing one N or O atom, it can be concluded that the B.E.E. method predicts that the inductive effect produced at a given point by either nitrogen or oxygen substitution is virtually independent of the structure of the rest of the hydrocarbon chain. For example, the inductive effect produced by N_{te} at the C_1-H bond is $\Delta i_{CH} = 2.1 \pm 0.2\%$. The Δi_{CH} data for the disubstituted alkanes listed in Tables I-XIX to I-XXII indicates that the inductive effect produced by multiple substitution in the alkanes is approximately additive, in agreement with experimental chemical and physical evidence regarding the effect of polysubstitution (72).

C-C Bonds

The C-C bond ionic characters for the amines, alcohols and ethers are listed in Table I-XXIII (for nitrogen derivatives) and Table I-XXIV (for oxygen derivatives). The sign convention used here is that i_{CC} is positive

TABLE I-XXIII: Carbon-Carbon Bond Ionic Characters in Amines

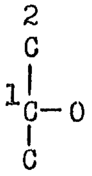
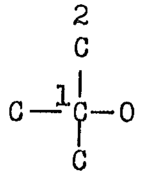
Molecular Framework	te Orbitals for N $i_{C_1C_2}$ %	 $i_{C_2C_3}$ %	 $\Delta i_{C_1C_2}$	p Orbitals for N $i_{C_1C_2}$ %	 $i_{C_2C_3}$ %	 $\Delta i_{C_1C_2}$
$\overset{2}{C}—\overset{1}{C}—N$	3.561		3.165	-0.065		-0.331
$\overset{3}{C}—\overset{2}{C}—\overset{1}{C}—N$	3.244	1.432	3.244	-0.472	0.374	-0.472
$\overset{2}{C}—\overset{1}{C}—N—C—C$	3.439		2.898	0.189		-0.352
	3.684		2.848	0.305		-0.431
	3.791		2.758	0.627		-0.406
$N—\overset{1}{C}—\overset{2}{C}—N$	0.000		0.000	0.000		0.000
$N—\overset{1}{C}—\overset{2}{C}—C—N$	2.195		2.081	-0.450		-0.336

Note:

a) In this table and the next,

$$\Delta i_{CC} = i_{CC} \text{ (in amine or alcohol)} - i_{CC} \text{ (in alkane)} .$$

TABLE I-XXIV: Carbon-Carbon Bond Ionic Characters in Alcohols and Ethers

Molecule	te Orbitals for O			p Orbitals for O		
	$i_{C_1C_2}$ %	$i_{C_2C_3}$ %	$\Delta i_{C_1C_2}$	$i_{C_1C_2}$ %	$i_{C_2C_3}$ %	$\Delta i_{C_1C_2}$
$\overset{2}{C}-\overset{1}{C}-O$	6.953		6.557	2.226		1.830
$\overset{3}{C}-\overset{2}{C}-\overset{1}{C}-O$	6.720	2.424	6.720	1.877	1.043	1.877
$\overset{2}{C}-\overset{1}{C}-O-C-C$	6.367		5.826	2.221		1.680
 $\begin{array}{c} \overset{2}{C} \\ \vert \\ {}^{1}C-O \\ \vert \\ C \end{array}$	6.825		6.089	2.445		1.709
 $\begin{array}{c} \overset{2}{C} \\ \vert \\ C-{}^{1}C-O \\ \vert \\ C \end{array}$	6.716		5.683	2.635		1.602
$O-\overset{1}{C}-\overset{2}{C}-O$	0.000		0.000	0.000		0.000
$O-\overset{1}{C}-\overset{2}{C}-C-O$	4.680		4.566	1.223		1.109

if the carbon atom nearest the substituent atom (N or O) is the negative end of the bond. The changes Δi_{CC} in C-C bond polarity due to substitution of carbon by nitrogen or oxygen are also listed for the C_1-C_2 bond in each case.

The ionic characters of the carbon-carbon bonds in the hydrocarbon derivatives are much greater than those in the unsubstituted alkanes. For each hybridization listed in the two tables, $\Delta i_{C_1-C_2}$ is almost independent of the molecular structure. The sign and magnitude of the $\Delta i_{C_1-C_2}$ terms are consistent with the relative electronegativities of N_{te}, N_p, O_{te}, O_p and C_{te} as discussed under "C-H Bonds."

The carbon atom net charges for the alkane derivatives with one substituent atom are listed in Tables I-XXV and I-XXVI. All the carbon atoms are predicted to carry a net negative charge, with the exception of those directly bonded to O_{te}. For N_{te}, O_p and O_{te} substituents, the net negative charges of carbon are less than those in the n-alkanes, whereas for an N_p substituent, the net negative charges are greater than in the alkanes. The trends in the carbon net negative charges in the disubstituted alkanes are similar to those found for the C-H bonds in these molecules.

TABLE I-XXV: Carbon Atom Net Charges in Some Amines

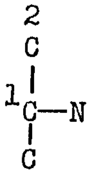
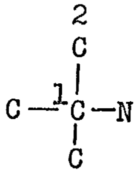
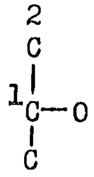
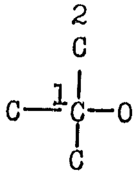
Molecular Framework	te Orbitals for Nitrogen Net Charge of Carbon Atoms			p Orbitals for Nitrogen Net Charge of Carbon Atoms		
	C_1	C_2	C_3	C_1	C_2	C_3
$\overset{1}{C}$—N	-0.0132			-0.0595		
$\overset{2}{C}$—$\overset{1}{C}$—N	-0.0114	-0.0403		-0.0543	-0.0538	
$\overset{1}{C}$—N—C	-0.0149			-0.0568		
$\overset{3}{C}$—$\overset{2}{C}$—$\overset{1}{C}$—N	-0.0104	-0.0366	-0.0482	-0.0530	-0.0491	-0.0522
$\overset{2}{C}$—$\overset{1}{C}$—N—C—C	-0.0129	-0.0407		-0.0513	-0.0529	
	-0.0163			-0.0546		
	-0.0100	-0.0398		-0.0499	-0.0524	
	-0.0088	-0.0394		-0.0461	-0.0512	
N—$\overset{1}{C}$—N	+0.0279			-0.0597		
N—$\overset{1}{C}$—C—N	+0.0009			-0.0546		
N—$\overset{1}{C}$—$\overset{2}{C}$—C—N	-0.0067	-0.0244		-0.0531	-0.0494	

TABLE I-XXVI: Carbon Atom Net Charges in Some Alcohols and Ethers

Molecular Framework	te Orbitals for Oxygen Net Charge of Carbon Atoms C_1	 C_2	 C_3	p Orbitals for Oxygen Net Charge of Carbon Atoms C_1	 C_2	 C_3
$\overset{1}{C}-O$	+0.0298			−0.0302		
$\overset{2}{C}-\overset{1}{C}-O$	+0.0280	−0.0276		−0.0272	−0.0452	
$\overset{1}{C}-O-C$	+0.0225			−0.0307		
$\overset{3}{C}-\overset{2}{C}-\overset{1}{C}-O$	+0.0289	−0.0248	−0.0445	−0.0260	−0.0412	−0.0497
$\overset{2}{C}-\overset{1}{C}-O-C-C$	+0.0213	−0.0298		−0.0272	−0.0453	
 $\begin{array}{l} \overset{2}{C} \\ \vert \\ {}^{1}C-O \\ \vert \\ C \end{array}$	+0.0267	−0.0281		−0.0246	−0.0444	
 $\begin{array}{l} \quad\ \overset{2}{C} \\ \quad\ \vert \\ C-{}^{1}C-O \\ \quad\ \vert \\ \quad\ C \end{array}$	+0.0253	−0.0285		−0.0223	−0.0437	
$O-\overset{1}{C}-O$	+0.1146			−0.0043		
$O-\overset{1}{C}-C-O$	+0.0532			−0.0194		
$O-\overset{1}{C}-\overset{2}{C}-C-O$	+0.0363	−0.0010		−0.0237	−0.0336	

I. 3. E CORRELATIONS OF THE CHARGE DENSITIES WITH N.M.R. CHEMICAL SHIFTS

The B.E.E. method charge distributions for saturated molecules may be "tested" to establish their validity by attempting to correlate the atomic charge densities with experimental properties which are known to be strongly dependent upon electron densities. For the molecular systems considered herein, the nuclear magnetic resonance (N.M.R.) chemical shift is the most convenient experimental measure of the electronic charge density about the various nuclei.

In N.M.R. spectroscopy, the shielding constant σ of the magnetic nucleus in a molecule is determined by the electronic environment about that nucleus (73). The strength of the local magnetic field, H, at a nucleus in an N.M.R. experiment is given by the expression (73):

$$H = H_o (1 - \sigma) \qquad (155)$$

where H_o is the strength of the externally-applied magnetic field. A chemical shift parameter, δ, is defined for each nuclear species relative to the shielding constant of that type of nucleus in a standard reference (73):

$$\delta = \sigma - \sigma_R = \frac{H - H_R}{H_R} \qquad (156)$$

In this equation, H_R and σ_R denote the required magnetic field at resonance, and the screening constant of the nucleus in the reference sample.

The shielding constant σ for a nuclei L in a molecule is conveniently subdivided into parts according to the approximate scheme of Saika and Slichter (74):

$$\sigma^L = \sigma_d^{LL} + \sigma_p^{LL} + \sum_{M \neq L} \sigma^{LM} + \sum_{ring} \sigma^{L,ring} . \qquad (157)$$

The terms σ_d^{LL} and σ_p^{LL} are those diamagnetic and paramagnetic contributions to σ^L which can be localized on atom L. The term $\sum_{M \neq L} \sigma^{LM}$ represents the anisotropic screening contribution to σ^L due to local electron currents on atoms other than L. The term $\sum_{ring} \sigma^{L,ring}$ is a screening term which is important only in molecules with substantial ring currents, and will be of negligible magnitude for the molecules to be considered (73).

The local diamagnetic screening term, σ_d, is given by the formula (75)

$$\sigma_d^{LL} = \frac{e^2}{3\,mc^2} \sum_a \left\langle r_a^{-1} \right\rangle \tag{158}$$

where e, m are the charge and mass of the electron, c is the speed of light, and $\left\langle r_a^{-1} \right\rangle$ is the mean inverse distance of electron a from the nucleus L. Since the summation over a is over all the electrons on the atom, the local diamagnetic screening contribution to σ will be directly proportional to the electron density of the atom. The rate of increase in σ_d with charge density is about 15-20 parts per million (p.p.m.) per electron for carbon and hydrogen (73,75).

Except for hydrogen nuclei, variations in the local paramagnetic screening term, σ_p^{LL}, are mainly responsible for the range of observed chemical shifts. According to Pople's LCAO-MO theory of diamagnetism (76), σ_p^{LL} may be approximately expressed for hydrogen and carbon as

$$\sigma_p^{LL} = \frac{-e^2\hbar^2}{2\,m^2\,c^2\,\Delta E} \left\langle r^{-3} \right\rangle_{2p} \sum_M Q_{LM} \quad . \tag{159}$$

In this equation, $\hbar$ is $(1/2\,\pi)$ times Planck's constant, h ; ΔE is an average electronic excitation energy, $\langle r^{-3} \rangle_{2p}$ is the mean inverse cube radius of the 2p atomic orbitals; and $\sum_{M} Q_{LM}$ is a term involving the bond orders of the occupied molecular orbitals (75,76). The σ_p^{LL} contribution to the screening constant σ^L is quite large for carbon atoms, and is dependent upon the total electronic charge density about the carbon atom, since as this charge density increases the 2p orbitals expand and the term $\langle r^{-3} \rangle_{2p}$ decreases. Pople (76) has shown that, if the net charge associated with the carbon atom L is $-q_L$ electrons, then for small values of q_L, $\langle r^{-3} \rangle_{2p}$ varies linearly with q_L :

$$\langle r^{-3} \rangle_{2p} = \frac{34.33}{a_o^3} (1 - 0.323\, q_L) \quad . \tag{160}$$

In this expression, a_o is the Bohr radius.

Provided that the variations in the terms ΔE, $\sum_{M} Q_{LM}$, and $\sum_{M \neq L} \sigma^{LM}$ are slight, the shielding constant σ for hydrogen and carbon atoms should be directly proportional to the charge density about these atoms, since both σ_d^{LL} and σ_p^{LL} increase linearly with the net atom charge. For the saturated molecules considered in the present work, the term $\sum_{M} Q_{LM}$ is almost constant if the bonds formed by atom L are not too ionic (76,77). Any deviations from linearity of charge density versus screening constant correlations will, therefore, be due to variations in the average electronic excitation energies, ΔE, and/or to variations in the neighbour anisotropy screening contribution $\sum_{M \neq L} \sigma^{LM}$, or to the inaccuracy of the calculated charge density distributions.

^{13}C N.M.R. Chemical Shift Correlations

The experimental ^{13}C N.M.R. chemical shifts in aromatic molecules are strongly dependent upon the electron charge density associated with the pi atomic orbitals of the conjugated carbon atoms (73,75,76,78). Spiesecke and Schneider (79) measured the ^{13}C N.M.R. chemical shifts in the series $C_5H_5^-$, C_6H_6, $C_7H_7^+$, $C_8H_8^{2-}$, and determined that the rate of change of the shielding constant with electron density is about 160 p.p.m. per pi electron. Other correlations of pi electron charge density with chemical shift have established this rate of variation to be in the range of 160-200 p.p.m. per electron (78).

Semi-quantitative correlations of the ^{13}C N.M.R. chemical shift with carbon atom charge density have been established for certain series of saturated and unsaturated hydrocarbon derivatives by using inductive effect parameters such as the Pauling electronegativity or Hammett σ value of the substituent atoms or groups (73). Any deviations encountered in such correlations are usually attributed to variations in the neighbour anisotropy screening contribution, $\sum_{M \neq L} \sigma^{LM}$.

Grant and Paul (80,81) measured the ^{13}C N.M.R. chemical shift (relative to benzene) of each inequivalent carbon atom in the n-alkanes C_3H_8 to $C_{10}H_{22}$, and in several branched hydrocarbons. The chemical shifts, δ_L, for the carbon atoms L in the n-alkanes can be accurately described (80,81) by the linear expression

$$\delta_L = 131.26 + \sum_M R_M N_{LM} \qquad (161)$$

where R_M is an empirical constant for the presence of a carbon atom in the

M^{th} position relative to carbon atom L, and N_{LM} is the number of carbon atoms in the M^{th} position. The summation $\sum_{M}$ runs over all the possible positions (α, β, . . .) relative to carbon atom L. The empirical constants R_M were fitted from the experimental data, and the standard deviation of the empirical fit for all thirty chemically inequivalent carbon atoms in the n-alkanes CH_4 through $C_{10}H_{22}$ was only 0.21 p.p.m. (80,81). The empirical correlation is less satisfactory when branched alkanes are also considered (80).

Grant and Paul (80) found that the empirical constants R_M correlate linearly with the estimated neighbour anisotropy variations due to carbon-carbon bonds. However, the magnitude of the neighbour anisotropy contribution, $\sum_{M \neq L} \sigma^{LM}$, is probably of minor importance in determining the chemical shifts in the alkanes (80). If the range of chemical shifts observed for the alkanes is due to variations in the neighbour anisotropy screening term, then $\Delta \chi_{C-C}$, the anisotropy of the magnetic susceptibility of a carbon-carbon single bond, would have to be approximately two orders of magnitude greater than all previous estimates (80,81).

The ^{13}C N.M.R. chemical shifts, δ_C, (relative to benzene) of the n-alkanes CH_4 through $C_{10}H_{22}$ listed by Grant and Paul are given in Table I-XXVII. This table of chemical shifts is set up so that comparisons with the corresponding carbon atom net charges (Table I-IX) can be easily made. The trends in the ^{13}C chemical shifts (Table I-XXVII) correlate qualitatively with the net atom charges (Table I-IX). Within each n-alkane molecule, both δ_C and the excess negative charge (q_C) of the carbon atoms decrease in magnitude as the centre of the molecule is approached.

TABLE I-XXVII: Experimental ^{13}C N.M.R. Chemical Shifts in p.p.m. for the n-Alkanes C_mH_{2m+2}

Value of m	Chemical Shift[a] (Relative to Benzene) at Position C_1	C_2	C_3	C_4	C_5
1	130.8				
2	122.8				
3	113.10	112.62			
4	115.48	103.68			
5	114.97	106.13	94.17		
6	114.82	105.78	96.66		
7	114.75	105.70	96.30	99.23	
8	114.65	105.67	96.32	99.02	
9	114.67	105.62	96.25	98.85	98.58
10	114.55	105.72	96.26	98.78	98.43

Note:

a) Data from reference 80.

For carbon atoms of a given position, for example C_1, both δ_C and q_C generally decrease with increasing chain length, and the changes in both quantities which occur between successive n-alkane molecules decrease rapidly with increasing chain length. Deviations from the parallel variation of δ_C and q_C consistently occur whenever the carbon atom concerned is bonded to one or more ethyl groups.

The chemical shifts and net charges of the carbon atoms in some branched hydrocarbons have been listed in Table I-VII. The chemical shifts of the carbon atoms of all the alkanes listed in Tables I-VII and I-XXVII are plotted in Figure I-7 against the corresponding carbon atom net charges. The darkened circles in this and in the next figure in this section denote points corresponding to two or more chemically inequivalent atoms which have almost identical values of the chemical shift and net charge.

Since the scatter of points in Figure I-7 is quite large, no single correlation curve has been drawn through the points. The correlation of the chemical shifts and the net charges of the carbon atoms is substantially improved if the points which correspond to any carbon atom which is bonded to a branched or unbranched chain of length two carbon atoms are not considered. The correlation plot for the remaining carbon atoms is given in Figure I-8.

The plot in Figure I-8 indicates the existence of an approximate linear correlation of δ_C with q_C for the restricted set of carbon atoms considered. As expected from previous theoretical and empirical considerations, the shielding constant of a carbon nucleus (as expressed in terms of its chemical shift) increases with increasing charge density around the nucleus. The slope of the correlation line, approximately 2100 p.p.m. per electron, is about ten times as large as previous estimates of this quantity (78).

Figure I-7:

PLOT OF ^{13}C N.M.R. CHEMICAL SHIFT AGAINST CARBON ATOM NET CHARGE FOR THE ALKANES

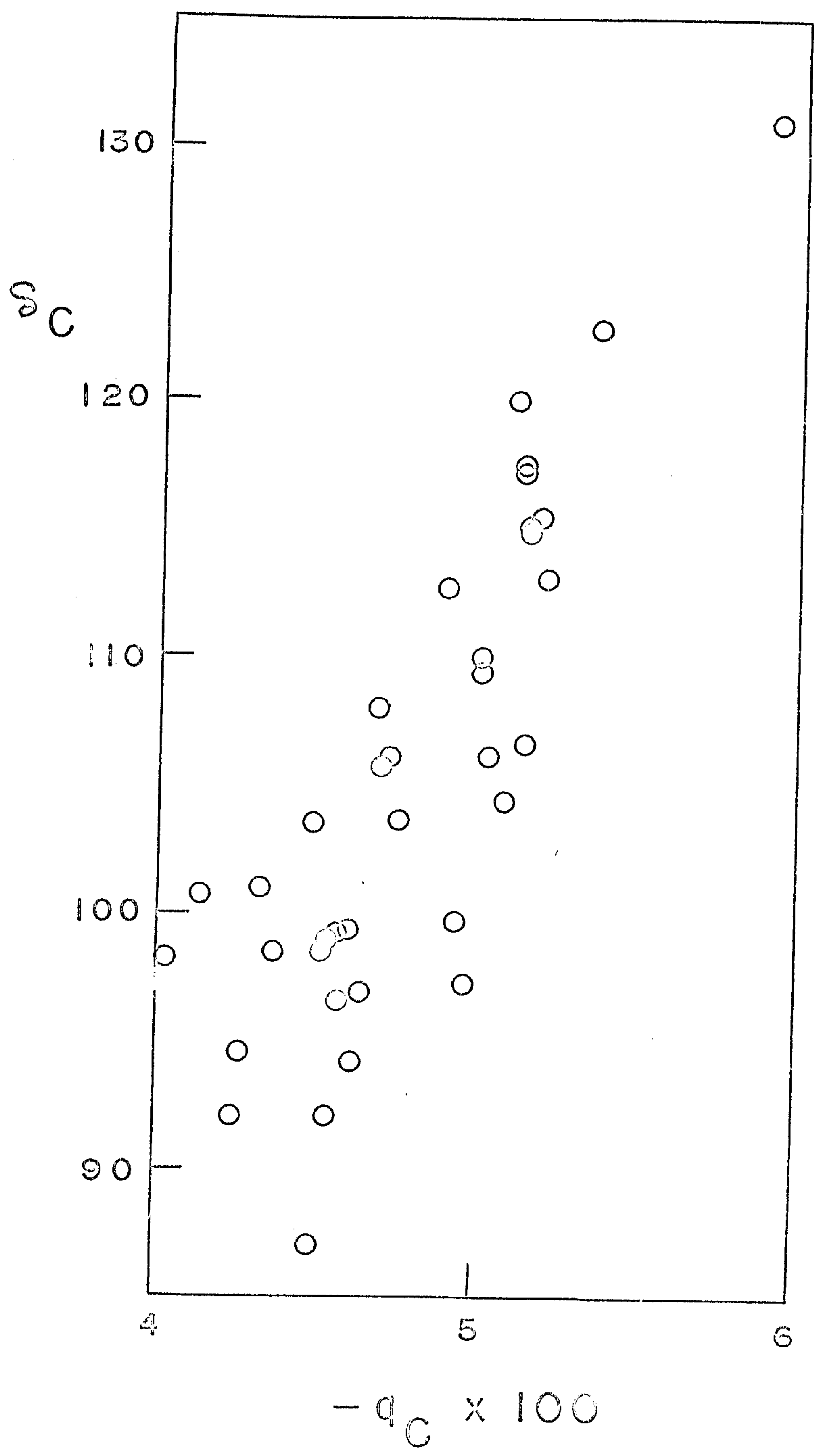
Notes:

a) δ_C is the ^{13}C chemical shift in p.p.m. relative to benzene.

b) q_C is the carbon atom net charge in electrons.

c) Filled-in points represent two or more carbon atoms with nearly identical q_C and δ_C values.

d) All carbon atoms in the alkanes listed in Tables I-VII and I-IX are represented on the graph.



δ_C
130
120
110
100
90
4
5
6
$-q_C \times 100$

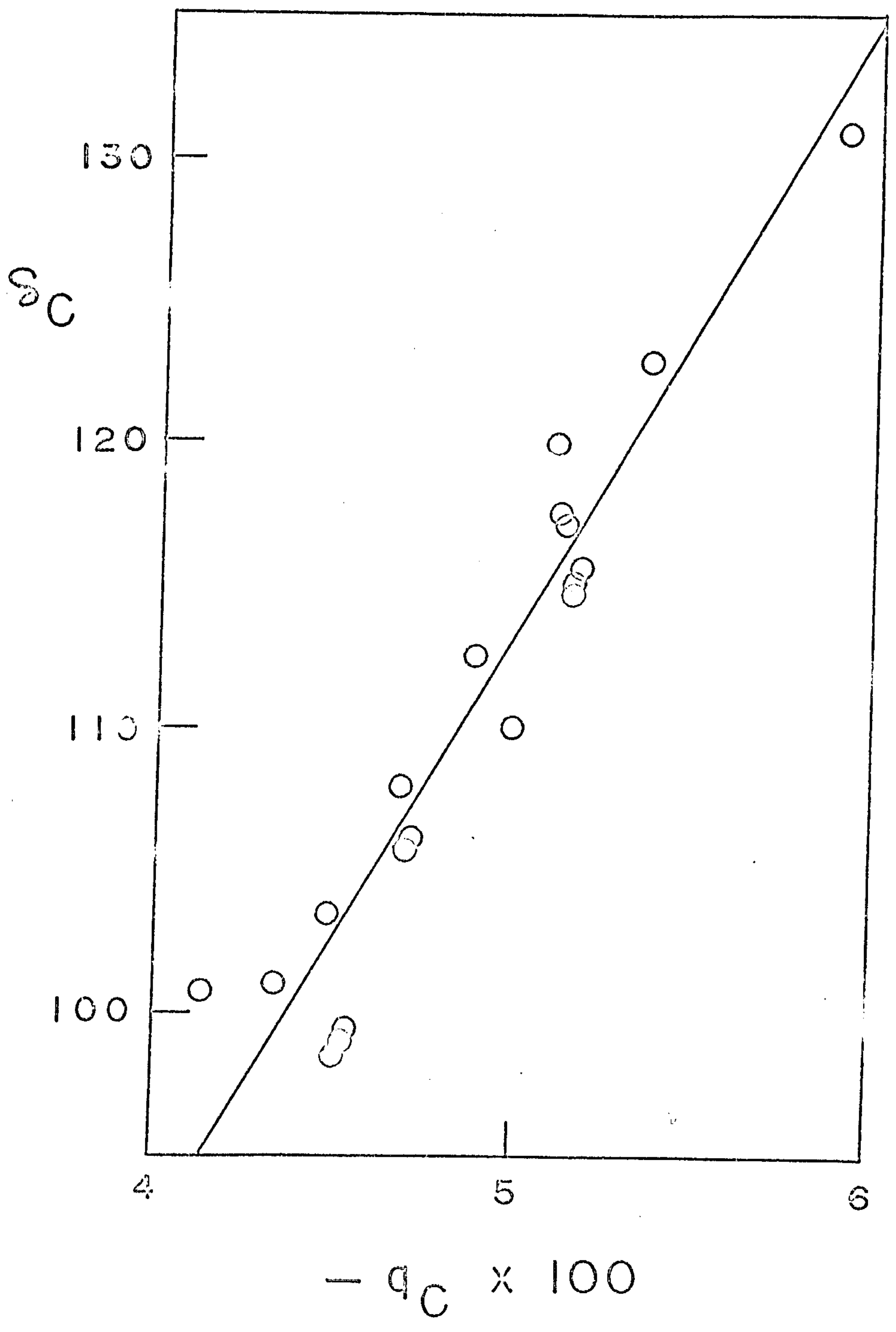
Figure I-8:

PLOT OF ^{13}C N.M.R. CHEMICAL SHIFT AGAINST CARBON ATOM NET CHARGE FOR SELECTED CARBON ATOMS IN ALKANE MOLECULES

Notes:

a) See notes a, b, and c for Figure I-7.

b) The carbon atoms represented are the same as those in Figure I-7, except that carbon atoms bonded to $-C(R_1)(R_2)CH_3$ groups (where the R are alkyl groups or hydrogen atoms) have been eliminated.


130
120
110
100
δ_C
4
5
6
$-q_C \times 100$

If the ^{13}C chemical shifts for the carbon atoms in specific series of alkane molecules are plotted against the corresponding charge densities, other correlation lines can be established. For example, two straight line correlations are found in the methylated methanes series, $(CH_3)_{4-m}\ CH_m$ (Figure I-9). Curve A represents the central carbon atoms in this series, while curve B represents the methyl group carbon atoms. The slope of line A is almost identical to the correlation line slope of Figure I-8, whereas the line B slope, 6000 p.p.m. per electron, is three times as large.

The slopes of the correlation lines in Figures I-8 and I-9 are of the expected sign, and this agreement between the calculated and "experimental" trends upon alkyl substitution represents a limited experimental confirmation of the electron withdrawing effect of substituting alkyl groups for hydrogen atoms in the alkanes. The fact that the correlation line slopes in Figures I-8 and I-9 are much greater than previous estimates indicates that the electronegativity equalization method probably underestimates the changes which occur in the ionic character of localized chemical bonds when the molecular environment is altered. The spread of points encountered in the correlation of Figure I-8 indicates

i) that the electronegativity equalization method correctly predicts the overall trends in the variation of electron density between the different carbon atoms but fails to assess the finer details of the charge density variations correctly, and/or

ii) that although the ^{13}C chemical shifts in the alkanes are primarily determined by the charge density variations, small differences in the neighbour anisotropies and in the average electronic excitation energies for different carbon atoms and for different alkanes do occur, and these

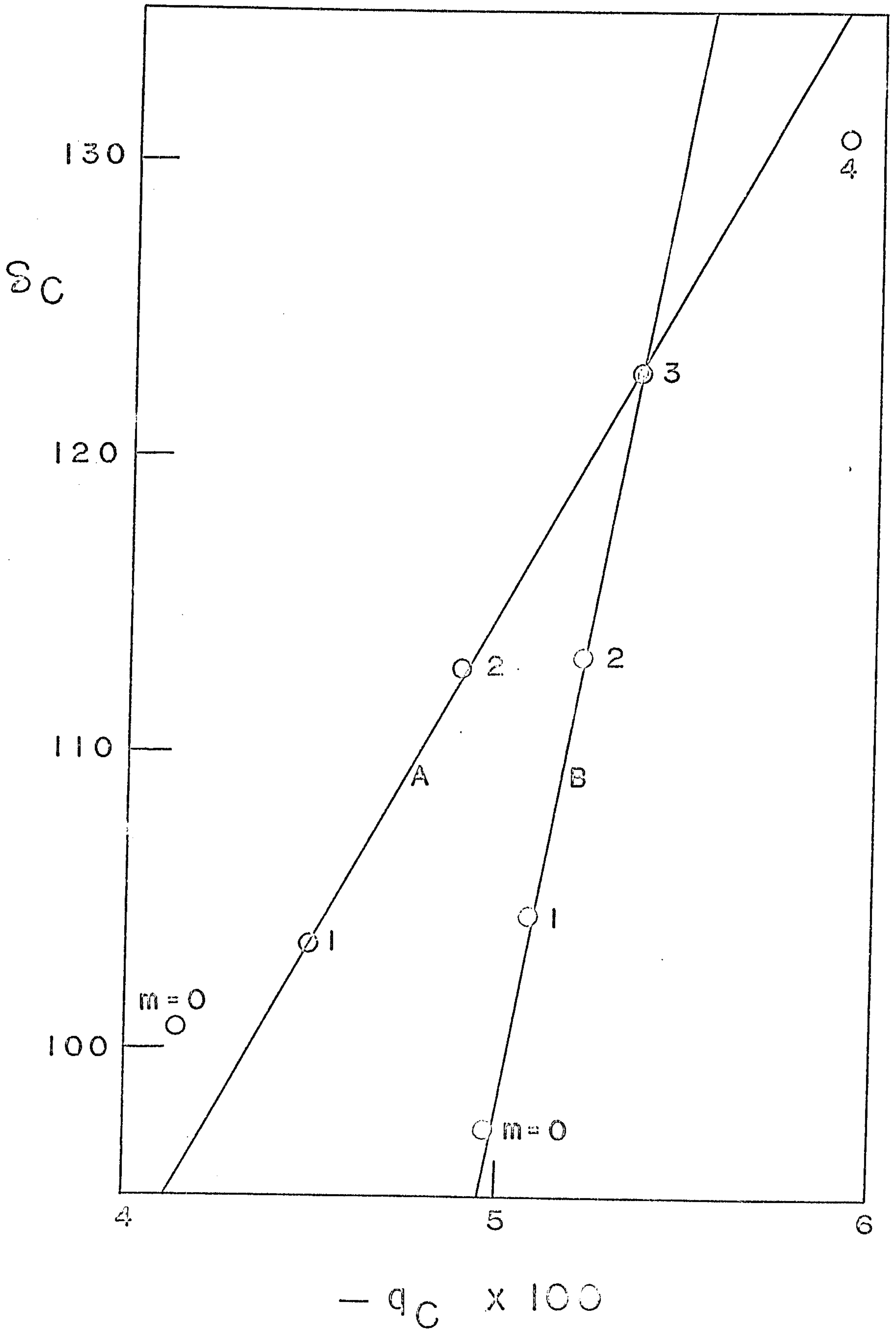
Figure I-9:

PLOT OF ^{13}C N.M.R. CHEMICAL SHIFT AGAINST CARBON ATOM NET CHARGE FOR THE SERIES $(CH_3)_{4-m}\,CH_m$

Notes: a) See notes a and b for Figure I-7.

b) Curve A represents the central carbon atoms.

Curve B represents the carbon atoms of the methyl group.


130
120
110
100
S_C
3
2
2
A
B
1
1
m = 0
m = 0
4
4
5
6
$-q_C$ x 100

changes do not parallel the variations in electronic density. There is no apparent reason why the carbon shifts of the carbon atoms associated with ethyl groups should fail to correlate with the electron densities in the same manner as the other carbon atoms. Grant and Paul (80,81) have also noted the peculiar trends in the chemical shifts for carbon atoms bonded to ethyl groups.

Savitsky and Namikawa (82) have measured the ^{13}C N.M.R. chemical shifts of the carbon atoms in a series of simple alcohols $(CH_3)_{3-m}CH_mOH$. The central carbon atom chemical shifts (relative to benzene) decrease as 80.7, 71.8, 66.1, and 61.3 p.p.m. for m = 3, 2, 1, and 0 respectively. The methyl group carbon atom chemical shifts in this series are substantially higher, and decrease as 111.9, 104.7, and 99.2 p.p.m. for m = 2, 1, and 0 respectively. The calculated carbon atom charge densities for these alcohols, assuming te oxygen atom hybridization (Table I-XXVI), increase as m decreases for both the central carbon atoms and the methyl group carbon atoms, in contrast to the trends in the shielding constants. The trends in the carbon atom charge densities, calculated for these alcohols in which the oxygen atom uses p bonding orbitals (Table I-XXVI), agree with the trends in the chemical shift data. The correlation between δ_C and q_C (with the oxygen atoms using p orbitals) is shown in Figure I-10. Two correlation lines can be established, curve A, of slope 2400 p.p.m. per electron for the central carbon atoms, and curve B, of slope 8300 p.p.m. per electron, for the methyl group carbon atoms. The existence of two separate lines, and the relative slopes of these lines, are similar to the correlations for the $(CH_3)_{4-m}CH_m$ series (Figure I-9). A correlation between δ_C and q_C for the chloromethane series CH_mCl_{4-m} (m = 4, 3, 2, 1, and 0) has been established

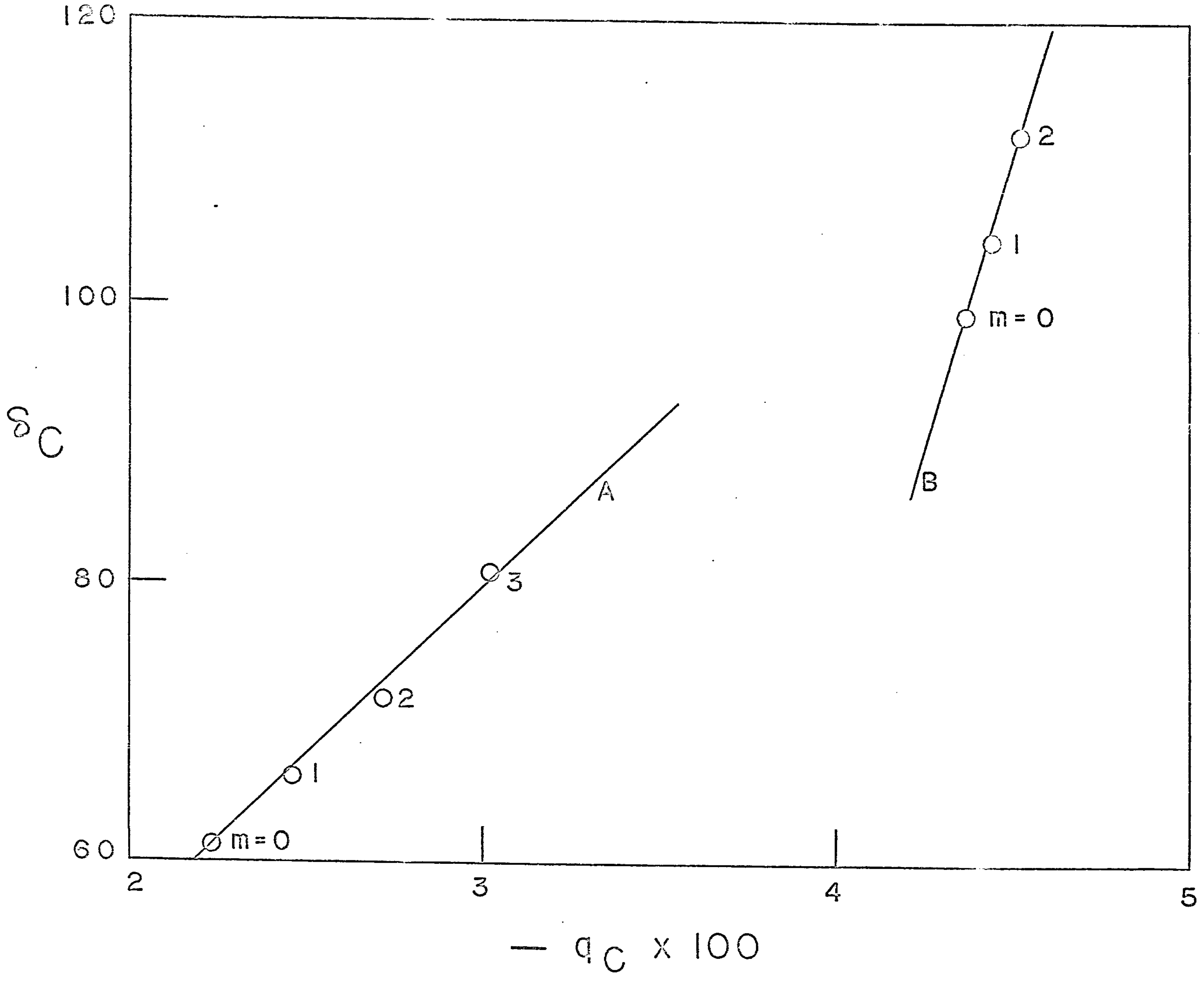
Figure I-10:

PLOT OF ^{13}C N.M.R. CHEMICAL SHIFT AGAINST CARBON ATOM NET CHARGE FOR THE ALCOHOLS $(CH_3)_{3-m}\,CH_mOH$

Notes:

a) See notes a and b for Figure I-7, and note b for Figure I-9.

b) The carbon atom charges are for the alcohols if p orbitals are used by oxygen for bonding.



120
100
80
60
δ_C
2
3
4
5
$-q_C \times 100$
A
m=0
1
2
3
B
m = 0
1
2

by Whitehead, Baird, and Kaplansky (54) who calculated the charge distributions in these molecules by the B.E.E. method. The chlorine atom bonding orbital hybridizations were established by the use of ^{35}Cl nuclear quadrupole resonance spectra. The points corresponding to the carbon atoms in ethyl chloride did not fall on the chloromethane correlation line, of slope 300 p.p.m. per electron, when calculated in the same manner (54).

^{1}H N.M.R. Chemical Shift Correlations

The range of chemical shifts for the proton is much smaller than for other nuclei, since the total electron density in the vicinity of the proton is very small, and because the local paramagnetic shielding term σ_p^{LL} is far less important for ^{1}H than for ^{13}C, ^{19}F, etc. (73). The proton chemical shifts are, consequently, determined by the local diamagnetic term σ_d^{LL}, which is dependent upon electron density about the proton to the extent of about 20 p.p.m. per electron, and by the neighbour anisotropy contribution to the shielding. The latter effect is expected to be very important for protons, since the electron density about this nucleus is relatively small, and the proton is quite exposed to currents flowing on the other atoms in the molecule.

The proton chemical shifts in some series of molecules have been correlated with the hydrogen atom charge densities either by a direct correspondence of the two parameters, or by means of relative charge density criteria such as the electronegativity or the inductive effect parameters of the neighbouring atoms in the molecule (73).

Pople (83) has noted that the screening constants σ of hydrogen nuclei bonded to carbon atoms in the alkanes are in the order

$$\sigma(CH_4) > \sigma(-CH_3) > \sigma(-CH_2) > \sigma(-CH) ,$$

and has suggested that these differences are due to changes in the electron density around the protons. The range of experimental ^1H chemical shifts, and the range of electron density around the proton, for the series of alkanes considered in the present study, are listed in Table I-XXVIII. The calculated hydrogen atom electron densities in this series decrease as the number of hydrogen atoms bonded to the carbon atom decreases, in agreement with the shielding constant variations. There is very little overlapping of either chemical shift or charge ranges between hydrogen atoms of different types. Although the screening constant and charge density trends between carbon atoms of different types are in agreement, there is no general correlation of these two quantities for different hydrogen atoms within each series.

The correlation between ^1H chemical shift and hydrogen atom charge density for the methylated methanes series, $(CH_3)_{4-m}CH_m$, is illustrated in Figure I-11. The slope of line A, the correlation line for the hydrogen atoms bonded to the central carbon atom, is in the correct direction, but is about ten times as large as expected (190 p.p.m. against 20 p.p.m. expected). The slope of correlation line B, about 30 p.p.m. per electron, is also in the correct direction, and is of the expected size. The variations in chemical shift in this series have been attributed by Moritz and Sheppard to variations in the neighbour anisotropy screening contributions to the screening constant (84). The neighbour anisotropy effect changes with m should be much larger for protons bonded to the central atom than for the hydrogen atoms associated with

TABLE I-XXVIII: ^{1}H N.M.R. Chemical Shift and C-H Bond Polarity Ranges in the Alkanes

Type of C-H Bond	Range of ^{1}H N.M.R. Chemical Shifts (a)	Range of C-H Bond Ionic Characters(%)	Range of H Atom Charge Density (in Electrons)
CH_4	6.95	1.48	0.9852
$-CH_3$	6.29 ± 0.04	1.90 ± 0.12	0.9810 ± 0.0012
$>CH_2$	5.92 ± 0.08	2.15 ± 0.11	0.9785 ± 0.0011
$\geqslant CH$	5.6 ± 0.2	2.34 ± 0.07	0.9766 ± 0.0007

Note:

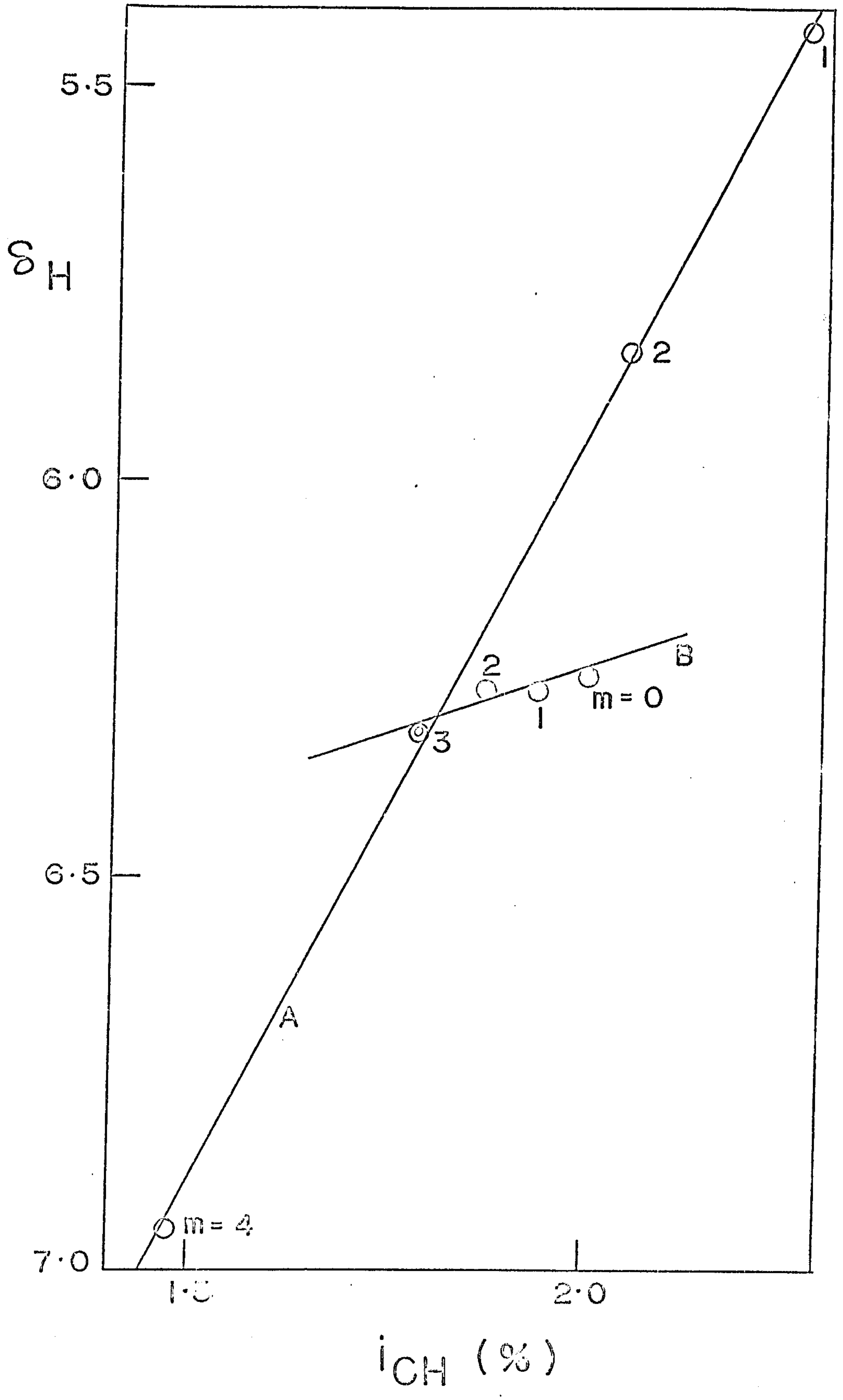
a) See footnotes of Table I-VII for the sources of N.M.R. chemical shifts (given in p.p.m. relative to benzene).

Figure I-11:

PLOT OF ^{1}H N.M.R. CHEMICAL SHIFT AGAINST C-H BOND POLARITY FOR THE SERIES $(CH_3)_{4-m}CH_m$

Notes: a) δ_H is the proton chemical shift in p.p.m. relative to benzene.

b) i_{CH} is the C-H bond ionic character in per cent, in the sense $H^{\delta+}$.


5·5
6·0
6·5
7·0
δ H
1
2
2
B
m = 0
1
3
A
m = 4
1·5
2·0
i CH (%)

the methyl groups. The very large slope of correlation line A may, then, be due to a combination of parallel variations in the contributions from the local diamagnetic and the neighbour anisotropy terms of the screening constant expression.

Further Discussion

Although the ^{1}H and ^{13}C N.M.R. chemical shift correlations with the hydrogen and carbon atom charge densities in the alkanes are only approximate, both sets of correlations clearly support the basic conclusion drawn from the electronegativity equalization calculations that alkyl groups are electron-withdrawing agents relative to hydrogen in the alkanes.

Schaefer and his co-workers (85) have shown that there is an excellent linear correlation of the proton chemical shifts with the B.E.E. method hydrogen atom charge densities for the chloroalkanes. In this correlation, the proton chemical shifts determined by McClellan and Nicksic (86) for both carbon tetrachloride and cyclohexane solutions were separately plotted against the hydrogen charge densities calculated by Whitehead, Baird, and Kaplansky (54). In an additional plot, the "hydrogen-bonded shifts" of four alkyl chloride hydrogen atoms were shown to be linearly dependent upon the calculated hydrogen atom charge densities. The slopes of the correlation lines for cyclohexane and carbon tetrachloride solutions of the chloroalkanes were both approximately 46 p.p.m. per electron (85).

Some chemical shift data has been reported for the ^{14}N nucleus in the saturated amines discussed in the previous section of this study. The ^{14}N chemical shift variations in such nitrogen compounds correlate with the changes in the average electronic excitation term of the local paramagnetic screening contribution (87). There is no correlation between the ^{14}N chemical shifts and the nitrogen atom charge densities calculated herein for either the amines or the protonated amines.

The ^{35}Cl N.M.R. chemical shifts in the chloromethanes have been recently reported by Saito (88). Kaplansky and Whitehead (70) have established a linear correlation between these ^{35}Cl chemical shifts and the corresponding chlorine atom net charges calculated by the electronegativity equalization method.

I. 4. FURTHER DISCUSSION AND CONCLUSIONS

In Part I. 2, the Principle of Electronegativity Equalization was analyzed using molecular orbital theory and the linear combination of atomic orbitals approximation. Defining electronegativity as the first derivative of the energy (molecular or atomic) with respect to the electron density (atomic or orbital) provided a direct link between the LCAO-MO theory and the electronegativity equalization concept. The introduction of the localized chemical bond concept (into this molecular orbital framework for electronegativity equalization), together with neglect of interatomic molecular energy terms, led to the B.E.E. method for the calculation of molecular electron densities.

The B.E.E. method is also related to earlier electronegativity—ionic character theories, such as that of Pauling, since the idea of localized, two-electron bonds is retained, and each bond has associated with it an ionic character determined by the electronegativity properties of its constituent atoms. The B.E.E. method differs from earlier electronegativity theory in that the ionic character of a bond is explicitly dependent on the polarities of the other bonds in the molecule.

The modification of earlier electronegativity and ionic character formulae for a bond to reflect the polarities of other bonds in the molecule, has been proposed by several workers (21,66,89,90). In the method of Daudel and Daudel (21), for example, the dependence of the "Pauling" electronegativity of an atom on its net charge was evaluated using the dependence of electronegativity on effective nuclear charge. A self-consistent field technique was used to calculate atomic net charges by combining the electronegativity-net charge function with Pauling's formula for the ionic character of a bond, equation 9 (90). The advantages of the B.E.E. method over this procedure are that

i) the dependence of electronegativity on atomic charge is a direct one, since the electronegativity function is defined explicitly by atomic properties (ionization potential and electron affinity) whose dependence on charge can be directly evaluated,

ii) the orbital nature of electronegativity is fully recognized in the electronegativity function used in the B.E.E. method, and

iii) there is some theoretical justification for the electronegativity-ionic character relationship used in the B.E.E. method, whereas Pauling's ionic character equation is based on an approximate, empirical correlation using dipole moments.

The "bond electronegativity equalization method" is then best regarded as a hybrid of molecular orbital theory with conventional electronegativity concepts. The molecular electronic distributions calculated by the B.E.E. method were shown (Part I. 3) to account semi-quantitatively for several known aspects of electronic effects in saturated molecules, such as the transmission of inductive effects through carbon-carbon bonds, the stabilization of carbonium ions by alkyl groups, the nature of the inductive effects produced by substitution of a heteroatom into an alkane molecule, etc. The correlations of atom charges calculated by the B.E.E. method with N.M.R. chemical shifts are as good as, or better than, the correlations obtained when the atom charges are estimated by standard LCAO-MO techniques such as the Extended Huckel Method (91).

Some of the more surprising aspects of the inductive effects predicted by the B.E.E. method are difficult to test due to the lack of relevant experimental evidence. For example, very little information is available about the relative inductive effects of alkyl groups and hydrogen atoms in the alkanes. The N.M.R. chemical shift trends in these molecules do provide some support for the prediction that alkyl groups are electron-withdrawing relative to hydrogen in such molecules. In addition, some recent chemical evidence concerning the reactivity (92,93,94) and dipole moments (95) of alkanes has been interpreted in terms compatible with the B.E.E. method predictions. In these studies, it was concluded that the normal inductive effects of methyl groups and hydrogen atoms can be reversed when there are no highly electronegative atoms close to the carbon atom at which the substitution occurs (94,95). It will be interesting to see how close the B.E.E. method results come in predicting the point at which the inductive effects of alkyl groups and hydrogen are reversed, when more chemical evidence concerning this effect is available.

One of the interesting features of the B.E.E. method calculations is the relatively wide range of values found for the electronegativity of a group in various chemical environments. Since the "Mulliken" electronegativity of a group of atoms is quite dependent on the group or atom to which it is bonded, it is impossible to construct a scale of relative group inductive effects applicable over a range of chemical environments from the B.E.E. calculations. The variation of group electronegativity with environment shows that empirical estimates of group electronegativity, such as the Taft σ^* parameters (72), are valid only for molecules in which the electronic environments of the groups are similar.

The B.E.E. calculations show that the Mulliken electronegativity of an atomic orbital of a polyvalent atom in a molecule is not necessarily close to that for the orbital in the valence state of the isolated atom. For example, X(1) for a te orbital of an oxygen atom in a molecule is usually lower than the isolated atom value, since the bonds to oxygen are quite polar in the sense $O^{\delta-}$. Hence, the ionic character of O_{te}-H bonds in alcohols is substantially lower than that predicted for an isolated O_{te}-H bond. Although the self-consistent field B.E.E. method ionic characters for a bond are generally quite different from the polarity of the same isolated bond, the S.C.F. ionic characters of a given bond in similar molecules are usually quite similar.

The greatest deficiency of the B.E.E. method lies in the difficulty of total molecular energy calculations. Since no interatomic energy terms are explicitly considered in the calculations, the extra ionic resonance energies calculated by this method (equation 83) will be very small in comparison with the experimental results. The inclusion of interatomic electrostatic and resonance energy terms into the bond electronegativity function, as suggested in Part I. 2, would partially relieve this difficulty. Such changes would also increase the magnitude of the ionic characters of bonds, and increase the changes in these ionic characters when the molecular environment is altered. The ionic characters of the halogen-alkali metal bonds would then be increased to more chemically reasonable values, and the rate of change of N.M.R. chemical shift with electronic density obtained from the correlations would be more in line with those expected from theoretical considerations.

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APPENDIX I:

DESCRIPTION OF THE COMPUTER PROGRAMME USED FOR ELECTRONEGATIVITY EQUALIZATION CALCULATIONS

An iterative, self-consistent field procedure must be used to calculate molecular charge distributions for polyatomic molecules by the bond electronegativity equalization (B.E.E.) method. A computer programme has been written in IBM Fortran IV language to automatically carry out these calculations, once certain information concerning the molecule has been supplied. This programme was used to calculate the charge density and electronegativity data required in Part I of the present study.

The programme is divided into two sections, the "main" programme called BEEM, and a "subroutine" termed PARAMT. The symbols used in both these segments are identical, and are listed in Table I-XXIX.

The input data required for each molecule may be discussed by reference to the "BEEM CALCULATION SHEET" given in Figure I-12. Such a sheet has been composed for each molecule considered. The sheet illustrated is that used for the methanol molecule CH_3OH.

In a molecule, each chemically inequivalent atom is assigned a number which is shown as a circled integer. The atomic orbitals forming each chemically inequivalent bond are also numbered such that the orbitals of the first bond are 1 and 2, those of the second bond are 3 and 4, etc. If two or more bonds formed by the same atom are chemically equivalent, then the same orbital number is assigned to each equivalent atomic orbital of the atom. For example, the three equivalent te hybrid orbitals of carbon which form C-H bonds in methanol are all numbered "5."

TABLE I-XXIX

Definition of the Symbols Used in the "BEEM" and "PARAMT" Fortran IV Computer Programmes

SYMBOL	DEFINITION
III	Determines type of valence state to be used for N, O, S.
NCASE	Code number for molecule (Integer between 1 and 299).
NATOT	Total number of chemically inequivalent atoms in the molecule.
IB	Total number of inequivalent bonding orbitals in the molecule.
IC	" " " " " " " "
NMAX	Maximum number of iterations allowed for one molecule.
NZ(I)	Atomic number of atom I.
N1(I)	Code numbers of the four valence-shell orbitals of atom I.
N2(I)	
N3(I)	
N4(I)	
M1	Initial, integral charge densities of the four valence-shell orbitals (N1(I), N2(I), N3(I), N4(I)) of atom I.
M2	
M3	
M4	
L1,L2,L3,L4	Same as N1(I), N2(I), N3(I), N4(I) respectively.
Q(I)	Charge density of orbital I for current iteration.
QA(I)	" " " " " " previous iteration.
NC(I)	Code number of atom to which orbital I belongs.

TABLE I-XXIX continued

SYMBOL	DEFINITION
D1(I)	Value of electronegativity parameter α for orbitals of atom I.
D2(I)	" " " " β " " " " "
D3(I)	" " " " γ " " " " "
F1(I)	" " " " δ " " " " "
F2(I)	" " " " ϵ " " " " "
F3(I)	" " " " ζ " " " " "
B(I)	" " " " b for orbital I.
C(I)	" " " " c " " "
XX(I)	Value of the electronegativity X " " "
NIT	Iteration number.
I1 I4 J1 J4	Code numbers of the four valence-shell orbitals of the same atom as orbital I, J.
NTI, NTJ	Sum of the charge densities Q of all the valence-shell orbitals except I (or J) on same atom as orbital I (or J).
PTI, PTJ	Ionization potential of orbital I (or J).
AFI, AFJ	Electron affinity " " " " "
Y	Total charge density of orbitals of an atom.

Figure I-12:

"BEEM" CALCULATION SHEET FOR
THE METHANOL MOLECULE

Notes: a) —— represents a bonding orbital

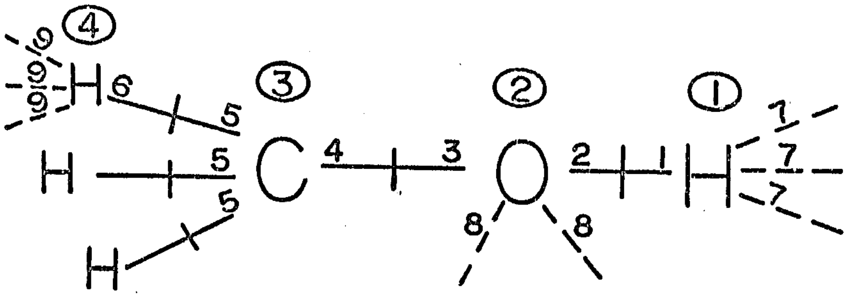
- - - - represents an "imaginary" orbital or a "lone-pair" orbital.

b) NZ is the atomic number; N1 to N4 are atomic orbital numbers; M1 to M4 are initial orbital charge densities.

B.E.E.M. CALCULATION SHEET

CASE NO.	51
MOLECULE CH_3OH	

MOLECULAR NUMBERING SYSTEM



CONTROL CARD

051	004	006	009

DATA CARDS

NZ	N1	N2	N3	N4	M1	M2	M3	M4
1	1	7	7	7	1	0	0	0
8	2	3	8	8	1	1	0	0
6	4	5	5	5	1	1	1	1
1	6	9	9	9	1	0	0	0

The first set of data supplied to the computer for a molecule is listed under the "control" card heading in the calculation sheet. The integer in the first block is the "case number" assigned to the molecule, and is entered into the computer as the variable NCASE. The integer in the second block represents NATOT, the total number of chemically inequivalent *atoms* in the molecule. The third block is used for IB, the total number of non-equivalent *bonding* atomic orbitals, and the fourth block represents IC, the total number of inequivalent atomic orbitals of all types.

In addition to the information punched on the "control" card, a "data" card must be punched for each inequivalent atom. The information on these data cards is given in each row which is divided into nine sections on the calculation sheet. The data for the i^{th} atom is listed in the i^{th} row in this matrix. The first variable of each row is NZ, which represents the "atomic number" of the atom. These "atomic numbers" correspond to the real atomic numbers of the atoms concerned with the following exceptions:

NZ = 66 for the $(trtrtr\pi^1)$ valence state of carbon

NZ = 67 for the $(trtrtr\pi^0)$ valence state of carbon

NZ = 68 for the $(didi\pi^1\pi^1)$ valence state of carbon

NZ = 77 for the (tetetete) valence state of nitrogen .

The entries N1, N2, N3, N4 correspond to the orbital numbers for the atom concerned. If two or more orbitals are equivalent, their numbers will be identical. Lone-pair, vacant and singly-occupied non-bonding orbitals are numbered from (IB + 1) upwards, and are listed under the N1 to N4 headings. The programme was devised for atoms which have four valence-shell orbitals, and therefore four orbital numbers N1, N2, N3 and N4 must be listed. In the case of the hydrogen atom which has only one valence-shell atomic orbital, an arbitrary integer between (IB + 1) and IC is listed in the columns N2, N3, and N4 for each hydrogen atom.

The entries M1, M2, M3, and M4 for each atom correspond to the initial, integral values used by the programme for the charge densities of the orbitals N1, N2, N3 and N4 respectively. Values of zero are listed for M2, M3, and M4 if the atom concerned is hydrogen. Initial charge densities of bonding orbitals can be listed as 0, 1 or 2 although it is usually more efficient to list then all as 1.

Some caution must be exercised in the assignment of M1 to M4 values to non-bonding orbitals. If the charge density of the orbital concerned is included in the sum T for the atom (see Part I. 3. A), its actual, integral charge density must be listed. If the charge density of the non-bonding orbital is not included in T, its initial charge density must be listed as zero.

A "data card" for each atom, and a "control card" for the molecule, are required for each molecule.

The manipulations executed by each part of the "BEEM" and "PARAMT" programmes are described in Table I-XXX by reference to the "INTERNAL STATEMENT NUMBERS" (ISN) concerned. "Source" listings of the BEEM and PARAMT sections of the programme are illustrated in Figures I-13 and I-14 respectively.

The input data which is transferred from the main programme to the PARAMT subroutine consists of the numerical values of the variables NZ(I), I, and III for the atom I. The function of the subroutine is to assign the values of D1(I), D2(I), D3(I), F1(I), F2(I), and F3(I) for atom I based upon

i) its atomic number NZ(I), and

ii) the type of valence state to be considered, as given by III.

TABLE I-XXX: Description of the "BEEM" Computer Programme

ISN (see Figure I-13)	Description
0—1	"Comment" statements. These are not operations but are simply comments listed to aid the user of the programme.
1	DIMENSION statement. This statement defines the maximum size of the one-dimensional matrices NZ . . . XX used in the programme.
2	REAL statement—converts the variables NTI, NTJ from integers to "floating point" variables.
3, 5	Before a set of molecules is considered, a parameter III is read. If III is equal to 1, (sppp) valence states are used for N, O, and S atoms. If III is 2, (tetetete) valence states are used for these atoms.
6, 13	Reading of the "control card" for each molecule.
14	The value of NCASE is automatically increased by 300 (from the value read in) for (tetetete) valence states of N, O, and S.
17	NMAX defines the maximum number of iterations to be used for any one molecule.
20, 21	The data read in at 6, 13 is printed out.
22	The "DO 40" loop is defined. Each operation from ISN 23 to ISN 50 is then repeated for each atom from 1 to NATOT.
23, 30	The "data card" for atom I is read.
31, 32	The data read in above is printed out.

TABLE I-XXX continued

ISN (see Figure I-13)	Description
33---36	Variables L1, L2, L3, and L4 are defined as the orbital numbers N1(I), N2(I), N3(I), and N4(I).
37---42	The initial charge densities M1 to M4 of orbitals L1 to L4 are entered into the QA matrix.
43---46	The NC matrix is defined. NC(J) represents the number of the atom associated with orbital J.
47	The subroutine PARAMT is called. This subroutine assigns the ionization potential and electron affinity parameters α, β, γ, δ, ϵ, and ζ to each atom I. In the programme, these parameters are called D1(I), D2(I), D3(I), F1(I), F2(I), and F3(I) respectively.
50	"DO 40" loop ended.
52, 53	Initial values of the matrix Q are defined as the corresponding values in the QA matrix.
57, 60	Some as ISN 52, 53 for iterations other than the first.
63	The "DO 10" loop is started; this loop ends at ISN 123. Since IZ has been defined as (IC - 1), this loop treats every <u>bond</u> in the molecule.
64	Assigns a value to J, the second orbital in the bond formed by orbitals I and J.

TABLE I-XXX continued

ISN (see Figure I-13)	Description
65, 66	IA and JA defined as the atom numbers to which orbitals I and J belong.
67---76	I1 to I4, and J1 to J4 defined as the orbital numbers associated with atoms IA and JA respectively.
77, 100	NTI, NTJ calculated for orbitals I, J from the charge density Q matrix. NTI and NTJ represent the sums of the charge densities of the valence-shell orbitals of atoms IA and JA respectively; NTI and NTJ do <u>not</u> include the charge densities of orbitals I and J respectively.
101---110	The operations in these statements define PTI, PTJ, AFI, AFJ, B(I), B(J), C(I), and C(J) which correspond to the electronegativity equation parameters I_I, I_J, A_I, A_J, b_I, b_J, c_I and c_J respectively.
111	Transfers control of program to ISN 121 if I, J are non-bonding orbitals.
114, 115	Define XX(I) and XX(J) corresponding to the electronegativities $X_I(1)$, and $X_J(1)$.
116, 117	New charge densities Q(I) and Q(J) defined by the ionic character equation.
120	Programme control transferred to ISN 123.

TABLE I-XXX continued

ISN (see Figure I-13)	Description
121, 122	Calculates bond electronegativities X_I and X_J (for the charge densities Q(I) and Q(J) for non-bonding orbitals I, J.
123	Defines end of "DO 10" loop.
125---133	The charge densities Q(I) are compared to those of the previous iteration, QA(I), for each I to establish whether a self-consistent charge density distribution has been found. The criterion for self-consistency is that all the terms $\lvert Q(I) - QA(I) \rvert$ are less than 0.000002 electrons. If self-consistency has been established, control of the programme is transferred to ISN 153. If not, the programme is transferred to ISN 134.
134---135	Calculates the iteration number and tests to see if the maximum number of iterations has been reached, since the charge densities do not yet form a self-consistent field. If the maximum number has been reached, control is transferred to ISN 140. If not, control is transferred back to ISN 57, and all the operations between ISN 57 and ISN 134 are repeated in a new iteration.
140---152	Since the maximum number of iterations has been reached without self-consistency if the control is transferred to this point, a message "NO CONV" is printed. The next molecule

TABLE I-XXX continued

ISN (see Figure I-13)	Description
	is then considered by transferring the control back to ISN 6.
153---154	Since an SCF set of orbital charge densities has been calculated if control is transferred to this point, the results must be printed out. These two statements, 153 and 154, print a heading concerning the total charge density of each atom.
155---170	The total charge density in the orbitals N1(I), N2(I), N3(I), and N4(I) of each atom I is defined as Y, and this density is printed out.
172-177	The first line on the second page of results is printed out. This line gives the case number, (NCASE), number of iterations required to achieve self-consistency (NIT), and the atomic numbers of each atom from 1 to NATOT.
200---201	Second line on second page of results printed. This line contains the headings for the successive lines to be printed.
202---211	The orbital number, number of the atom, atomic number of the atom, SCF charge density, and electronegativity XX of each orbital (except the "imaginary" hydrogen orbitals) are printed out. The manipulations for the molecule are now complete.
213	Transfers control back to ISN 6 so that a new molecule may be considered.
214	Required "END" statement for the BEEM programme.

Figure I-13:

FORTRAN IV SOURCE LISTING FOR THE
"BEEM" MAIN COMPUTER PROGRAMME

```
 ISN        SOURCE STATEMENT

  0 $IBFTC MAIN
    C        BAIRD  GENERALIZED BOND ELECTRONEGATIVITY EQUALIZATION METHOD
    C        BEEM  PROGRAM,BY N.C.BAIRD   APRIL 1966
    C        ATOMIC NUMBERS NZ ARE 1 FOR H(S),6 FOR C(TE TE TE TE),
    C        66 FOR C(TR TR TR PI(1)),67 FOR C(TR TR TR PI(0)),
    C        14 FOR SI(TE TE TE TE)
    C        68 FOR C(DI DI PI(1)PI(1)),7 FOR N, 8 FOR O
    C        N CAN BE (S(2)P P P) OR (TE TE TE TE(2))
    C        O CAN BE (S(2)P(2) P P) OR (TE TE TE(2)TE(2))
    C        S CAN BE (S(2)P(2) P P) OR (TE TE TE(2)TE(2))
    C        IF III IS 1, SPPP STATES USED FOR N,O,S
    C        IF III IS 2, TE TE TE TE STATES USED FOR N,O,S
    C        FOR N,O,S TE STATES,NCASE IS AUTOMATICALLY INCREASED BY 300
    C        NOTE THAT ANY ORBITALS WHOSE CHARGE DENSITIES ARE NOT INCLUDED
    C        IN THE SUM MUST BE LISTED INITIALLY WITH ZERO CHARGE DENSITY.
    C        SINCE THE PROGRAM ASSUMES EACH ATOM HAS FOUR VALENCE SHELL
    C        ORBITALS,THREE IMAGINARY NON-BONDING ORBITALS WITH ZERO CHARGE
    C        DENSITY MUST BE LISTED FOR EACH HYDROGEN ATOM.
  1          DIMENSION NZ(100),N1(100),N2(100),N3(100),N4(100),NC(100),
           1 D1(100),D2(100),D3(100),F1(100),F2(100),F3(100),Q(100),QA(100),
           2 B(100),C(100),XX(100)
  2          REAL NTI,NTJ
    C        DATA READING SECTION
  3          READ(5,90)III
  5     90   FORMAT(I1)
  6     16   READ(5,1)NCASE,NATOT,IB,IC
 13      1   FORMAT(4I3)
```

```
      IF(III.EQ.2)NCASE=NCASE+300
      NMAX=100
      WRITE(6,8)NCASE
    8 FORMAT(1H1,11HCASE NUMBER,I8,3X,6HBEGINS)
      DO 40 I=1,NATOT
      READ(5,3)NZ(I),N1(I),N2(I),N3(I),N4(I),M1,M2,M3,M4
    3 FORMAT(9I2)
      WRITE(6,50)NZ(I),N1(I),N2(I),N3(I),N4(I),M1,M2,M3,M4
   50 FORMAT(1H0,9I5)
      L1=N1(I)
      L2=N2(I)
      L3=N3(I)
      L4=N4(I)
      QA(L1)=M1
      QA(L2)=M2
      QA(L3)=M3
      QA(L4)=M4
      NC(L1)=I
      NC(L2)=I
      NC(L3)=I
      NC(L4)=I
C     PARAMETER ASSIGNMENT SECTION
      CALL PARAMT(NZ,I,III,D1,D2,D3,F1,F2,F3)
   40 CONTINUE
      DO 7 I=1,IC
    7 Q(I)=QA(I)
      NIT=0
      GOTO9
```

Mc

```
       ISN        SOURCE STATEMENT

        57     14 DO 22 I=1,IB
        60     22 QA(I)=Q(I)
        62      9 IZ=IC-1
             C    IONIC CHARACTER AND ORBITAL CHARGE DENSITY CALCULATION SECTION
        63        DO 10 I=1,IZ,2
        64        J=I+1
        65        IA=NC(I)
        66        JA=NC(J)
        67        I1=N1(IA)
        70        I2=N2(IA)
        71        I3=N3(IA)
        72        I4=N4(IA)
        73        J1=N1(JA)
        74        J2=N2(JA)
        75        J3=N3(JA)
        76        J4=N4(JA)
        77        NTI=Q(I1)+Q(I2)+Q(I3)+Q(I4)-Q(I)
       100        NTJ=Q(J1)+Q(J2)+Q(J3)+Q(J4)-Q(J)
       101        PTI=D1(IA)+D2(IA)*NTI+D3(IA)*(NTI**2)
       102        PTJ=D1(JA)+D2(JA)*NTJ+D3(JA)*(NTJ**2)
       103        AFI=F1(IA)+F2(IA)*NTI+F3(IA)*(NTI**2)
       104        AFJ=F1(JA)+F2(JA)*NTJ+F3(JA)*(NTJ**2)
       105        B(I)=1.5*PTI-0.5*AFI
       106        B(J)=1.5*PTJ-0.5*AFJ
       107        C(I)=0.5*(AFI-PTI)
       110        C(J)=0.5*(AFJ-PTJ)
```

```
      IF(I.GT.IB)GOTO43
      XX(I)=B(I)+2.*C(I)
      XX(J)=B(J)+2.*C(J)
      Q(I)=1.0+((XX(J)-XX(I))/(2.*(C(I)+C(J))))
      Q(J)=2.0-Q(I)
      GOTO10
C     NOTE-IF IC IS EVEN,ITS BOND X IS NOT CALCULATED
   43 XX(I)=B(I)+2.*C(I)*Q(I)
      XX(J)=B(J)+2.*C(J)*Q(J)
   10 CONTINUE
C     TEST FOR SELF-CONSISTENT FIELD
      DO 11 I=1,IB
      IF(ABS(Q(I)-QA(I)).GT.0.000002)GOTO12
   11 CONTINUE
      GOTO13
   12 NIT=NIT+1
      IF(NIT.LE.NMAX)GOTO14
      WRITE(6,15)NCASE,NIT,(Q(I),I=1,IB),(QA(I),I=1,IB)
   15 FORMAT(1H0,7HNC CONV,2I5,20F5.3/1H0,20F5.3/1H0,20F5.3)
      GOTO16
C     CALCULATION OF ATOM CHARGE DENSITIES(BONDING ORBITALS ONLY)
   13 WRITE(6,70)
   70 FORMAT(1H0,46HTOTAL CHARGE DENSITY IN ATOMS BONDING ORBITALS)
      DO 71 I=1,NATOT
      IF(NZ(I).EQ.1)GOTO71
      L1=N1(I)
      L2=N2(I)
      L3=N3(I)
      L4=N4(I)
```

```
 ISN          SOURCE STATEMENT

 165          Y=Q(L1)+Q(L2)+Q(L3)+Q(L4)
          C   PRINTING OF RESULTS(FIRST PAGE)
 166          WRITE(6,72)I,Y
 167       72 FORMAT(1H0,I8,F17.5)
 170       71 CONTINUE
          C   PRINTING OF RESULTS(SECOND PAGE)
 172          WRITE(6,17)NCASE,NIT,(NZ(I),I=1,NATOT)
 177       17 FORMAT(1H1,25I4)
 200          WRITE(6,31)
 201       31 FORMAT(1H0,7HORBITAL,2X,8HATOM NO.,2X,10HATOMIC NO.,5X,
             1 6HCHARGE,12X,13HBOND(0,1,2) X)
 202          DO 19 I=1,IC
 203          J=NC(I)
 204          IF(Q(I).EQ.0.0.AND.NZ(J).EQ.1)GOTO19
 207          WRITE(6,30)I,J,NZ(J),Q(I),XX(I)
 210       30 FORMAT(1H0,3I7,4X,F16.5,3X,F16.5)
 211       19 CONTINUE
 213          GOTO16
 214          END

NO MESSAGES FOR ABOVE ASSEMBLY
```

Figure I-14:

FORTRAN IV SOURCE LISTING FOR

THE "PARAMT" SUBROUTINE

```
BAIRD BEEM THESIS PRDN.                        FORTRAN SOURCE LIST                              07/23/66
     ISN       SOURCE STATEMENT

       0 $IBFTC PARAMT
       1          SUBROUTINE PARAMT(NZ,I,III,D1,D2,D3,F1,F2,F3)
       2          DIMENSION NZ(100),D1(100),D2(100),D3(100),F1(100),F2(100),F3(100)
        C         THIS SUBROUTINE ASSIGNS D1 TO F3 FOR ATOM I
       3          IF(NZ(I).NE.77)GOTO12
       6          D1(I)=100.057
       7          D2(I)=-28.1695
      10          D3(I)=1.9715
      11          F1(I)=70.500
      12          F2(I)=-25.395
      13          F3(I)=2.202
      14          RETURN
      15       12 IF(NZ(I).NE.1)GOTO1
      20          D1(I)=13.60
      21          D2(I)=0.0
      22          D3(I)=0.0
      23          F1(I)=0.75
      24          F2(I)=0.0
      25          F3(I)=0.0
      26          RETURN
      27        1 IF(NZ(I).NE.6)GOTO2
      32          D1(I)=57.067
      33          D2(I)=-17.240
      34          D3(I)=1.029
      35          F1(I)=44.465
      36          F2(I)=-20.8795
      37          F3(I)=2.1685
      40          RETURN
```

```
 41      2 IF(NZ(I).NE.66)GOTO3
 44        D1(I)=40.853
 45        D2(I)=-14.3865
 46        D3(I)=0.8855
 47        F1(I)=26.049
 50        F2(I)=-16.226
 51        F3(I)=2.089
 52        RETURN
 53      3 IF(NZ(I).NE.67)GOTO4
 56        D1(I)=60.373
 57        D2(I)=-19.081
 60        D3(I)=1.482
 61        F1(I)=37.478
 62        F2(I)=-15.1255
 63        F3(I)=1.1515
 64        RETURN
 65      4 IF(NZ(I).NE.68)GOTO5
 70        D1(I)=28.153
 71        D2(I)=-11.282
 72        D3(I)=0.554
 73        F1(I)=12.965
 74        F2(I)=-11.4555
 75        F3(I)=1.8355
 76        RETURN
 77      5 IF(NZ(I).NE.14)GOTO6
102        D1(I)=32.822
103        D2(I)=-6.7785
```

```
BAIRD BEEM THESIS PRDN.                               FORTRAN SOURCE LIST PARAM
   ISN        SOURCE STATEMENT

   104        D3(I)=-0.0745
   105        F1(I)=26.566
   106        F2(I)=-8.8725
   107        F3(I)=0.3145
   110        RETURN
   111      6 IF(III.EQ.2)GOTO9
   114        IF(NZ(I).NE.7)GOTO7
   117        D1(I)=48.229
   120        D2(I)=-21.101
   121        D3(I)=1.977
   122        F1(I)=29.017
   123        F2(I)=-19.921
   124        F3(I)=2.902
   125        RETURN
   126      7 IF(NZ(I).NE.8)GOTO8
   131        D1(I)=34.284
   132        D2(I)=-18.9065
   133        D3(I)=1.9005
   134        F1(I)=15.207
   135        F2(I)=-14.8685
   136        F3(I)=1.6635
   137        RETURN
   140      8 IF(NZ(I).NE.16)GOTO100
   143        D1(I)=23.052
   144        D2(I)=-11.6615
   145        D3(I)=1.0025
   146        F1(I)=11.033
   147        F2(I)=-8.5815
   150        F3(I)=-0.0725
   151        RETURN
   152      9 IF(NZ(I).NE.7)GOTO10
   155        D1(I)=53.752
   156        D2(I)=-22.0735
   157        D3(I)=2.3295
   160        F1(I)=29.853
   161        F2(I)=-17.6995
   162        F3(I)=2.4245
   163        RETURN
   164     10 IF(NZ(I).NE.8)GOTO11
   167        D1(I)=40.798
   170        D2(I)=-17.4515
   171        D3(I)=1.0445
   172        F1(I)=20.427
   173        F2(I)=-16.3625
   174        F3(I)=2.0445
   175        RETURN
   176     11 IF(NZ(I).NE.16)GOTO100
   201        D1(I)=29.248
   202        D2(I)=-16.154
   203        D3(I)=2.403
   204        F1(I)=13.715
   205        F2(I)=-8.826
   206        F3(I)=-0.119
   207    100 RETURN
   210        END

   NO MESSAGES FOR ABOVE ASSEMBLY

OBJECT PROGRAM IS BEING ENTERED INTO STORAGE.
```

If III is 2, the (tetetete) valence state parameters are assigned to atom I, if I is a nitrogen, oxygen or sulphur atom; if III is 1, the (sppp) valence state parameters are assigned to these atoms.

The subroutine PARAMT is capable of assigning the parameters D1(I) through F3(I) for the following atoms and valence states: H(s), C(tetetete), C(trtrtrπ^1), C(trtrtrπ^o), C(didi$\pi^1\pi^1$), Si(tetetete), N(s^2ppp), O(s^2p^2pp), S(s^2p^2pp), N(tetetete^2), N(tetetete), O(tetete^{2}te^2) and S(tetete^{2}te^2). After assigning the parameters to a given atom, control is returned to the main programme by the "RETURN" statements.

The print-out from the BEEM PROGRAM for a typical molecule is illustrated in Figure I-15 for the methanol molecule. On each page of results, the value of the parameter NCASE is the first number to be printed. The input data used for the molecule is printed out under NCASE on the first page. The atom number and total bonding orbital charge density of each atom (other than hydrogen atoms) are listed below the input data on the first page of results for a molecule.

The first, untitled, row of figures on the second page of print-out for the molecule represent the numerical values of NCASE, NIT (the number of iterations used to achieve a self-consistent field), and the atomic numbers NZ(I) of all the atoms from 1 to NATOT. The remaining data on the second page consists of the orbital number, the atom number of the atom associated with the orbital, the atomic number of this atom, the self-consistent field charge density, and the electronegativity, XX(I), for the orbital. Each orbital except the "imaginary" orbitals of hydrogen are listed in order. Note that the programme does not calculate the electronegativities of non-bonded orbitals which are not included in the charge density sum T of each atom,

Figure I-15:

COMPUTER PRINT-OUT FROM THE "BEEM" PROGRAMME

FOR THE METHANOL MOLECULE

Note: p bonding orbitals used for oxygen.

```
CASE NUMBER       51   BEGINS
     1    1    7    7    7    1    0    0    0
     8    2    3    8    8    1    1    0    0
     6    4    5    5    5    1    1    1    1
     1    6    9    9    9    1    0    0    0
TOTAL CHARGE DENSITY IN ATOMS BONDING ORBITALS
         2          2.12125
         3          4.03020
```

```
  51   14    1    8   6    1
ORBITAL  ATOM NO.  ATOMIC NO.     CHARGE              BOND(0,1,2) X
      1        1        1         0.94126              7.17500
      2        2        8         1.05874              8.81403
      3        2        8         1.06252              8.86356
      4        3        6         0.93748              7.11148
      5        3        6         1.03091              7.98218
      6        4        1         0.96909              7.17500
      8        2        8         0.00000              8.51914
END-OF-DATA ENCOUNTERED ON SYSTEM INPUT FILE.
```

so that the listing under "BOND (0, 1, 2) X" for such orbitals has no meaning. Since the programme treats all the atomic orbitals in pairs, the electronegativity of the last non-bonding orbital IC is not calculated if IC is even. The electronegativity listing for such an orbital has no significance.

By use of the programme BEEM, with the subroutine PARAMT, discussed above, the self-consistent field electronegativity equalization charge densities of more than one hundred molecular species have been calculated. The entire set of "BEEM CALCULATION SHEETS" and results printed out by the computer for these systems is available, along with "SOURCE" and "OBJECT" card decks of the two programmes (96). About five to fifteen iterations were generally sufficient to achieve self-consistent charge densities. The average calculation time required for a molecule on the IBM 7044 computer was 1.5 seconds. No cases were encountered where self-consistency was not obtained within the limit of one hundred iterations.

PART II

APPLICATIONS OF BOND ELECTRONEGATIVITY IN THE CALCULATION OF MOLECULAR ORBITALS FOR PI ELECTRON NETWORKS

PREFACE TO PART II

The theory and calculations in Part I illustrate the technique by which the bond electronegativity function for atomic orbitals can be combined with the electronegativity equalization principle to calculate molecular charge density distributions in saturated molecules. The bond electronegativity function can also be applied in other molecular orbital methods. In Part II of this thesis, the use of this function to evaluate "Coulomb" integrals for MO techniques which deal with the "pi" electrons of conjugated molecules is developed, and these Coulomb integrals are used to study some pi-bonded molecules which contain boron atoms.

II. 1 INTRODUCTION: MOLECULAR ORBITAL THEORY FOR PI ELECTRON NETWORKS

As discussed in part I, the purpose of molecular orbital theory is to find approximate electronic wave functions for a molecule by assigning a one-electron wave function to each extranuclear electron.

In the LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO) approach, the one-electron molecular orbitals ψ_i are approximated as a linear combination of atomic orbitals (AOs) ϕ_u associated with each atom α in the molecule,

$$\psi_i = \sum_u c_{iu} \phi_u \qquad (1)$$

where the coefficients c_{iu} of atomic orbital ϕ_u in the MOs ψ_i are to be determined. In order to determine the best MOs, ψ_i, for a particular molecule in its ground state, a variational treatment which minimizes the total electronic energy of the molecule with respect to the coefficients c_{iu} is carried out (1) by using the expansions in equation 1. If the electronic wave function is approximated by a single Slater determinant for the closed shell of electrons, then the energy minimization procedure described by Roothaan (1) leads to a set of SECULAR EQUATIONS for the coefficients c_{iu}:

$$\sum_v F_{uv} c_{iv} = E_i \sum_v S_{uv} c_{iv} \qquad (2)$$

for each ϕ_u. The sum v is over all the atomic orbitals to be considered. In equation 2, the elements F_{uv} of the F matrix are defined (2) as:

$$F_{uv} = H_{uv} + \sum_{w,x} P_{wx} \left[(uw \mid G \mid vx) - \frac{1}{2} (uw \mid G \mid xv) \right] \qquad (3)$$

where

$$H_{uv} = \int \phi_u^* \left[-\frac{1}{2} \nabla^2 - \sum_\alpha V_\alpha \right] \phi_v \, d\tau \qquad (4)$$

and

$$(uw|G|vx) = \iint \phi_u^{*}(1)\,\phi_w^{*}(2)\left(\frac{1}{r_{12}}\right)\phi_v(1)\,\phi_x(2)\,d\tau(1)\,d\tau(2) \quad . \tag{5}$$

The sums over w, x are over all the atomic orbitals considered. Complex conjugates of the orbitals are denoted by stars *. In equation 3, the P_{wx} are the elements of the bond order matrix P:

$$P_{wx} = 2 \sum_{i}^{occ} c_{iw}\, c_{ix} \tag{6}$$

where the sum is over all the doubly-occupied molecular orbitals. The ∇^2 term in equation 4 is the Laplacian operator, and V_α represents the potential due to nucleus α. The r_{12} factor in equation 5 represents the distance between electrons 1 and 2.

The elements S_{uv} of the overlap matrix S in equation 2 are defined as

$$S_{uv} = \int \phi_u^{*}\,\phi_v\, d\tau \quad . \tag{7}$$

The E_i of equation 2 are the one-electron energy levels of the molecular orbitals ψ_i. The E_i may be found by solving the SECULAR DETERMINANT based on equation 2:

$$\left| F_{uv} - E\, S_{uv} \right| = 0 \quad . \tag{8}$$

The roots, E, of the determinant equation 8 represent the N possible values of E_i for which non-trivial solutions of the secular equations are possible. The total electronic energy, $\mathcal{E}$, of the molecule is given (2) by:

$$\mathcal{E} = \frac{1}{2} \sum_{u,v} P_{uv}\,(H_{uv} + F_{uv}) \quad . \tag{9}$$

For conjugated molecules which are completely planar at the equilibrium positions, the ψ_i for the molecule can be separated into a set of "pi" MOs and a set of "sigma" MOs, according to whether the ψ_i are antisymmetric or symmetric with respect to reflection through the plane of the molecule. Two standard methods of treating the electrons associated with the pi MOs will now be considered.

Pople's Method for Pi Electrons

In the approximate self-consistent field method developed for pi electrons, Pople (2) assumed that the effect of the sigma electrons upon the pi electron system can be represented by a rigid, non-polarizable "core." The potential of this core is included in the elements of the H matrix (equation 4) associated with the pi system atomic orbitals.[☆] The orbitals $\phi_u, \phi_v, \ldots\ldots$ to be considered are the valence-shell p_π atomic orbitals, one from each atom in the conjugated system.

In order to simplify the treatment of pi electron systems, two "overlap" approximations are made (2):

i) The overlap integrals S_{uv} are approximated by the Kroneker delta δ_{uv}:

$$\begin{aligned} S_{uv} = \delta_{uv} &= 1 \quad \text{if} \quad u = v \\ &= 0 \quad \text{if} \quad u \neq v \end{aligned} \tag{10}$$

ii) All the two-electron integrals $(uw\,|\,G\,|\,vx)$, defined in equation 5 are set equal to zero unless $u = v$ and $w = x$:

$$(uw|G|vx) = \delta_{uv}\,\delta_{wx}\,(ux|G|ux)\;. \tag{11}$$

Only two types of the two-electron integrals are then non-zero, $(uu\,|\,G\,|\,uu)$ and $(uv\,|\,G\,|uv)$.

For simplicity the two integrals will be written in terms of γ:

$$\begin{aligned} \gamma_{uu} &= (uu\,|\,G\,|\,uu) \\ \gamma_{uv} &= (uv\,|\,G\,|\,uv)\,. \end{aligned} \tag{12}$$

One effect of the above approximations is that the F matrix elements, F_{uv},

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[☆] The "sigma-pi" separation of this type is rigorously examined and justified by Lykos and Parr, reference 3.

defined in equation 3 are simplified (2,4,5) to:

$$F_{uu} = H_{uu} + \frac{1}{2} P_{uu} \gamma_{uu} + \sum_{w \neq u} P_{ww} \gamma_{uw} \quad , \tag{13}$$

$$F_{uv} = H_{uv} - \frac{1}{2} P_{uv} \gamma_{uv} \qquad (u \neq v) \quad . \tag{14}$$

Pople (2) expanded the core integral H_{uu}, (equation 4) into two parts,

$$H_{uu} = \int \phi_u^* \left[-\frac{1}{2}\nabla^2 - \sum_\alpha V_\alpha \right] \phi_u \, d\tau$$

$$= \int \phi_u^* \left[-\frac{1}{2}\nabla^2 - V_u \right] \phi_u \, d\tau - \sum_{\alpha \neq u} \int \phi_u^* \, V_\alpha \, \phi_u \, d\tau$$

$$= U_{uu} - \sum_{\alpha \neq u} (u \,|\, V_\alpha \,|\, u) \; . \tag{15}$$

U_{uu} is the diagonal matrix element of orbital ϕ_u with respect to the one-electron Hamiltonian $\left[-\frac{1}{2}\nabla^2 - V_u \right]$. This Hamiltonian contains the kinetic energy and the interaction of an electron in ϕ_u with the core of the atom associated with ϕ_u, since V_u is the potential due to this core. In most semi-empirical methods, the term U_{uu} is not calculated explicitly, but is evaluated from the "experimental" valence-state ionization potential I_u associated with ϕ_u (6,7):

$$U_{uu} = - I_u \quad . \tag{16}$$

Pople (2) simplified the F_{uu} equation further by approximating that the interaction of an electron in ϕ_u with the singly-charged core of atom α (with which ϕ_v is associated) is equal and opposite to the interaction of an electron in ϕ_u with an electron in ϕ_v :

$$\frac{1}{Z_\alpha} \int \phi_u^* \, V_\alpha \, \phi_u \, d\tau = -\gamma_{uv} \qquad (u \neq v) \quad . \tag{17}$$

Since Z_α (or Z_v) is the "core charge" of atom α, then

$$- Z_v \gamma_{uv} = \int \phi_u^* \; V_\alpha \; \phi_u \, d\tau \; . \tag{18}$$

By introducing the above expressions involving U_{uu} into the equation 13, the F_{uu} expression is simplified considerably:

$$\begin{aligned} F_{uu} &= H_{uu} + \tfrac{1}{2} P_{uu} \gamma_{uu} + \sum_{w \neq u} P_{ww} \gamma_{uw} \\ &= U_{uu} - \sum_{\alpha \neq u} \int \phi_u^* \; V_\alpha \; \phi_u \, d\tau + \tfrac{1}{2} P_{uu} \gamma_{uu} + \sum_{w \neq u} P_{ww} \gamma_{uw} \\ &= -I_u - \sum_{w \neq u} Z_w \gamma_{uw} + \tfrac{1}{2} P_{uu} \gamma_{uu} + \sum_{w \neq u} P_{ww} \gamma_{uw} \\ &= -I_u + \tfrac{1}{2} P_{uu} \gamma_{uu} + \sum_{w \neq u} (P_{ww} - Z_w) \gamma_{uw} \; . \end{aligned} \tag{19}$$

In semi-empirical pi-electron methods, the one-center repulsion integrals γ_{uu} are usually approximately evaluated from the ionization potential I_u, and the valence-state electron affinity, A_u, associated with ϕ_u (5,8):

$$\gamma_{uu} = I_u - A_u \; . \tag{20}$$

Since the zero overlap condition (equation 10) is used in the Pople method, the electronic charge density, q_u, of orbital ϕ_u may be associated with the bond order matrix diagonal terms F_{uu} :

$$q_u = F_{uu} \; . \tag{21}$$

If equations 20 and 21 are combined with the expression for F_{uu} in equation 19, the F matrix diagonal elements become:

$$F_{uu} = -I_u + \tfrac{1}{2} q_u (I_u - A_u) + \sum_{w \neq u} (q_w - Z_w) \gamma_{uw} \tag{22}$$

In Pople's method, the expressions for F_{uu} and F_{uv} are evaluated for each pair of atomic orbitals in the pi system by use of equations 22 and 14 respectively.[☆] The resulting secular determinant equation,

$$\left| F_{uv} - E\,\delta_{uv} \right| = 0 \qquad (23)$$

may then be solved for the N energy levels, E_i, and these energies used in the set of secular equations 2 to calculate the coefficient matrix C. Since the F matrix elements are dependent upon the elements of C, an iterative process is used in Pople's method to establish the self-consistent field energy levels and C matrix.

[☆] See also footnote (b) of Table II-I.

The Huckel Method for Pi Electrons

An alternative method to Pople's procedure for the study of pi electron networks is the "simple Huckel" technique. The general theory of the Huckel method is extensively discussed by Coulson and Longuet-Higgins (9). A shorter review of the technique is contained in Streitwieser's book (10).

The Huckel method is similar to that developed by Pople since, in both approaches, the one-electron molecular orbitals ψ_i are approximated by a linear combination of valence shell p_π atomic orbitals ϕ_u :

$$\psi_i = \sum_u c_{iu} \phi_u \quad . \tag{24}$$

The bond order matrix P is defined from the coefficients

$$P_{uv} = 2 \sum_i^{occ} c_{iu} c_{iv} \tag{25}$$

and the overlap integrals S_{uv} are normally (in the simplest Huckel treatments) approximated as follows:

$$\begin{aligned} S_{uv} = \delta_{uv} &= 1 \quad \text{if} \quad u = v \\ &= 0 \quad \text{if} \quad u \neq v \quad . \end{aligned} \tag{26}$$

The secular determinant to be solved is then of the form:

$$\left| F_{uv} - E\, \delta_{uv} \right| = 0 \quad . \tag{27}$$

The main difference between the Huckel and Pople methods is the evaluation of the F matrix elements. In the Huckel treatments, all the terms F_{uu} and F_{uv} are defined with respect to an EFFECTIVE HAMILTONIAN $\overset{o}{H}_{eff}$ (11,12):

$$F_{uu} = \alpha_u = \int \phi_u \, \hat{\overset{o}{H}}_{eff} \, \phi_u \, d\tau \tag{28}$$

$$F_{uv} = \beta_{uv} = \int \phi_u^{*} \overset{o}{H}_{eff} \phi_v \, d\tau \qquad (u \neq v) . \tag{29}$$

The F matrix terms α_u and β_{uv} are not evaluated explicitly, but are treated as semi-empirical parameters. The "resonance integrals" β_{uv} are taken to be zero <u>unless</u> ϕ_u, ϕ_v are the p_π AOs of atoms which have a localized sigma bond between them (i.e. ϕ_u, ϕ_v are "bonded" or "nearest neighbours" in the molecule).

The parameters α_u and β_{uv} are usually expressed in terms of "standard" Coulomb and resonance integrals α^o and β^o which represent the α_u and "bonded" β_{uv} for the benzene pi system in the following manner:

$$\alpha_u = \alpha^o + h_u \beta^o \tag{30}$$

$$\beta_{uv} = k_{uv} \beta^o . \tag{31}$$

Many methods have been proposed to evaluate h_u and k_{uv} for different p_π AOs (12). One common procedure is to adjust the various values of h_u and k_{uv} in a molecule in order that some experimental property of the molecule, or of a series of molecules, is reproduced by the Huckel calculations. The Huckel method Coulomb parameters, h_u, have been associated with the difference between the Pauling electronegativity, X_C^P, of the atom associated with ϕ_u, and the electronegativity of carbon, X_C^P,

$$h_u = \frac{\alpha_u - \alpha^o}{\beta^o} = A\,(X_u^P - X_C^P) \tag{32}$$

where A is usually taken to be unity.

Mulliken (13) has shown on the basis of some theoretical calculations that the Coulomb integral, α_u, for a singly-occupied atomic orbital ϕ_u, is roughly proportional to the Mulliken electronegativity, X_u^M, of the orbital ϕ_u:

$$X_u^M = \frac{1}{2}(I_u + A_u) \quad . \tag{33}$$

On the basis of this analysis, valence-state ionization potentials, electron affinities and Mulliken electronegativities have been used to estimate Huckel method Coulomb integrals by various techniques in the past.

Attempts have been made (12,14,15) to find Coulomb and resonance integrals which, when used in the Huckel method, would closely reproduce some property (e.g. charge distribution) calculated by Pople's method or methods closely related to it.

Molecular ionization potentials have been extensively employed as a property which can be used to "fit" Coulomb and resonance integrals, especially in a variant of the Huckel method commonly known as the OMEGA (ω) TECHNIQUE (16). In omega technique calculations, the Coulomb integral of a p_π AO ϕ_u is assumed to be linearly dependent upon the charge density, q_u, of that orbital:

$$\alpha_u = \alpha^o + h_u \beta^o + (Z_u - q_u)\,\omega\,\beta^o \, . \tag{34}$$

In this expression, Z_u is the core charge of the atom associated with ϕ_u, and ω is an empirical constant. A range of values from 0.33 to 1.8 (12,17,18) has been proposed for the term ω, but Streitwieser's estimate of $\omega = 1.4$ (16) for carbon is now generally accepted and is used for the p_π atomic orbitals of all atoms.

The wide range of h_u and k_{uv} values that have been used for various heteroatoms in the simple Huckel method have been compiled and discussed by Streitwieser (12). From such data, he has been able to determine "average" or "best" values of the Huckel parameters h_u and k_{uv} for a variety of systems, and these "best" values are now in wide use in simple Huckel method calculations. The object of the next section will be to analyze the nature of the effective Hamiltonian $\overset{o}{H}_{eff}$ of equations 28, 29 which generates such a set of parameters.

II. 2 COULOMB INTEGRAL PARAMETERS FROM BOND ELECTRONEGATIVITY FUNCTIONS

The review of molecular orbital methods for pi-electron systems in the previous section has indicated that the simple Huckel, omega technique, and Pople methods are similar, and differ mainly in the determination of the elements of the matrix F used in the LCAO - MO secular equation. In this section, various schemes will be advanced whereby the Pople method F matrix elements may be APPROXIMATELY calculated, and the relationships between these schemes and the simple Huckel and omega techniques will be discussed. The relationships will be exploited to provide Huckel method Coulomb integral parameters, h_u, for a variety of atoms.

Approximation Method A

The F matrix diagonal elements, F_{uu}, of the secular determinant have been found to reduce to the following equation in Pople's molecular orbital method:

$$F_{uu} = -I_u + \frac{1}{2} q_u (I_u - A_u) + \sum_{w \neq u} (q_w - Z_w) \gamma_{uw} \quad . \tag{35}$$

By introducing Z_u, the core charge of the atom associated with atomic orbital ϕ_u, into equation 35, F_{uu} may be rewritten as a sum of three expressions:

$$F_{uu} = \left[-I_u + \frac{Z_u}{2} (I_u - A_u) \right] + \left[\frac{(q_u - Z_u)}{2} (I_u - A_u) \right] + \left[\sum_{w \neq u} (q_w - Z_w) \gamma_{uw} \right] , \tag{36}$$

$$F_{uu} = J(u) + K(u, q_u) + L(u, q_w) , \tag{37}$$

In equation 37, the terms $J(u)$, $K(u, q_u)$ and $L(u, q_w)$ represent the first, second and third expressions respectively in the square brackets of the right-hand side of equation 36.

Part of the F_{uu} expressions in equations 36 and 37 bear a strong resemblance to the molecular orbital bond electronegativity function, X_u, for an atomic orbital ϕ_u which was defined in part I (page 40). This definition for X_u is of the form

$$X_u = I_u + \frac{1}{2} q_u (A_u - I_u) . \tag{38}$$

By substituting X_u of equation 38 into equation 36, F_{uu} may be defined in terms of X_u :

$$F_{uu} = -X_u + \sum_{w \neq u} (q_w - Z_w) \gamma_{uw} \tag{39}$$

since

$$-X_u = J(u) + K(u, q_u) . \tag{40}$$

If $q_u = Z_u$, then the term $K(u, q_u)$ is zero, and for such situations $-J(u)$ represents the bond electronegativity of orbital ϕ_u for the "neutral" orbital ϕ_u (i.e. an orbital for which $q_u = Z_u$). Further relations between X_u and F_{uu} will be discussed later in this section.

For the purposes of the present analysis, it is convenient to define some new parameters ϵ_{uv} for the orbital pairs such that when $u = v$, then

$$\epsilon_{uu} = \frac{1}{2} \gamma_{uu} = \frac{1}{2} (I_u - A_u) \tag{41}$$

and for $u \neq v$,

$$\epsilon_{uv} = \gamma_{uv} . \tag{42}$$

By using the ϵ terms instead of γ_{uu} and γ_{uv}, the expression for F_{uu} in equation 36 can be rewritten in the following forms:

$$F_{uu} = -I_u + \frac{Z_u}{2}(I_u - A_u) + (q_u - Z_u)\,\epsilon_{uu} + \sum_{w \neq u}(q_w - Z_w)\,\epsilon_{uw} \; ; \tag{43}$$

$$F_{uu} = J(u) + \sum_w (q_w - Z_w)\,\epsilon_{uw} \, . \tag{44}$$

The sum w is now over <u>ALL</u> the pi atomic orbitals, including ϕ_u.

In approximation method A, the term $\sum_w (q_w - Z_w)\,\epsilon_{uw}$ of equation 43 will be assumed to be equal to zero. The F_{uu} expression of equation 43 is then reduced to the term J(u):

$$F_{uu} = J(u) = -I_u + \frac{Z_u}{2}(I_u - A_u) \, . \tag{45}$$

The validity of neglecting the term $\sum_w (q_w - Z_w)\,\epsilon_{uw}$ may be discussed by first defining the terms $\Delta\epsilon_{uw}$ such that each ϵ_{uw} is defined relative to a term ϵ :

$$\epsilon_{uw} = \epsilon + \Delta\epsilon_{uw} \, . \tag{46}$$

In equation 46, ϵ is some average of all the ϵ_{uw} for a given orbital ϕ_u. Using this type of expansion for each ϵ_{uw} term, the expression $\sum_w (q_w - Z_w)\,\epsilon_{uw}$ may be split into two parts as follows:

$$\begin{aligned}\sum_w (q_w - Z_w)\,\epsilon_{uw} &= \sum_w (q_w - Z_w)\,(\epsilon + \Delta\epsilon_{uw}) \\ &= \sum_w (q_w - Z_w)\,\epsilon + \sum_w (q_w - Z_w)\,\Delta\epsilon_{uw} \\ &= \epsilon \sum_w (q_w - Z_w) + \sum_w (q_w - Z_w)\,\Delta\epsilon_{uw} \, . \end{aligned} \tag{47}$$

For pi-electron networks in which there is no <u>net</u> charge associated with the pi system, the sum of the orbital charge densities q_w must be equal to the sum of the core charges Z_w:

$$\sum_w q_w = \sum_w Z_w \tag{48}$$

or

$$\sum_w (q_w - Z_w) = 0 \, . \tag{49}$$

Due to the equality expressed in equation 49, the right-hand side of equation 47 is simplified to one term:

$$\sum_w (q_w - Z_w) \, \epsilon_{uw} = \sum_w (q_w - Z_w) \, \Delta \epsilon_{uw} \, . \tag{50}$$

If, the system being considered, all the ϵ_{uw} terms for orbital ϕ_u were exactly equal, all the $\Delta \epsilon_{uw}$ would be zero and the remaining term in the expansion in equation 47 would disappear.

In this case, the approximation expression for F_{uu} in equation 45 would be exact. In general, all the ϵ_{uw} are not identical, although for many common small ring molecules these terms are all similar in magnitude. In the benzene molecule, for example, Pariser and Parr (8) give the following γ_{uv} values from which the ϵ_{uw} terms may be calculated according to equations 41 and 42:

$$\gamma_{11} = 10.53 \text{ e.v.} \qquad \therefore \quad \epsilon_{11} = 5.265 \text{ e.v.}$$

$$\gamma_{12} = \gamma_{16} = 7.30 \text{ e.v.} \qquad \therefore \quad \epsilon_{12} = \epsilon_{16} = 7.30 \text{ e.v.}$$

$$\gamma_{13} = \gamma_{15} = 5.46 \text{ e.v.} \qquad \therefore \quad \epsilon_{13} = \epsilon_{15} = 5.46 \text{ e.v.}$$

$$\gamma_{14} = 4.90 \text{ e.v.} \qquad \therefore \quad \epsilon_{14} = 4.90 \text{ e.v.}$$

If the average, 5.95 e.v., of the six ϵ_{uw} values is taken as ϵ, the terms $\Delta \epsilon_{uw}$ are small relative to ϵ itself:

$$\Delta \in_{11} = -0.69 \text{ e.v.}$$

$$\Delta \in_{12} = \Delta \in_{16} = +1.35 \text{ e.v.}$$

$$\Delta \in_{13} = \Delta \in_{15} = -0.49 \text{ e.v.}$$

$$\Delta \in_{16} = -1.05 \text{ e.v.}$$

The second approximation which will be employed in method A concerns the off-diagonal F matrix elements, F_{uv}, of the Pople scheme. These F_{uv} are defined as

$$F_{uv} = H_{uv} - \frac{1}{2} P_{uv} \gamma_{uv} \qquad (u \neq v) . \tag{51}$$

The approximation which will be used concerning the off-diagonal F_{uv} terms is that F_{uv} is taken as zero <u>unless</u> the atomic orbitals ϕ_u, ϕ_v belong to atoms which have a sigma bond between them (i.e. ϕ_u and ϕ_v are "bonded" or "nearest neighbours"). If the two orbitals ϕ_u and ϕ_v are "bonded" and are both p_π atomic orbitals of carbon, then F_{uv} will be taken to be equal to $F_{cc'}$, which is the F_{uv} value for the bonded atomic orbitals in benzene. For two carbon atom p_π AOs ϕ_u and ϕ_v, then,

$$\begin{aligned} F_{uv} &= F_{cc'} && \text{if } u, v \text{ are bonded} \\ \text{and } F_{uv} &= 0 && \text{if } u, v \text{ are not bonded.} \end{aligned} \tag{52}$$

The assumption regarding non-bonded F_{uv} is not a drastic approximation, since even in the full Pople method, the term H_{uv} is taken to be zero if the orbitals ϕ_u and ϕ_v are not bonded (2), in which case the matrix element F_{uv} reduces to $-\frac{1}{2} P_{uv} \gamma_{uv}$, which is usually small.

The Coulomb integrals J(u) of "method A" may be expressed in terms of the term $F_{cc'}$, which will be used as the unit of energy in the method. By defining J(C) as the value of J(u) for a carbon atom, the general expression

$J(u)$ may be written in terms of $J(C)$ and $F_{cc'}$:

$$J(u) = J(C) + h_u F_{cc'} \tag{53}$$

or

$$h_u = \frac{J(u) - J(C)}{F_{cc'}} . \tag{54}$$

The Coulomb integral parameters h_u may be calculated for a variety of atoms and valence states from the ionization potential (I_u) and electron affinity (A_u) data of Hinze (19). The terms I_u, A_u, $J(u)$, and $\left[J(u) - J(C)\right]$ are listed in Table II - I. The evaluation of the h_u terms requires the numerical value of $F_{cc'}$. Since $P_{cc'}$, the bonded bond order in the benzene ground state, is 2/3, and since $\gamma_{cc'}$, the repulsion integral for the bonded AOs is 7.30 e.v. (Pariser and Parr (8)), then the term $F_{cc'}$ is:

$$\begin{aligned} F_{cc'} &= H_{cc'} - \frac{1}{2} P_{cc'} \gamma_{cc'} \\ &= H_{cc'} - 2.43 \text{ e.v.} \end{aligned} \tag{55}$$

The bonded core integral, $H_{cc'}$, for benzene is normally estimated empirically from some experimentally observable property of the molecule. From the ultraviolet spectrum of benzene, Pariser and Parr (8) have derived $H_{cc'} = -2.3_9$ e.v., while Chung and Dewar (20) obtained $H_{cc'} = -1.7_5$ e.v. from an empirical relation between bond order and bond length. An alternative procedure by which $H_{cc'}$ can be estimated is by fitting the experimental first ionization potential $I_{BENZENE}$ of benzene, 9.52 e.v. (electron impact value, reference 21) to the prediction of this quantity made by method A:

$$I_{BENZENE} = F_{cc} + F_{cc'} = -5.59 + H_{cc'} - 2.43 = -9.52 \text{ e.v.} \tag{56}$$

This fitting procedure leads to a $H_{cc'}$ value of -1.5_0 e.v. Several other methods can be used to determine the magnitude of $H_{cc'}$, but most estimates, like those above, cluster in the region -1.5 to -2.5 e.v. (6,11). The

TABLE II-I: Coulomb Integral Parameters for Methods "A" and "B"

Atom	Valence State of σ Core	Z_u	I_u (a) (e.v.)	A_u (b) (e.v.)	$I_u - A_u$ (b) (e.v.)	J(u) (e.v.)	J(u)-J(C) (e.v.)	h_u	Empirical h_u (c)	ω_u
Be	di^1di^1	0	0.17	-0.85	1.02	-0.17	+5.42	-1.2_8		0.1_2
B	$tr^1tr^1tr^1$	0	1.06	-5.32	6.38	-1.06	+4.53	-1.0_7	-1	0.7_5
C	$tr^1tr^1tr^1$	1	11.16	0.03	11.13	-5.59	0.00	0.0_0	0	1.3_2
N	$tr^2tr^1tr^1$	1	14.12	1.78	12.34	-7.95	-2.36	0.5_6	0.5	1.4_6
N	$tr^1tr^1tr^1$	2	28.71	11.95	16.76	-11.95	-6.36	1.5_0	1.5	1.9_8
O	$s^2p^2p^1$	1	17.28	2.01	15.27	-9.65	-4.06	0.9_6	1	1.8_0
O	$s^2p^1p^1$	2	34.15	14.61	19.54	-14.61	-9.02	2.1_3	2	2.3_1
F	$s^2p^2p^1$	2	39.67	18.11	21.56	-18.11	-12.52	2.9_6	3	2.5_5
Mg	di^1di^1	0	0.16	-1.94	2.10	-0.16	+5.43	-1.2_8		0.2_5
Al	$tr^1tr^1tr^1$	0	1.62	-2.51	4.13	-1.62	+3.97	-0.9_4		0.4_9
Si	$tr^1tr^1tr^1$	1	9.17	2.00	7.17	-5.59	0.00	0.0_0		0.8_5
P	$tr^2tr^1tr^1$	1	11.14	1.80	9.34	-6.47	-0.88	0.2_1		1.1_0

TABLE II-I continued

Atom	Valence State of σ Core	Z_u	I_u (a) (e.v.)	A_u (b) (e.v.)	I_u-A_u (b) (e.v.)	J(u) (e.v.)	J(u)-J(C) (e.v.)	h_u	Empirical h_u (c)	ω_u
P	$tr^1tr^1tr^1$	2	20.68	10.26	10.42	-10.26	-4.67	1.1_0		1.2_3
S	$s^2p^2p^1$	1	12.39	2.38	10.01	-7.39	-1.80	0.4_3		1.1_8
S	$s^2p^1p^1$	2	22.97	11.05	11.92	-11.05	-5.46	1.2_9		1.4_1
Cl	$s^2p^2p^1$	2	26.36	13.38	12.98	-13.38	-7.79	1.8_4	2	1.5_3
Ge	$tr^1tr^1tr^1$	1	8.72	4.11	4.61	-6.41	-0.82	0.1_9		0.5_5
As	$tr^2tr^1tr^1$	1	11.24	2.64	8.60	-6.94	-1.35	0.3_2		1.0_2
Se	$s^2p^2p^1$	1	11.68	2.52	9.16	-7.10	-1.51	0.3_6		1.0_8
Sn	$tr^1tr^1tr^1$	1	8.02	4.89	3.13	-6.46	-0.87	0.2_1		0.3_7
Sb	$tr^2tr^1tr^1$	1	10.51	2.77	7.74	-6.64	-1.05	0.2_5		0.9_1
Te	$s^2p^2p^1$	1	11.04	2.58	8.46	-6.81	-1.22	0.2_9		1.0_0

TABLE II-I continued

Notes:

a) Energy data from reference 19.

b) The calculation of γ_{uu} by the "I_u-A_u" formula is not rigorously justifiable for atoms having less than half-filled valence shells (see, for example, reference 29), but the "I_u-A_u" formula is used for all atoms considered herein since it is sufficiently accurate for the purposes of this study.

c) Empirical h_u data from p. 135 of reference 10.

range of F_{cc}, is therefore approximately -3.9 to -4.9 e.v.

The expression for J(u) in method A, equation 53, is similar in form to the simple Huckel method expression for α_u (equation 30). The Coulomb integrals for the two methods will be identical if the following conditions are met:

i) The Huckel method empirical h_u values are a linear function of the method A h_u values determined from the valence-state energies,

ii) The magnitude of the slope of the line for the plot of Huckel h_u against the term $\left[J(u) - J(C)\right]$ lies within the range of F_{cc}, discussed above.

In order to establish whether the above conditions are in fact valid, the empirical Huckel h_u are plotted against the terms $\left[J(u) - J(C)\right]$ in Figure II-1. The Huckel h_u are the "best" values listed by Streitwieser (12). Since these values are given by Streitwieser to the nearest 0.5 unit, each empirical h_u has an uncertainty of ±0.25.

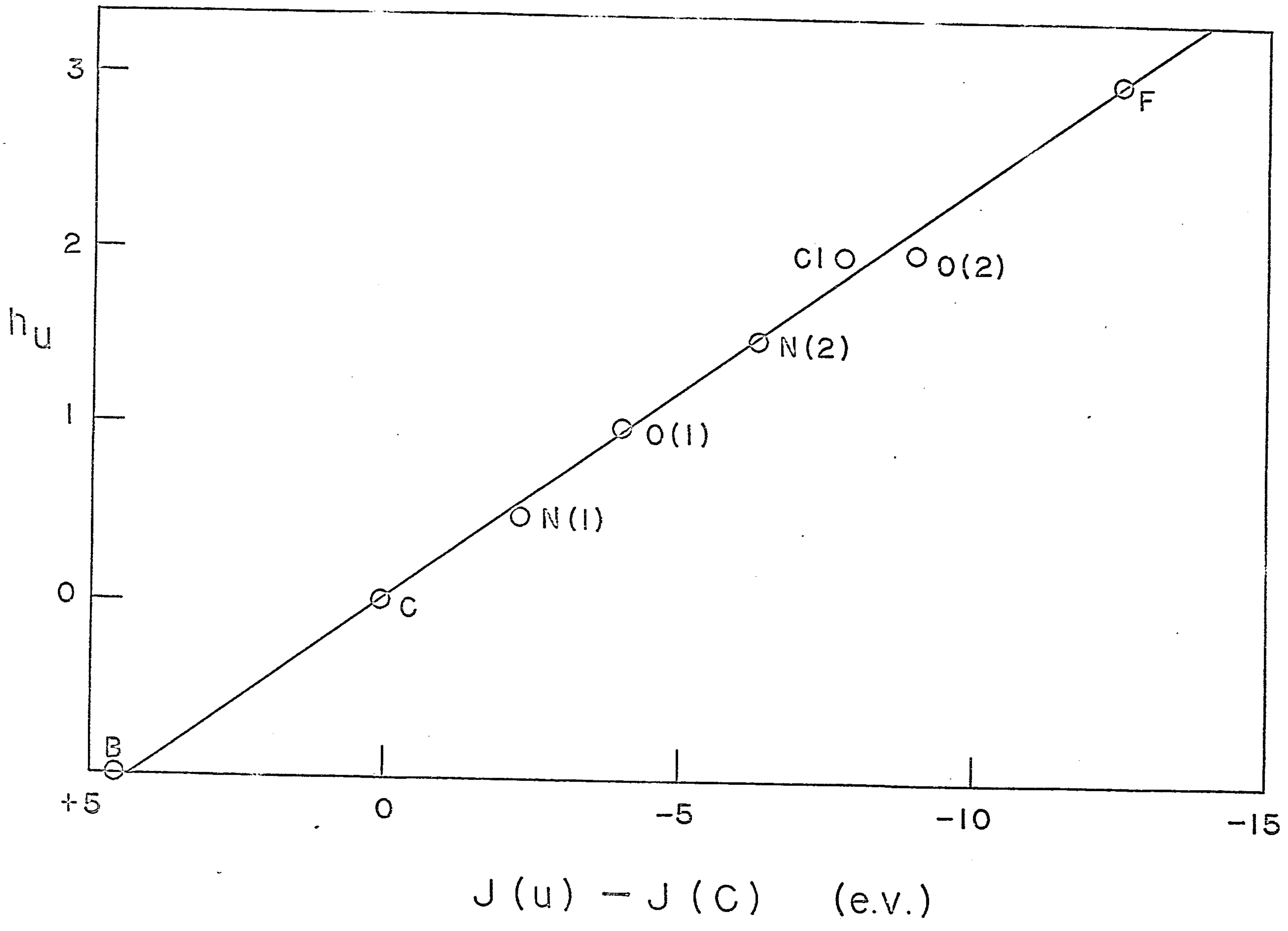
The correlation line in Figure II-1 is excellent, and yields a slope of -4.2_3 e.v., which is roughly in the middle of the range of F_{cc}, discussed above. From these correlations, it may be concluded that method A will lead to the same results as the simple Huckel method (using the "best" Huckel h_u) for the molecular orbital treatment of any particular molecule. The effective Hamiltonian, $\overset{o}{H}_{eff}$, of the Huckel method Coulomb integrals is therefore identical to the Pople technique Hamiltonian <u>calculated for the particular charge density distribution in which all the atoms are "neutral"</u> (i.e. all $q_w = Z_w$).

Since the method A J(u) values correspond to the negative of the bond electronegativities for the neutral A O (equation 40), the Huckel

Figure II-1:

VARIATION OF $\left[J(u)-J(C)\right]$ WITH EMPIRICAL h_u PARAMETERS

Note: Core charges for orbitals are listed in brackets after the atom symbol, if parameters for more than one core charge have been calculated.


3
2
1
0
h_u
+5
0
-5
-10
-15
$J(u) - J(C)$ (e.v.)
B
C
N(1)
O(1)
N(2)
Cl
O(2)
F

Coulomb integrals will also correspond to the electronegativities. In general, the relation between the Huckel Coulomb integrals and the bond electronegativity function may be expressed as follows:

$$h_u \text{ (Huckel) } \equiv -X_u \text{ (for all } q_w = Z_w) .$$

All the J(u) listed in Table II-I are calculated from the various sigma orbital valence states noted. All the sigma valence states employed correspond to what may be termed a "neutral" sigma system. The neutral sigma systems represent sigma bond charge distributions in which no charge transfer has taken place in any of the localized sigma bonds on the atoms associated with the p_π atomic orbitals . A second characteristic of the Huckel method $\overset{0}{H}_{eff}$ is that it corresponds to a completely non-polar charge density distribution in the sigma electron system of each atom.

The changes to the individual h_u values caused by polarity in the sigma bonds can be estimated by using valence-state ionization potential and electron affinity data (used to calculate J(u)) of the p_π atomic orbitals evaluated under conditions for which charge transfer has occured in the sigma bonded framework. By using the power series expansions of I_u, A_u, in terms of the <u>net</u> sigma charge, Q_σ, of a particular atom (see part I, page 60), the terms h_u may be expressed in terms of Q_σ. For the carbon, nitrogen and oxygen p_π orbitals having core charge $Z_u = 1$, this dependence is:

$$h_C = 0.00 + 2.28\, Q_\sigma + 0.43\, Q_\sigma^2 , \qquad (57)$$

$$h_N = 0.56 + 2.43\, Q_\sigma + 0.49\, Q_\sigma^2 , \qquad (58)$$

$$h_O = 0.96 + 3.17\, Q_\sigma + 0.32\, Q_\sigma^2 . \qquad (59)$$

The magnitude of the dependence of h_u upon Q_σ is about 2-3 units per electron, and will be important for tetravalent nitrogen and trivalent oxygen atoms. Streitwieser (12) lists h_u for these two particular species as +2.0 and +2.5 respectively, corresponding to a sigma system net charge Q_{σ} of approximately +0.5 electron in each case. This net charge appears to be quite reasonable, since the sigma bonds of the nitrogen and oxygen atoms will be quite polar in these species, reducing the net positive charges from unity.

The expression for h_C in terms of Q_{σ} may be combined with the sigma system net charges calculated by the B.E.E. method for various hydrocarbons to yield Coulomb integrals for the pi orbitals in such molecules. The values of h_C calculated in this manner are given in Table II-II along with the h_C relative to the pi orbital of benzene. The Coulomb integrals relative to benzene fall into three classes:

i) $h_C \approx 0$ for the benzenes

ii) $h_C \approx -0.06$ for the ethylenes

iii) $h_C \approx -0.13$ to -0.17 for the acetylenes .

Within the benzene and ethylene series, the effect of alkyl substitution upon the magnitude of h_C is very small.

The expression for h_u in method A (equation 54 with $F_{cc'} = -4.2_3$ e.v.) may be used to generate Coulomb integrals appropriate to simple Huckel method calculations for a variety of atoms with "neutral" sigma cores. The values of these Huckel Coulomb integral parameters h_u are listed in Table II-I. The p_{π} orbitals of the atoms of the second and third groups of the periodic table (Be, Mg, B and Aℓ), have quite low h_u, about -1, for the core charge $Z_u = 0$ valence states. The group four atom h_u terms are somewhat larger, in the range $0 \leqslant h_u \leqslant 1$. For the p_{π} orbitals of the group five, six and seven

TABLE II-II: Effect of Sigma Core Charge on the Coulomb Integrals of a Carbon p_π Orbital

Molecule	Sigma Core Net Charge (in Electrons)[a]	h_C Relative to a Neutral Carbon Atom (in β^o)	h_C Relative to pi Orbital of Benzene (in β^o)
Benzene	-0.0608	-0.13_7	0.00_0
Hexamethylbenzene	-0.0631	-0.14_2	-0.00_5
$H_2C = CH_2$	-0.0904	-0.20_3	-0.06_6
MeHC = CHMe	-0.0888	-0.19_9	-0.06_2
$Me_2C = CMe_2$	-0.0875	-0.19_7	-0.06_0
EtHC = CHEt	-0.0872	-0.19_6	-0.05_9
HC≡CH	-0.1192	-0.26_6	-0.12_9
MeC≡CMe	-0.1378	-0.30_6	-0.16_9
EtC≡CEt	-0.1373	-0.30_5	-0.16_8

Note:

a) From Table I-X.

atoms, the variation of h_u for different atoms in the same group, and for different Z_u of the same atom, is quite marked.

Approximation Method B

In approximation method A, the Coulomb integrals were calculated by retaining only the term J(u) in the Pople expression for the F matrix elements F_{uu}, equation 37. In approximation method B, the two terms J(u) and K(u, q_u) of Pople's expression for F_{uu} will be retained in the approximate form for the Coulomb integrals. The other approximation used in method A, that concerning the off-diagonal F matrix elements, will also be used in method B. Hence the F matrix elements in method B are given by the expressions:

$$F_{uu} = J(u) + K(u, q_u) = -X_u (q_u) ; \qquad (60)$$

$$F_{uv} = F_{cc'} \quad \text{if u, v are bonded} ; \qquad (61)$$

$$F_{uv} = 0 \quad \text{if u, v are not bonded} . \qquad (62)$$

The expression for F_{uu} in method B, equation 60, may be converted into a computationally convenient form in the following manner. In method A, the term J(u) was recast in terms of J(C) and $F_{cc'}$:

$$J(u) = J(C) + h_u F_{cc'} . \qquad (63)$$

The term K(u, q_u) of equation 60

$$K(u, q_u) = (q_u - Z_u) \left(\frac{I_u - A_u}{2}\right) \qquad (64)$$

may also be expressed in terms of $F_{cc'}$ by defining a term ω_u by the equation:

$$\omega_u = \frac{A_u - I_u}{2 F_{cc'}} = \frac{I_u - A_u}{(-2 F_{cc'})} . \qquad (65)$$

The expression for $K(u, q_u)$ then becomes

$$K(u, q_u) = (Z_u - q_u)\ \omega_u F_{cc'} , \tag{66}$$

and the equation for the F matrix diagonal elements in method B is of the following form:

$$F_{uu} = J(C) + h_u F_{cc'} + (Z_u - q_u)\ \omega_u F_{cc'} . \tag{67}$$

Using the value of $F_{cc'}$, -4.2_3 e.v., found in method A, and the ionization potential and electron affinities listed in Table II-I, the parameters ω_u may be calculated for each type of p_π atomic orbital. Numerical values of ω_u for several types of orbitals are listed in Table II-I.

All the ω_u terms calculated are positive, indicating that the magnitude of the Coulomb integrals decrease (in the sense of becoming less negative) as the orbital charge density q_u increases. The values for the terms ω_u for different atoms are quite dissimilar, ranging from 0.1 to 2.6. Within each row of the Periodic Table, the terms ω_u are found to be linearly dependent upon the corresponding h_u parameters, if only group three to group seven atoms are considered. The plot in Figure II-2 illustrates this dependence for the first period atoms B to F. For the pi orbitals ω_u of these atoms,

$$\omega_u = 0.45\ h_u + 1.3_0 . \tag{68}$$

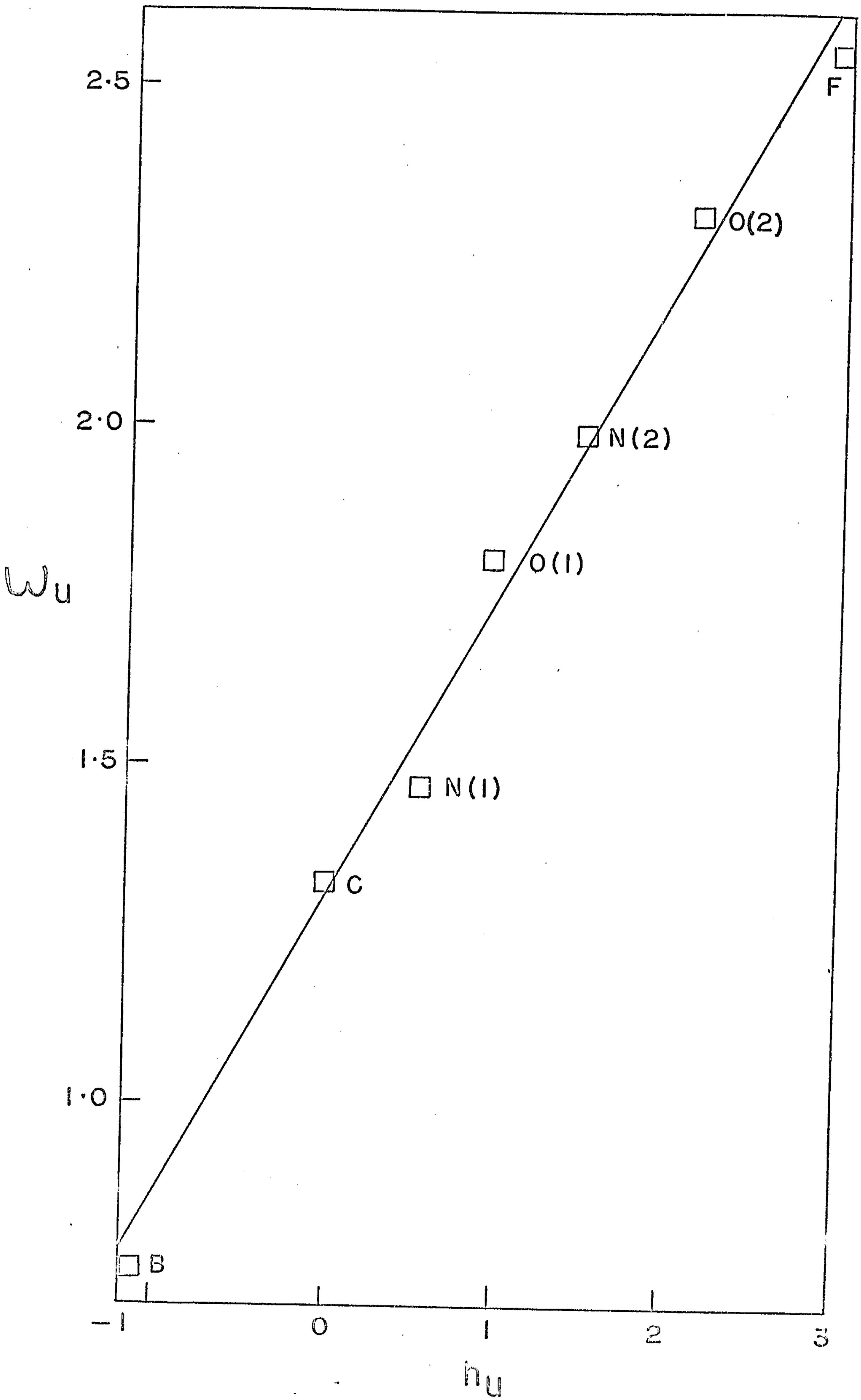
For the second period atoms Al to Cl, a correlation line between ω_u and h_u which is almost parallel to that for the first row atoms is found. For the pi orbitals of these atoms, ω_u may be expressed in terms of h_u by the following equation:

$$\omega_u = 0.42\ h_u + 0.8_6 . \tag{69}$$

By using these equations relating ω_u with h_u the expression for F_{uu},

Figure II-2:

VARIATION OF ω_u WITH h_u FOR FIRST PERIOD ATOMS


2·5
2·0
1·5
1·0
ω_u
F
O(2)
N(2)
O(1)
N(1)
C
B
−1
0
1
2
3
h_u

equation 60, may be rewritten in terms of a function h_u^{*} :

$$F_{uu} = J(C) + h_u^{*} F_{cc'} \quad . \tag{70}$$

Here h_u^{*} is defined for the orbitals of the atoms B to F by the expression

$$h_u^{*} = h_u + (0.45\, h_u + 1.3)\ (Z_u - q_u) \tag{71}$$

and for the orbitals of the atoms from Al to Cl by

$$h_u^{*} = h_u + (0.42\, h_u + 0.86)\ (Z_u - q_u) \quad . \tag{72}$$

The improved simple Huckel method, termed the omega technique by Streitwieser (16), is similar in form to the method B of this study. As previously discussed, the omega technique Coulomb integrals α_u are given by

$$\alpha_u = \alpha^o + h_u\, \beta^o + (Z_u - q_u)\, \omega\, \beta^o \quad . \tag{73}$$

In the discussion of method A, it was shown that the term $(\alpha^o + h_u\, \beta^o)$ corresponds to the expression $(J(C) + h_u\, F_{cc'})$. The omega technique will then correspond to method B if the term $\omega\, \beta^o$ of equation 73 is equivalent to the term $\omega_u\, F_{cc'}$ of equation 66. In the previous discussion, it was shown that β^o may be equated with $F_{cc'}$, and hence the omega technique will be identical to method B providing the magnitudes of ω and ω_u are identical. In the omega technique, the "best" empirical value of ω for carbon is 1.4. The magnitude of the term ω_u for carbon in method B is calculated to be 1.3_2 (Table II-I), in excellent agreement with the empirical result.

The empirical omega technique developed by Streitwieser is in fact almost computationally identical with approximation method B for hydrocarbon systems, since the ω and ω_u for carbon are virtually identical in magnitude. The effective Hamiltonian, $\overset{o}{H}_{eff}$, of the empirical omega technique for the Coulomb integrals corresponds to the Pople method Hamiltonian, evaluated for the condition:

$$L(u, q_w) = \sum_{w \neq u} (q_w - Z_w) \gamma_{uw} = 0 \qquad (73a)$$

since only the $L(u, q_w)$ term has been dropped from the Pople expression for F_{uu} in method B (see equations 37 and 60). The omega technique Coulomb integrals, therefore, represent the NEGATIVE of the bond electronegativity for atomic orbital ϕ_u (equation 60).

Although the empirical omega technique value for the term ω was evaluated for hydrocarbon systems, the same $\omega = 1.4$ has been used for other pi orbitals ϕ_u which are not p_π orbitals of carbon, but are associated with heteroatoms. The widely different ω_u for many atoms listed in Table II-I indicate that the extension of the carbon ω value to other atoms is not valid, and the different values in Table II-I should be used for heteroatoms. The specific dependence of the magnitude of the ω parameter upon the nature of the orbital ϕ_u has been previously considered by Pritchard and Sumner (22), and by Klopman (23). Klopman also briefly considered the correspondence between the omega technique Coulomb integrals and the bond electronegativity function (23).

In the main paper discussing the development of the omega technique, Streitwieser (16) attempted to make a comparison between Pople's expression for the term F_{uu}, and the Coulomb integral equation of the omega technique. Using a β^o value of -2.11 e.v. obtained from a correlation of some experimental molecular ionization potentials with those calculated by the omega technique, Streitwieser noted that the magnitude of the term $-\omega \beta^o$, 2.9 e.v., was much smaller than the value of the corresponding term $\frac{1}{2}\gamma_{uu}$, 5.3 e.v., of

Pople's expression. Streitwieser concluded from this that, by using this low value of $-\omega\beta^{o}$, the omega technique in fact compensated in an average way for the omission of the $L(u, q_w)$ term of Pople's expression for F_{uu}. This conclusion is in contrast to the discussion of the present study, where it was concluded that the omega technique does not compensate in any way for the omission of the $L(u, q_w)$ term.

The basis of disagreement between these opposing views lies in the different values of β^{o} and F_{cc}, used in the comparisons. Streitwieser employed a value of β^{o} obtained from a correlation line in which the omega technique molecular ionization potentials, I_m, were calculated from the difference in pi system energies between the original hydrocarbon R, and the ion R^{+} produced in the ionization process (16):

$$I_m = E_{\pi}(R) - E_{\pi}(R^{+}) \quad . \tag{74}$$

The $E_{\pi}(R)$ and $E_{\pi}(R^{+})$ were calculated using the normal Huckel hypothesis that the pi energy is given simply by the sum of the energies of the occupied one-electron molecular spin orbitals. This method of calculating the pi system energies is not valid for any molecular orbital scheme which includes electron repulsion, such as the Pople technique and methods A and B of the present study. Such correlation line values of β^{o} do not necessarily reflect the effective value of the term β^{o} used in the Coulomb integral expression, and the use of such values may lead to erroneous results when Coulomb integrals are analyzed.

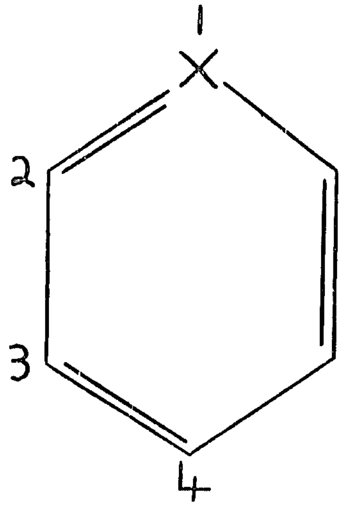
Comparison of Charge Density Predictions by Molecular Orbital Methods

All the molecular orbital methods for conjugated systems that have been discussed in this section are generally termed "semi-empirical" techniques. Such methods are traditionally tested for validity by establishing the extent to which they are capable of rationalizing experimental data, as well as by studying the rigor of the approximations employed. It is generally accepted that the Pople method does represent an improvement over the simple Huckel procedure. This conclusion has been reached by the use of both criteria given above. In the next few pages, an attempt will be made to ascertain the validity of the omega technique relative to the Pople and Huckel methods by establishing the extent to which the omega technique represents an improvement over the Huckel method towards Pople's procedure when applied to pi electron systems. Although a comparison between the three methods could be made for any and all pi electron systems, only certain arbitrarily chosen examples can be discussed in a limited amount of space. For this reason, a very common type of pi electron system will be used in the discussion. This typical pi network to be analyzed is that of a conjugated six-member ring system, with each atom in the ring contributing one p_π atomic orbital and one pi electron to the network. The molecule chosen is shown on the following page. Since the system contains five carbon atoms (atoms 2 to 6), and one heteroatom (atom 1), it represents a prototype of the pyridine molecule.

Since atoms 2 to 6 are carbon atoms, the "Huckel" method F matrix term constants are given simply by $h_2 = h_3 = h_4 = h_5 = h_6 = 0.0$ and $k_{23} = k_{34} = k_{45} = k_{56} = +1.0$. The heteroatom parameters are arbitrarily, but typically, chosen as

$$h_1 = +1.0$$

$$k_{12} = k_{16} = +1.0$$



The Huckel method charge distribution (24) based on this set of parameters is listed in the Table II-III.

Each of the molecular orbital methods (Pople, omega and Huckel) starts with this initial Huckel charge density distribution as a basis for further calculations. These Huckel charges are employed in each method to calculate new Coulomb integrals F_{uu} (or α_u). The parameters ΔF_{uu} is defined as the difference between the Huckel F_{uu} term and the F_{uu} based upon the Huckel charge density for each orbital ϕ_u:

$$\Delta F_{uu} = F_{uu} - F_{uu}\,(\text{Huckel}) \tag{75}$$

The molecular orbital methods may then be compared on the basis of the relative magnitudes of ΔF_{uu} terms predicted.

TABLE II-III: Calculated ΔF_{uu} and Huckel Charges for Pyridine-Like Molecule

Atom Number	Huckel Charge $(Z_u - q_v)$	ΔF_{uu}				
		Simple Huckel	ω Type Technique	ω + Nearest Neighbours	ω + 1st + 2nd Neighbours	Pople Method[a]
1	−0.3697	0.00	+1.95	−0.17	−0.08	−0.55
2	+0.1452	0.00	−0.76	+1.99	+0.68	+0.72
3	−0.0082	0.00	+0.04	−1.72	+0.35	−0.36
4	+0.0957	0.00	−0.50	−0.38	−1.97	−0.16

Note:

a) Equivalent to ω + all neighbours.

Since the Huckel method Coulomb integrals are independent of the charge densities q_u, all the terms ΔF_{uu} are equal to zero. The Pople method values of ΔF_{uu} for each inequivalent orbital are listed in Table II-III and were calculated by using the Huckel charge densities together with the appropriate repulsion integrals γ_{uw} according to equation 19. The values of the γ_{uw} integrals used were taken to be those listed for benzene (X = C) by Pariser and Parr (8). The parameters ΔF_{uu} values corresponding to the omega technique are also listed in Table II-III, and were calculated using $\gamma_{uu} = 10.53$ e.v., the Pariser and Parr value (8).

The corrections ΔF_{uu} calculated for the omega technique bear little resemblance in sign, magnitude or relative order to those calculated by Pople's method. In general, the omega technique ΔF_{uu} terms cannot be considered to lie between the Huckel and the Pople ΔF_{uu} terms since they are all outside of this range. The agreement between the omega technique and Pople ΔF_{uu} is not substantially improved by adding only the nearest neighbour $L(u, q_w)$ terms of equation 37 (Table II-III) nor only the nearest and second nearest neighbour $L(u, q_w)$ terms to the omega technique ΔF_{uu} terms. The inclusion of nearest neighbour, or first and second nearest neighbour, terms to the omega technique has been suggested in the literature as the ω' and ω'' methods (25,26).

From this analysis, it may be concluded that use of the omega technique will not result in charge distributions which are midway between those of the Huckel and Pople methods, but will yield distributions which are quite different from both of these procedures.

The present discussion concerning the validity of the omega technique may be concluded with a quotation from a review paper by M. J. S. Dewar (6):

> "If one is going to make allowance for the terms in F_{ii} $\left[F_{uu}\right]$ involving the charge densities q_i $\left[q_u\right]$, one might as well do the thing properly and use the full Pople expression."

II. 3. MOLECULAR ORBITAL CALCULATIONS FOR CONJUGATED MOLECULES CONTAINING BORON

II. 3. A. INTRODUCTION

The very large number of molecular orbital calculations for pi electron systems which are given in the chemical literature are mainly for aromatic hydrocarbons and their simple derivatives, since most of the known conjugated molecules are organic rather than inorganic. Recently, some inorganic analogues of the common rings and chains formed by carbon atoms have been synthesized (27). Conjugated pi electron systems, extending over several inorganic atoms, may be present in some of these molecules (27).

The pi electron systems in those compounds containing trivalent boron atoms are similar to aromatic hydrocarbons in some respects, since the atoms participating in the conjugated networks are coplanar, and can use valence-shell p_π atomic orbitals for pi bonding. In many molecules, the unoccupied p_π orbitals of boron atoms can conjugate with the p_π orbitals of nitrogen, oxygen, fluorine, chlorine, etc. which are doubly-occupied. These pi electron systems differ from those in organic aromatic molecules since the Coulomb integrals of the different p_π orbitals in the inorganic systems are generally quite different in magnitude, whereas the Coulomb integrals in the organic systems are quite similar.

Since Coulomb integrals for the p_π orbitals of many atoms have been "derived" in Part II. 2, simple molecular orbital treatments of many inorganic conjugated systems can be made. Such calculations are reported herein for pi electron systems formed by boron (B) atoms and atoms (X) which have lone pairs of electrons in their valence-shell p_π orbitals.

The model of the B-X pi electron systems considered has each boron atom contributing one p_π atomic orbital and zero pi electrons to the conjugated network, and each "lone-pair" atom, X, contributing one p_π orbital and two pi electrons. The sigma electron systems of these molecules are assumed to be composed of non-polar B-X bonds, since several authors (28, 29) have shown that this assumption is superior to models which assume substantial polarities in the B-X sigma bonds.

The molecules considered explicitly contain boron and nitrogen atoms (i.e. $X \equiv N$). Many of the B-N networks discussed have B-O, B-S, B-F, B-Cl, and B-Br analogues. The Coulomb integrals of these other lone-pair atoms are similar to that of nitrogen, and most of the results presented for B-N systems are directly applicable to these other systems.

Molecular orbital calculations by the Huckel and/or Pariser-Parr-Pople methods have been reported in the literature for the best-known boron-nitrogen conjugated system, borazine (28-36). LCAO-MO treatments for some aminoborane derivatives, and for the boron-nitrogen analogues of naphthalene and biphenyl, have also been reported (29,37). Both the sigma and pi bonds in several B-N rings and chains have been treated by the Extended Huckel Method (38,39), and the boron trihalides have been treated by a similar method (40). Several workers have also done molecular orbital calculations on some aromatic organic molecules which contain boron and nitrogen atoms (37-39,41).

In all the LCAO-MO calculations which have been reported for B-N pi systems, only a few conjugated systems have been considered in each report. In the present study, an attempt is made to consider a large variety of B-N systems by LCAO-MO methods with a consistent set of parameters, in order that direct comparisons between different B-N pi networks can be made.

In all the molecules to be considered, it is assumed, for simplicity, that a single, continuous pi electron network is present. For example, atoms having two lone-pairs of electrons are assumed to use only one of these pairs for pi bonding.

II. 3. B. METHOD OF CALCULATION

Both the simple Huckel method and the "omega technique" (see Part II. 2) were used in the LCAO-MO calculations for all the B-N networks considered herein. The calculations were done by means of the computer programme described in Appendix II. The main steps in the computer programme are as follows:

i) the "input data" for the molecule to be considered is read in to the computer,

ii) the matrix elements F_{uv} for each pi atomic orbital are calculated,

iii) the secular determinant (equation 27) is solved for the eigenvalues and eigenvectors,

iv) the eigenvalues (and corresponding eigenvectors) are sorted in order of decreasing stability,

v) the charge-density and bond-order matrix (equation 25) is calculated,

vi) in omega technique calculations, steps (ii) through (v) are iterated until a self-consistent field is produced,

vii) the molecular orbital results for the molecule are printed out.

The parameters required for these calculations are the Coulomb integrals for boron and nitrogen, the ω values for these atoms, and the B-N, B-B, and N-N resonance integrals. The Coulomb integral parameters h_B and h_N (see equation 30) were taken as those listed for $B(Z_u = 0)$ and $N(Z_u = 2)$ in Table II-I, and were rounded off to two significant figures (i.e. $h_B = -1.1$, $h_N = +1.5$). The ω values for B and N were obtained by substituting h_B and h_N above into equation 71. The resonance integral parameter k_{BN} (see equation 31) for a B-N bond has been estimated previously (30,33,37,41,42) to be in the range

$$0.5 < k_{BN} < 1 \quad .$$

The value $k_{BN} = 0.9$ has been arbitrarily adopted in all the present calculations. The use of a slightly different k_{BN} changes the absolute magnitudes of the molecular orbital parameters, but the TRENDS in bond order, charge, energy, etc. in different molecules are not affected greatly. In a few of the networks considered, k_{BB} and k_{NN} are required. In order to facilitate comparisons with molecules containing B-N bonds, k_{BB} and k_{NN} were also taken as 0.9. Non-zero resonance integrals were only used for "bonded" atoms in the Huckel and omega calculations.

Pople method self-consistent field calculations were also performed for the pi systems of several of the smaller molecules in their ground states. The distance between bonded B and N atoms was taken to be equal to that for borazine, 1.44 Å (36), in all cases, since structural data for the other B-N systems is not yet available. The B-N-B and N-B-N bond angles were assumed to be 120°, except in the four-membered ring where 90° bond angles were used. All the conjugating B and N atoms were assumed to be coplanar.

The Pople method calculations for the B-N networks were accomplished by using a slightly modified version of the "SCF-1" computer programme devised by J.M. Sichel (43). This programme is similar to that used for the Huckel and omega calculations. The evaluation of the F matrix elements is, however, more complicated in the Pople technique programme than in the Huckel-omega programme.

Several similar sets of parameters and integrals for Pariser-Parr-Pople calculations on borazine have been given in the literature (28,29,36).

The most recent set, that given by Perkins and Wall (36) who considered several borazine derivatives as well as the parent molecule, were used for the Pople calculations reported herein. Hence, the two-centre repulsion integrals γ_{uv} were calculated by Ohno's formula (44):

$$\gamma_{uv} = \frac{14.397}{(r^2 + a^2)^{1/2}} \tag{76}$$

where r is the distance in Å between the atoms of orbitals ϕ_u and ϕ_v, and

$$a = \frac{28.794}{\gamma_{uu} + \gamma_{vv}} \quad . \tag{77}$$

Perkins and Wall (36) give the following values for the one-centre repulsion integrals γ_{uu} and γ_{vv} and for the core integrals U_{uu} and U_{vv}:

γ_{BB} = 5.97 e.v.

γ_{NN} = 11.07 e.v.

U_{BB} = -1.061 e.v.

U_{NN} = -23.02 e.v.

The core integral H_{BN} (equation 14) for nearest-neighbours B and N was found to be -2.198 e.v. (36). All the Pople method calculations reported herein have been generated by use of the parameter set given above. No configuration interaction is included for the ground states of the molecules.

The indices of the LCAO-MO calculations reported are:

i) the bond orders P_{uv} between "bonded" orbitals,

ii) the net charges associated with the p_π atomic orbitals,

iii) the ionization potential of the pi network, which is taken to be the energy of the highest occupied pi molecular orbital,

iv) the pi BONDING energy, defined as the total pi energy of the network minus the pi energy of the separated atomic orbitals (i.e. $E_{\pi}(\beta_{BN} = 0.9) - E_{\pi}(\beta_{BN} = 0.0)$) (Simple Huckel method only),

v) the pi bonding energy per atomic orbital in the network (Simple Huckel method only), and

vi) the pi bonding energy is also reported in terms of the "resonance energy." The resonance energy is defined as the pi bonding energy for the pi system minus the pi bonding energy of the component B-N pairs if the latter were isolated from each other.

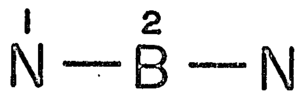
The boron and nitrogen atom frameworks of the conjugated systems considered are given in Figure II-3 for B-N chains, and in Figure II-4 for B-N rings. The numbering systems used in these figures are chosen for convenience in reporting the LCAO-MO calculations, and do not necessarily correspond to the numbering systems conventionally used for such molecules. Some examples of real molecules containing the pi networks given in Figures II-3 and II-4 are illustrated in Figure II-5. In all three figures, II-3, II-4, and II-5, all the B-N bonds are represented by single dashes, since full double B-N bonds are not present in these molecules. The B-N chains are classified according to the longest, continuous pi network that can exist in the molecule. For example, structure IX of Figure II-3 is considered as a branched derivative of the four-membered N-B-B-N chain.

Figure II-3:

BORON-NITROGEN CHAIN STRUCTURES

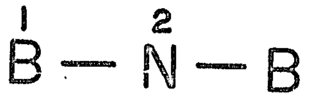
$\overset{1}{B}-\overset{2}{N}$

I



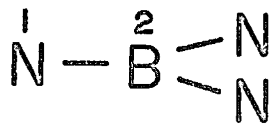
$\overset{1}{N}-\overset{2}{B}-N$

II

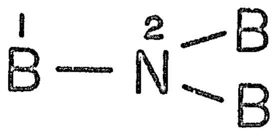


$\overset{1}{B}-\overset{2}{N}-B$

III



IV



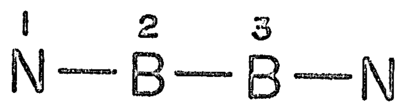
V

$\overset{1}{B}-\overset{2}{N}-\overset{3}{B}-\overset{4}{N}$

VI

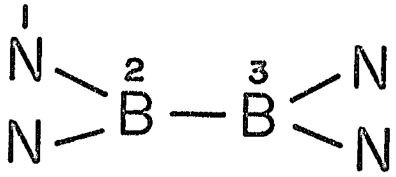
$\overset{1}{B}-\overset{2}{N}-\overset{3}{N}-B$

VII

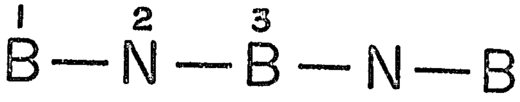


$\overset{1}{N}-\overset{2}{B}-\overset{3}{B}-N$

VIII

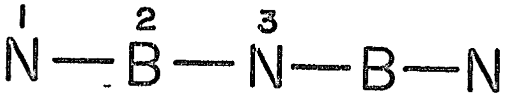


IX



$\overset{1}{B}-\overset{2}{N}-\overset{3}{B}-N-B$

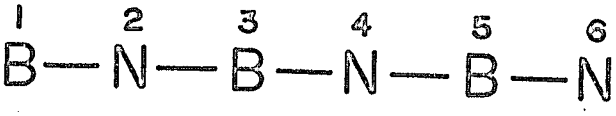
X



$\overset{1}{N}-\overset{2}{B}-\overset{3}{N}-B-N$

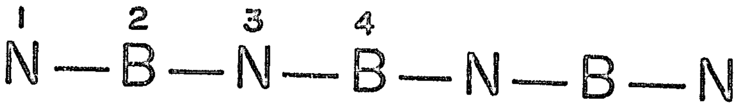
XI

XII



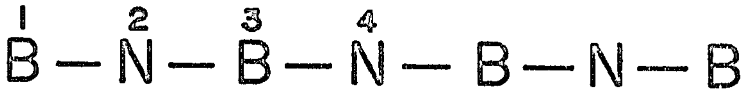
$\overset{1}{B}-\overset{2}{N}-\overset{3}{B}-\overset{4}{N}-\overset{5}{B}-\overset{6}{N}$

XIII



$\overset{1}{N}-\overset{2}{B}-\overset{3}{N}-\overset{4}{B}-N-B-N$

XIV



$$\overset{1}{B}-\overset{2}{N}-\overset{3}{B}-\overset{4}{N}-B-N-B$$

XV

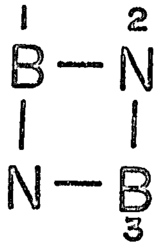
$$\overset{1}{B}-\overset{2}{N}-\overset{3}{B}-\overset{4}{N}-\overset{5}{B}-\overset{6}{N}-\overset{7}{B}-\overset{8}{N}$$

XVI

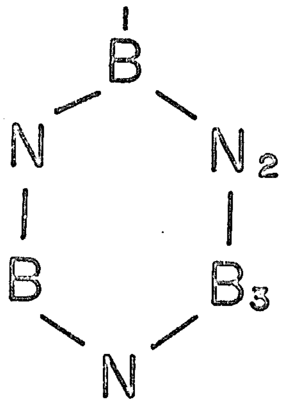
Figure II-4:

BORON-NITROGEN RING STRUCTURES

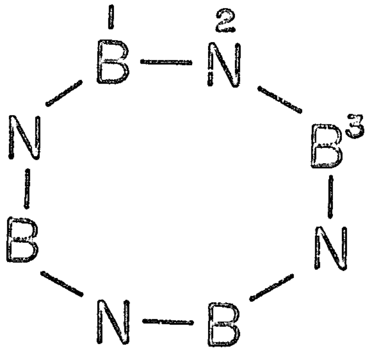
XVII



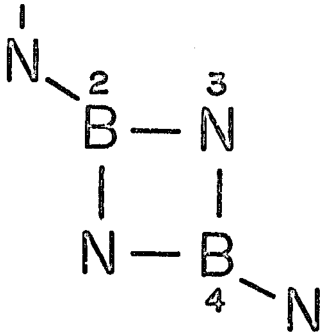
XVIII



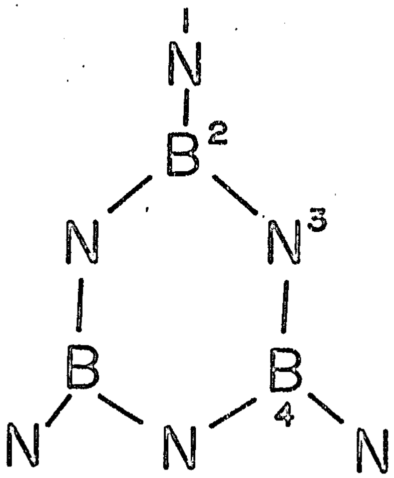
XIX



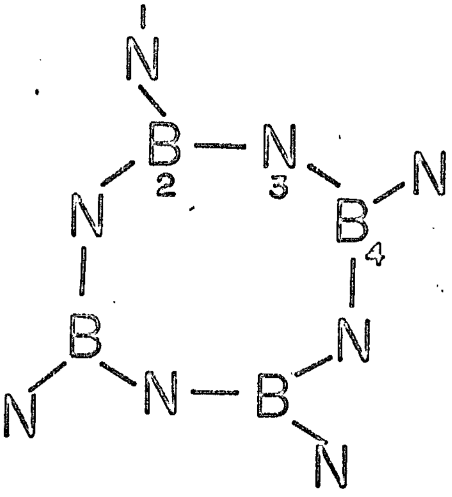
XX



XXI



XXII



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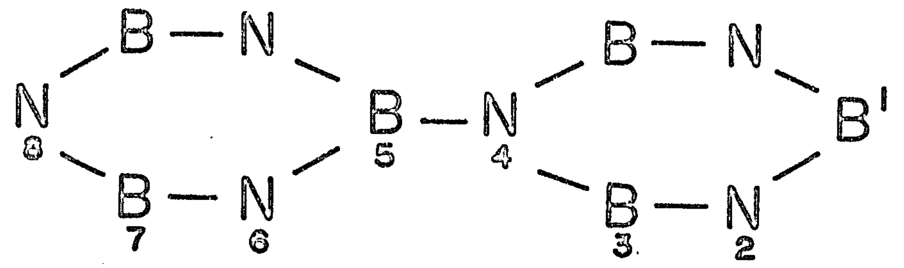
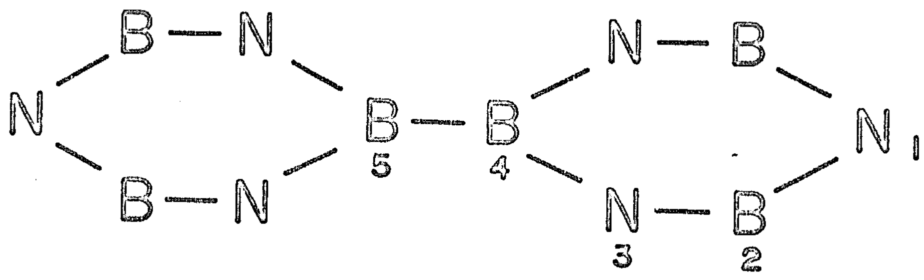
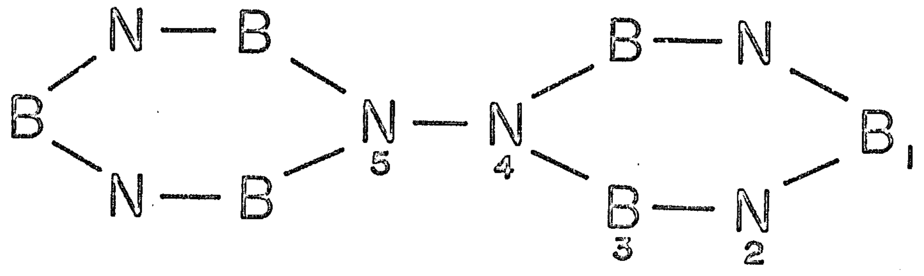


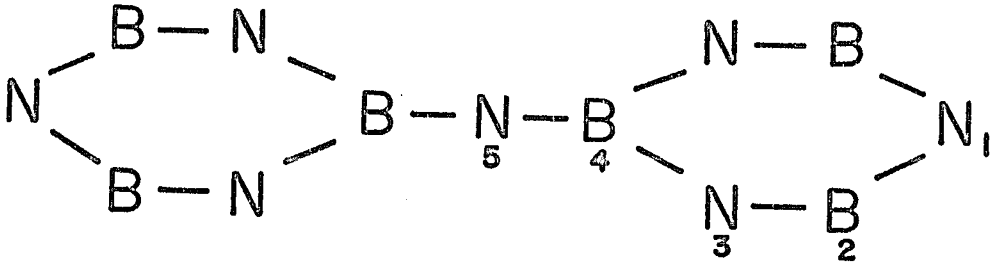
XXIV



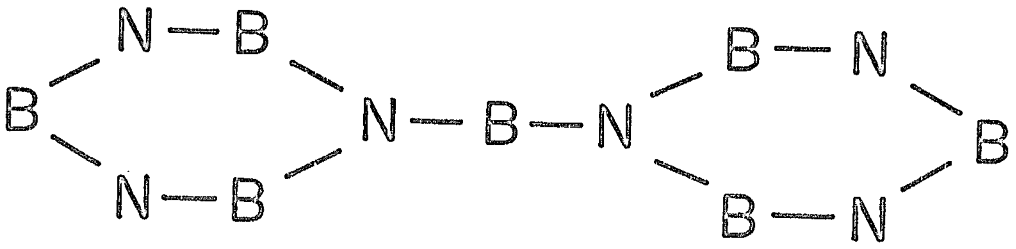
XXV



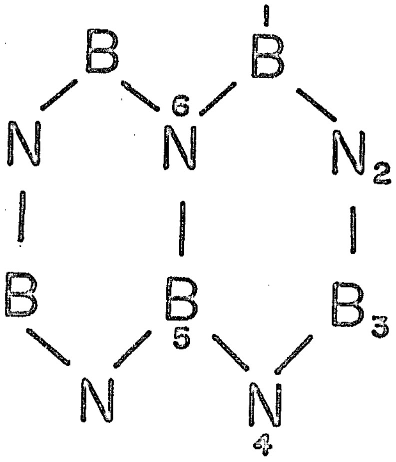
XXVI



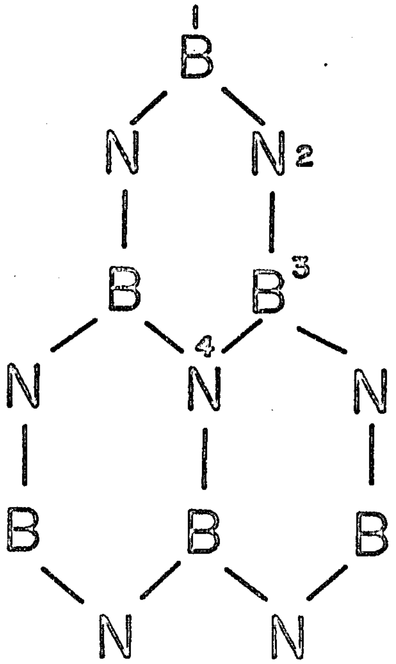
XXVII



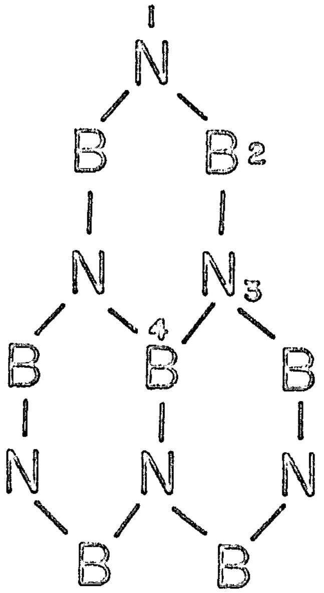
XVIII



XXIX



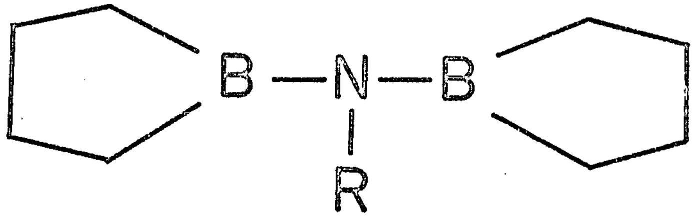
XXX



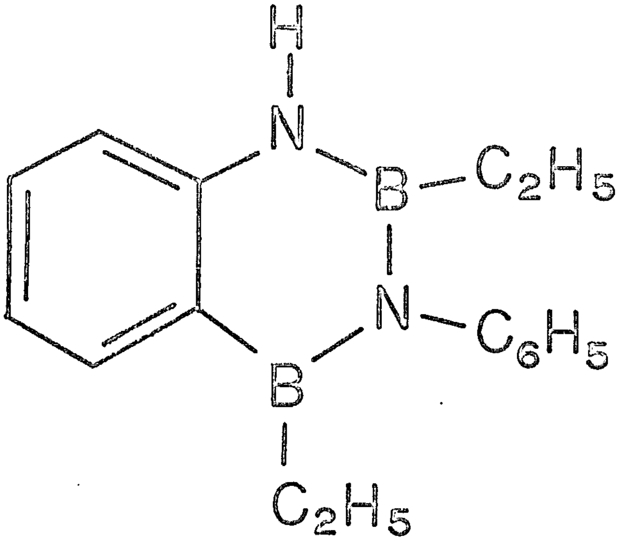
XXXI

Figure II-5:

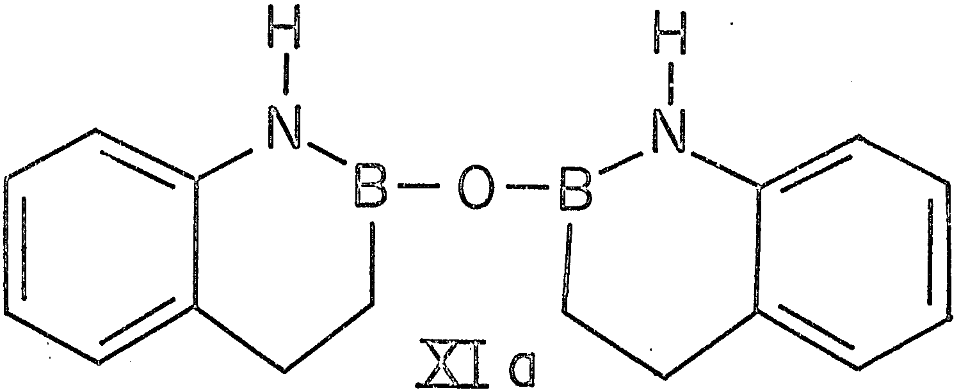
SOME EXAMPLES OF SYNTHESIZED MOLECULES WITH B-X Pi ELECTRON SYSTEMS



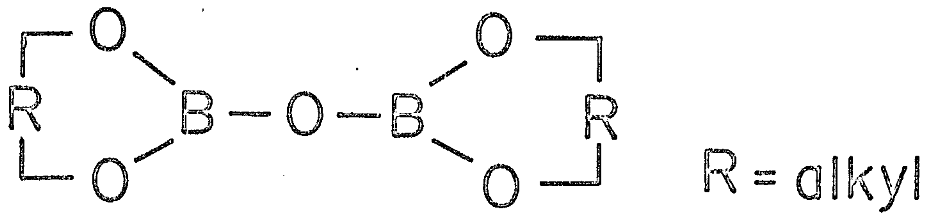
III a



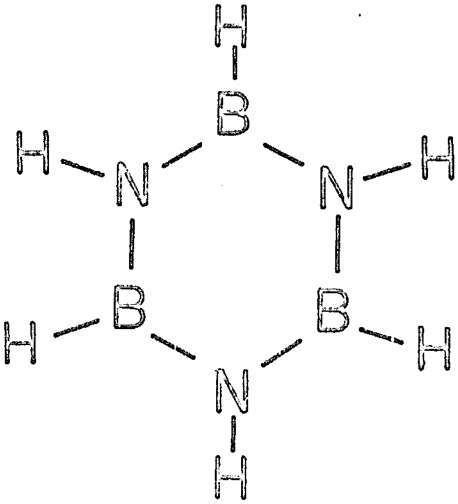
VI a



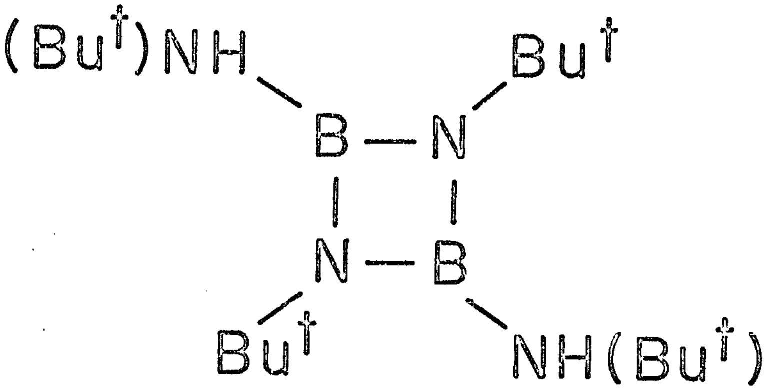
XI a



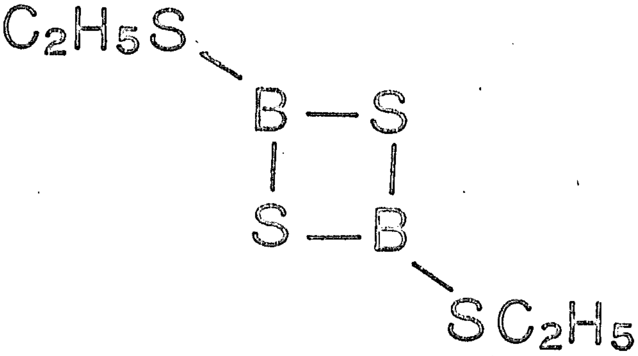
XII a



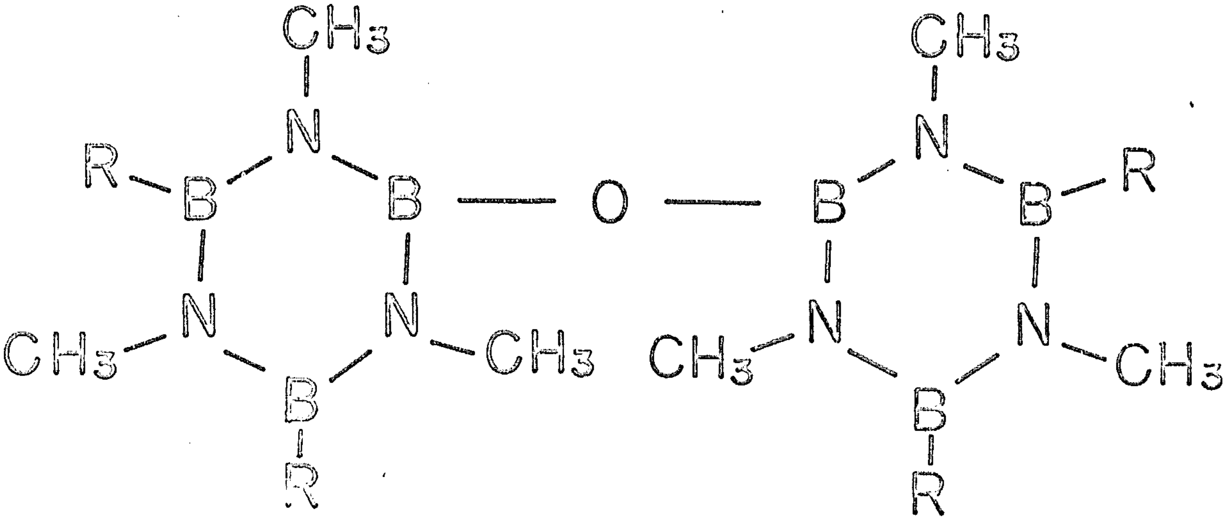
XIX a



XXI a



XXI b



XXVII a

R = CH_3,
$CH_2Si(CH_3)_3$

II. 3. C DISCUSSION AND RESULTS

In the conjugated pi electron networks formed by B and N atoms, each boron atom contributes zero electrons to the network, and each nitrogen atom contributes two electrons. Thus the total number of pi electrons is always an even number for such systems. In carbon-carbon pi networks, each C atom usually contributes one electron, and the total number of electrons is an even number only if there are an even number of carbon atoms present. Since an even number of pi electrons is required to obtain a closed-shell ground-state configuration, and since a closed shell is usually required for a stable system, it is theoretically possible to obtain a greater variety of B-N pi systems than C-C pi systems. This factor is especially evident in B-N conjugated chains, where a closed shell of pi electrons is obtained regardless of the chain length. In carbon-carbon straight chains, the conjugated system usually extends over only an even number of carbon atoms in the neutral molecules.

B-N CONJUGATED CHAINS

The fundamental pi electron unit formed by boron and nitrogen is the two-membered chain, B-N, which contains two pi electrons and is in some respects similar to the two-electron carbon-carbon double bond. Since the Coulomb integral of nitrogen is greater than that of boron, the pi electron pair in B-N is not shared equally between the two atomic orbitals, but is mainly centered on nitrogen. The molecular orbital calculations on B-N indicate that only about 0.2 electron is transferred to the initially unoccupied boron pi orbital from the initially doubly-occupied nitrogen pi orbital (Structure I, Tables II-VII, II-VIII, II-IX). Since the pi electrons are not shared equally in B-N, the B-N mobile bond order is only 0.5 to 0.6 (I, Tables II-IV, II-V, II-VI), which is much less than that of 1.0 in ethylene.

The pi bonding imparts additional energetic stability above that of a single boron-nitrogen sigma bond in the B-N molecule. The calculated Huckel pi bond energy for B-N of 0.56 β^{o} (I, Table II-X) is, however, much less than that of 1.80 β^{o} for a B-N bond in which the Coulomb integrals of the two atoms are equal. If the B and N units in the B-N type of molecule are twisted such that the pi atomic orbitals are at an angle of 90° to each other, the B-N resonance integral goes to zero and the pi bonding energy is zero. Therefore, a barrier to rotation about the B-N bond should exist. This barrier has been studied by nuclear magnetic resonance experiments for some substituted aminoboranes, $R_1R_2N\text{-}BR_3R_4$, and has been found to be about 15 Kcal. mole^{-1} (45), which is approximately one-sixth of that estimated for the carbon-carbon double bond in ethylene (46). In molecules with carbon-carbon double bonds, the barrier to rotation is sufficiently large so that cis and trans isomers in substituted alkenes can be physically separated. Since the rotation barrier for B-N is much smaller than that of a carbon-carbon double bond, the average lifetime of the cis and trans isomers is much smaller. For example, the mean lifetime of the isomers in $(C_6H_5)(CH_3)\ N\text{-}B\ (CH_3)_2$ is only approximately 10^{-2} seconds at 100°C (45), and individual isomers have not been isolated.

The parent molecule H_2BNH_2 of the simple B-N pi system, and the other B-X counterparts such as H_2BSH, etc., are found to be dimers and polymers rather than monomers (47,48). The pi bonding energy in these molecules is evidently insufficient to stabilize the monomers. Several organo-substituted derivatives of the parent molecules, such as $(CH_3)_2\ BNH_2$ and $(CH_3)_2BN(CH_3)_2$,

TABLE II-IV: Bond Orders (Huckel Method) for B-N Chains

Molecule Number	Pi Bond Orders for Orbital Pairs 1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	Others
I	0.569					
II	.495					
III	.495					
IV	.443					
V	.443					
VI	.510	.431	.510			
VII	.592	.101				
VIII	.592	.101				
IX	.502	.127				
X	.506	.443				
XI	.506	.443				
XII	.450	.405				
XIII	.507	.441	.456	.441	.507	
XIV	.507	.441	.454			
XV	.507	.441	.454			
XVI	.507	.441	.454	.451	.454	.441 (a) .507 (b)

Notes:

a) 6 - 7 Bond

b) 7 - 8 Bond

TABLE II-V: Bond Orders (<u>Omega Technique</u>) for B-N Chains

Molecule Number	Pi Bond Orders for Orbital Pairs 1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	Others
I	0.515					
II	.456					
III	.446					
IV	.413					
V	.401					
VI	.458	.393	.468			
VII	.528	.072				
VIII	.528	.072				
IX	.461	.097				
X	.455	.404				
XI	.466	.404				
XII	.420	.373				
XIII	.456	.402	.415	.402	.466	
XIV	.466	.402	.413			
XV	.456	.402	.413			
XVI	.456	.402	.413	.411	.414	.402 (a) .466 (b)

Notes:

a) 6 - 7 Bond

b) 7 - 8 Bond

TABLE II-VI: Bond Orders (Pople Method) for Selected B-N Chains and Rings

Molecule Number	Pi Bond Orders for Orbital Pairs 1 - 2	2 - 3	3 - 4
I	0.666		
II	0.567		
IV	0.499		
VI[(a)]	0.603	0.459	
XVIII	0.443	0.443	
XIX	0.542	0.542	
XXI	0.558	0.411	0.411
XXII	0.522	0.481	0.481

Note:

a) cis isomer

TABLE II-VII: Pi Orbital Net Charges (<u>Huckel Method</u>) for B-N Chains

Molecule Number	Net Charges (in Electrons) for Atomic Orbitals 1	2	3	4	5	6	Others
I	-.178	+.178					
II	+.143	-.286					
III	-.143	+.286					
IV	+.120	-.360					
V	-.120	+.360					
VI	-.151	+.264	-.264	+.151			
VII	-.212	+.212					
VIII	+.212	-.212					
IX	+.159	-.318					
X	-.149	+.269	-.240				
XI	+.149	-.269	+.240				
XII	+.123	-.350	+.207				
XIII	-.149	+.268	-.245	+.245	-.268	+.149	
XIV	+.149	-.268	+.244	-.250			
XV	-.149	+.268	-.244	+.250			
XVI	-.149	+.268	-.244	+.249	-.249	+.244	-.268 (a) +.149 (b)

Notes:

a) Orbital 7

b) Orbital 8

TABLE II-VIII: Pi Orbital Net Charges (Omega Technique) for B-N Chains

Molecule	Net Charges (in Electrons) for Atomic Orbitals						
Number	1	2	3	4	5	6	Others
I	-0.143	+0.143					
II	+.118	-.235					
III	-.112	+.224					
IV	+.101	-.302					
V	-.094	+.281					
VI	-.118	+.209	-.214	+.123			
VII	-.162	+.162					
VIII	+.162	-.162					
IX	+.128	-.256					
X	-.116	+.212	-.191				
XI	+.122	-.218	+.191				
XII	+.103	-.291	+.168				
XIII	-.117	+.211	-.195	+.195	-.217	+.122	
XIV	+.122	-.217	+.194	-.199			
XV	-.117	+.211	-.194	+.199			
XVI	-.117	+.211	-.194	+.198	-.198	+.194	-.217 (a) +.122 (b)

Notes:

a) Orbital 7

b) Orbital 8

TABLE II-IX: Pi Orbital Net Charges (Pople Method) for Selected B-N Chains and Rings

Molecule Number	Net Charges (in Electrons) for Atomic Orbitals 1	2	3	4
I	-0.254	+0.254		
II	+0.201	-0.403		
IV	+0.166	-0.497		
VI[(a)]	-0.225	+0.364	-0.378	+0.239
XVIII	-0.267	+0.267		
XIX	-0.397	+0.397		
XXI	+0.204	-0.448	+0.244	
XXII	+0.185	-0.515	+0.330	

Notes:

a) cis isomer

TABLE II-X: Pi Bonding Energy Data (Huckel Method) for B-N Chains

Molecule Number	Total Pi Bonding Energy (in β^o)	Resonance Energy (in β^o)	Bonding Energy per Pi Atomic Orbital (in β^o)
I	0.562	0.000	0.28
II	1.039	0.476	0.35
III	1.039	0.476	0.35
IV	1.460	0.897	0.37
V	1.460	0.897	0.37
VI	1.532	0.408	0.38
VII	1.212	0.087	0.30
VIII	1.212	0.087	0.30
IX	2.189	1.064	0.36
X	2.022	0.897	0.40
XI	2.022	0.897	0.40
XII	2.879	1.755	0.41
XIII	2.512	0.826	0.42
XIV	3.003	1.316	0.43
XV	3.003	1.316	0.43
XVI	3.493	1.244	0.44

are known to be monomeric (48).

The Pi Networks BN_m and NB_m

The pi electron system B-N can be extended by the addition of B or N atoms. If nitrogen atoms are added to the central boron atom, the series BN, BN_2, and BN_3 (II and IV of Figure II-3) is produced. If boron atoms are added to the nitrogen atom in B-N, then the series NB, NB_2, and NB_3 (III and V, Figure II-3) results. The pi networks in these series correspond to the two-membered chain, the three-membered chain, and the three-membered chain with a branched chain of unit length at the central atom. For the purposes of the simple Huckel and omega technique calculations, the p_π orbitals of the atoms in these series BN_m and NB_m can be considered to transform according to the rotation point groups C_m. The pi molecular orbitals in these molecules can be discussed by reference to the irreducible representations of the point groups C_m (49). For the set BN_m, the boron p_π orbital and the group orbital ϕ_1

$$\phi_1 = \frac{1}{m} \sum_i \phi_{Ni} \tag{78}$$

transform according to the "A" irreducible representation of the point group C_m. The boron and the group pi orbitals can be combined (49) to form two molecular orbitals of the type

$$\psi_A = c\,\phi_B + \frac{c_1}{m} \sum_i \phi_{Ni} \quad . \tag{79}$$

The energy levels for these molecular orbitals ψ_A are given by

$$E = \frac{\alpha_B + \alpha_N}{2} \pm \frac{1}{2} \left((\alpha_B - \alpha_N)^2 + 4m\beta_{BN}^2 \right)^{1/2} \quad . \tag{80}$$

The stability of the bonding MO increases with m for given Coulomb integrals α_B and α_N and for a given resonance integral β_{BN}. The energy levels for the MOs ψ_A in the system NB_m are given by the same formula.

For the BN_2 and NB_2 networks, a second group orbital ϕ_2, corresponding to the "B" irreducible representation of the group C_2, can be made:

$$\phi_2 = \frac{1}{2}(\phi_{N_1} - \phi_{N_2}) \qquad \text{for } BN_2 \qquad (81)$$

$$\phi_2 = \frac{1}{2}(\phi_{B_1} - \phi_{B_2}) \qquad \text{for } NB_2 \ . \qquad (82)$$

The group orbital ϕ_2 cannot mix with the p_π orbital of the central atom, since the two orbitals belong to different irreducible representations. The group orbital ϕ_2 represents a non-bonding MO with energy α_N for BN_2 and energy α_B for NB_2.

For the BN_3 and NB_3 systems, two group orbitals, ϕ_2 and ϕ_3, can be formed corresponding to the "E" representation of the point group C_3 (49). These group orbitals cannot mix with the p_π orbital of the central atom, and therefore ϕ_2 and ϕ_3 represent a degenerate pair of non-bonding molecular orbitals with $E = \alpha_N$ for BN_3, and $E = \alpha_B$ for NB_3.

The results of the molecular orbital calculations for BN_2 and NB_2 are reported in Tables II-IV to II-X as items II and III. Since these two networks are related by a complete interchange of atoms, the Huckel method calculations for II and III are identical. The bond orders P_{BN}, and the terminal atom net charges, in II and III are less than those in B-N, whereas the net charge of the central atom is higher.

Both the Huckel total pi bonding energy and the energy per atom for II and III are greater than that in B-N (1.04 β^o versus 0.56 β^o, and 0.35 β^o versus 0.28β^o). The pi system of a three-membered BN chain then imparts substantially greater stability to the molecule than the pi system in the two-membered chain. Indeed, the N-B-N chains (and generally the X-B-X systems) appear to be more common and stable than the B-N counterparts. For example, no well-defined, monomeric monoalkoxyboranes $ROBH_2$ have been reported, but dialkoxyboranes, $(RO)_2BH$ are common and are monomeric (50). Some monomeric compounds with the N-B-N linkage have also been synthesized, such as $(RR'N)_2BR''$ where R and R' are alkyl groups, and R'' is either an alkyl group or hydrogen (48). The three-membered chain with terminal boron atoms is present in such molecules as $(n\text{-}Bu)_2BOB(n\text{-}Bu)_2$ (51) and the molecule labelled IIIa in Figure II-5 (52).

The pi bonding energy calculated by the Huckel method for BN_3 and NB_3, $1.46\ \beta^o$, represents an increase of $0.42\ \beta^o$ over that for BN_2 and NB_2 (Table II-X). The pi bonding energy per atomic orbital is also increased, from $0.346\ \beta^o$ to $0.365\ \beta^o$. The B-N bond orders for BN_3 and NB_3 are slightly lower than those for BN_2 and NB_2 (Tables II-IV, II-V, II-VI). The net charge of the central atomic orbital in BN_3 and NB_3 is the highest found for any of the B-N systems considered (Structures IV and V, Tables II-VII, II-VIII, II-IX).

Since the pi bonding energy in BN_3 is relatively large, molecules containing the BX_3 grouping should be rather stable. Indeed, all four boron trihalides - BF_3, BCl_3, BBr_3, and BI_3 - are stable, monomeric compounds in which the four atoms are coplanar (53). Boron also forms a series of monomeric trialkoxyboranes, $(RO)_3B$, in which the B atom and the three O atoms are coplanar (54). Well-characterized nitrogen and sulphur derivatives, $(RR'N)_3B$ and $(RS)_3B$, are known and are usually monomeric (47,48). Even the parent molecule $B(NH_2)_3$ is known (48).

BN Chains with Four Atoms

The conjugated systems B-N-B-N and C=C-C=C are similar in some respects. In both "BN butadiene" and "CC butadiene," the pi bonding between the central orbitals is not as strong as that between the terminal orbital pairs, since the bond orders P_{23} are smaller than P_{12} and P_{34} (Structure VI, Tables II-IV, II-V, II-VI). The alternation of bond orders in BN butadiene (0.51, 0.43, and 0.51 for P_{12}, P_{23}, and P_{34} by the Huckel method) is not nearly as pronounced as that in CC butadiene (0.89, 0.45, and 0.89 by the Huckel method). The 36% increase in pi bonding energy in B-N-B-N relative to two B-N units (Table II-X), is significantly greater than the 12% increase for C=C-C=C relative to two C=C units (24). All three molecular orbital methods predict that the net charges of the p_π AOs of central atoms in B-N-B-N are greater than those for the p_π AOs of the terminal atoms (VI, Tables II-VII, II-VIII, II-IX). The net charges in C=C-C=C are all zero (2,24).

Although the conjugated B-N-B-N system is predicted to be stabilized relative to two B-N units, few molecules with the B-X-B-X network have been synthesized. One known example is VIa of Figure II-5 (52), in which the terminal B and N atoms are bonded to the benzene ring.

Two B-N units could also combine by B-B or N-N bonding to give the chains N-B-B-N and B-N-N-B. Some examples of both types are known; for example, $(CH_3)_2NB(R)B(R)N(CH_3)_2$ where R is an alkyl group (55), and $H_2BN(H)N(H)BH_2$ (56). There are many more compounds known of the type X_2BBX_2, which can be considered as two BX_2 units joined by a B-B bond to yield a branched chain of length four atoms. For example, the diboron tetrahalides B_2F_4, B_2Cl_4, B_2Br_4, and B_2I_4, as well as molecules of the type $B_2(NR_2)_4$ and $B_2(OR)_4$, have all been synthesized, and all contain B-B bonds (55).

Molecular orbital calculations for the units B-N-N-B, N-B-B-N, and N_2B-BN_2 are reported as structures VII, VIII and IX in the tables. The B-B and N-N bond orders are very small in these molecules (VII, VIII, and IX in Tables II-IV and II-V). Since these bond orders are small, the pi bonding energy increase of the units relative to separated BN or BN_2 units is very small (Table II-X). For example, the pi bonding energy increases by only 5% when two BN_2 units are joined by a B-B bond.

Since the pi bonding energy increase is small, the barrier to rotation due to pi bonding around the B-B and N-N bonds should be small. Solid-state X-ray measurements on crystalline B_2F_4 and B_2Cl_4 have indicated that the BX_2 units in these molecules are coplanar (57,58,59). In the gaseous phase, however, the two BCl_2 groups in B_2Cl_4 are perpendicular to each other (60). Infrared and Raman spectroscopic studies of gaseous and liquid B_2Cl_4, and of liquid $B_2(N(CH_3)_2)_4$ indicated that the BX_2 units are not coplanar (60,61,62), whereas the spectra of $B_2(OCH_3)_4$ is consistent with a planar arrangement of the B, O, and C atoms (62). These contradictory results are not surprising in the light of the molecular orbital calculations for N-B-B-N and N_2B-BN_2, since the conjugation between the two BN or BN_2 units is very weak, and will probably be of minor importance compared to steric effects, crystal packing requirements, etc. in determing the molecular geometry.

Brotherton (55) has noted that the higher B-O bond force constant in $B_2(OCH_3)_4$, compared to that in $B(OCH_3)_3$, indicates a greater double bond character for the B-O bond in the former molecule, compared to the latter. The LCAO-MO calculations are in agreement with this observation, since the B-N bond order in N_2B-BN_2 is greater than that in BN_3 (IX and IV, Tables II-IV and II-V).

Longer B-N Chains

The Huckel method energy levels, E_j, of unbranched chains of any length which have alternating B and N atoms can be found by the formula of Bochvar et al. (63):

$$E_j = \frac{\alpha_B + \alpha_N}{2} \pm \frac{1}{2}\left[(\alpha_B - \alpha_N)^2 + 16\,\beta_{BX}^2 \cos^2\left(\frac{j\pi}{m+1}\right)\right]^{\frac{1}{2}} \qquad (83)$$

where m is the chain length, and j = 1, 2, ... For chains having an odd number of p_π atomic orbitals, there are two possible molecules—that with terminal boron atoms and that with terminal nitrogen atoms. The Huckel method charges, bond orders, and pi bonding energies for the two possibilities are identical.

Some examples of the chain of length five are known. For example, the molecule number XIa of Figure II-5 (64) can be considered to include the N-B-O-B-N conjugated network joined at each end to a benzene ring. The branched chain X_2B-X-BX_2 is more common, however, and many molecules of the type illustrated in Figure II-5 (Structure XIIa) have been prepared (65). The Huckel pi bonding energy per p_π atomic orbital of $0.404\beta^o$ and $0.411\beta^o$ for these branched and unbranched chains respectively are significantly greater than those calculated for the BN, BN_2 and BN_3 units (Table II-X). The branched and unbranched chains should be quite stable with respect to their BN, BN_2, and BN_3 components.

The molecular orbital calculations reported in Tables II-IV, II-V, II-VII, II-VIII, and II-X for the unbranched chain of length five atoms, and for the longer unbranched chains, can be summarized as follows:

i) each boron pi orbital carries a net negative charge, the result of charge transfer from the nitrogen p_π orbitals. The net charges of the p_π orbitals of the terminal B and N atoms in each chain are less than the net charges of the other (internal) p_π atomic orbitals,

ii) the B-N bond orders in the boron-nitrogen chains display the same type of alternation as that established for conjugated carbon-carbon chains, but to a lesser degree, and

iii) the total pi bonding energy of the B-N chains increases smoothly with chain length. The pi bonding energy per p_π atomic orbital also increases with chain length, although the increases become smaller as the chain is lengthened.

B-N CONJUGATED RINGS

The B-N units can be joined together to form conjugated rings as well as chains. Until recently, only the six-membered rings were known in boron chemistry. Intensive research in the past decade, however, has resulted in the synthesis of many more B-X ring systems.

Both experimental evidence and molecular orbital calculations have indicated that planar, monocyclic ring systems, composed of trivalent carbon atoms, are especially stabilized by pi bonding when the number of pi electrons present equals $4n + 2$, where n is an integer (66). The extra stability of these systems is due to the complete filling of the bonding pi electron energy levels by the $4n + 2$ electrons, with the result that the pi bonding energy is a maximum for the system.

Craig (31) has shown that the "$4n + 2$" rule is also applicable to some extent for monocyclic, planar rings with alternating atoms X and Y whose p_π orbitals can form a pi electron system. He showed that the extra stability of such systems with $4n + 2$ pi electrons, relative to those with $4n$ pi electrons, decreases as the difference in Coulomb integrals between X and Y increases (31). In the rings discussed herein, the Coulomb integral difference between the p_π orbitals is quite large, and the "$4n + 2$" rule is not as important for such systems as it is with carbon-carbon networks.

The monocyclic ring systems $(BX)_m$, containing alternating B and X atoms, can be considered by the Huckel method by use of the C_m point group symmetry of the molecules. The Huckel method energy levels are more easily obtained by the formula of Davies (67) for such systems:

$$E_{\ell} = \left[(\alpha_B - \alpha_X)^2 + 8\beta_{BX}^2 \left\{ 1 + \cos \left(\frac{2\pi\ell}{n} \right) \right\} \right]^{1/2} \qquad (84)$$

where $\ell = 0, \pm 1, \ldots \pm q$. Here $q = n/2$ for even n, and $(n-1)/2$ for odd n, where n is the number of p_{π} orbitals in the ring. The total Huckel pi electron bonding energies for the $(BN)_2$, $(BN)_3$, and $(BN)_4$ rings (i.e. structures XVIII, XIX, and XX of Figure II-4) are listed in Table II-XV.

Monocyclic Rings

The pi bonding energy increase in $(BN)_2$, relative to that for two B-N units, is $0.72\beta^o$, corresponding to a 64% increase due to ring formation. The Huckel method predicts a zero pi energy increase when two carbon-carbon double bonds are joined to form cyclobutadiene (66). The Huckel pi energy levels for $(BN)_2$ and cyclobutadiene are illustrated in Figure II-6. In the carbon-carbon system, the energy levels for ethylene are split by equal and opposite amounts in cyclobutadiene, resulting in non-degenerate levels of energy $E = \alpha^o + 2\beta^o$ and $E = \alpha^o - 2\beta^o$, and a pair of degenerate, non-bonding levels of energy $E = \alpha^o$. The net increase in pi bonding energy is therefore zero, and cyclobutadiene should exist as a diradical. The bonding level for B-N, $E = \alpha^o + 1.781\beta^o$, and the anti-bonding level $E = \alpha^o - 1.381\beta^o$, are changed in $(BN)_2$ to give four non-degenerate pi energy levels. Since the extra stabilization of the first bonding level is greater than the destabilization of the other bonding level, the total pi bonding energy is increased. Since the $(BN)_2$ levels are not degenerate, the molecule should not be a diradical.

In both the carbon-carbon and boron-nitrogen four-membered rings,

TABLE II-XI: Bond Orders (Huckel Method) for B-N Rings

Molecule Number	Pi Bond Orders for Orbital Pairs					
	1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	Others
XVII	0.000	0.569	0.000			
XVIII	.405	.405				
XIX	.460	.460				
XX	.450	.450				
XXI	.472	.376	.376			
XXII	.455	.415	.415			
XXIII	.458	.410	.410			
XXIV	.458	.465	.425	.370	.425	.465 (a) .458 (b)
XXV	.461	.458	.469	.116		
XXVI	.461	.458	.469	.116		
XXVII	.458	.466	.418	.415		
XXVIII	.458	.466	.418	.415		
XXIX	.465	.455	.465	.421	.389	.421 (c)
XXX	.463	.419	.395			
XXXI	.463	.419	.395			

Notes:

a) 6 - 7 Bond

b) 7 - 8 Bond

c) 1 - 6 Bond

TABLE II-XII: Bond Orders (Omega Technique) for B-N Rings

Molecule	Pi Bond Orders for Orbital Pairs					
Number	1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	Others
XVII	0.000	0.515	0.000			
XVIII	.380	.380				
XIX	.416	.416				
XX	.411	.411				
XXI	.436	.353	.353			
XXII	.426	.380	.380			
XXIII	.427	.377	.377			
XXIV	.414	.420	.383	.342	.387	.421 (a) .414 (b)
XXV	.416	.413	.422	.082		
XXVI	.416	.414	.421	.082		
XXVII	.414	.422	.381	.383		
XXVIII	.414	.421	.377	.378		
XXIX	.420	.412	.421	.385	.352	.381 (c)
XXX	.419	.384	.358			
XXI	.419	.380	.358			

Notes:

a) 6 - 7 Bond

b) 7 - 8 Bond

c) 1 - 6 Bond

TABLE II-XIII: Pi Orbital Net Charges (Huckel Method) for B-N Rings

Molecule	Net Charges (in Electrons) for Atomic Orbitals						
Number	1	2	3	4	5	6	Others
XVII	-.178	-.178	+.178	+.178			
XVIII	-.207	+.207					
XIX	-.257	+.257					
XX	-.246	+.246					
XXI	+.135	-.318	+.183				
XXII	+.126	-.343	+.217				
XXIII	+.127	-.339	+.211				
XXIV	-.255	+.258	-.245	+.316	-.316	+.245	-.258 (a) +.255 (b)
XXV	+.259	-.257	+.271	-.288			
XXVI	-.259	+.257	-.271	+.288			
XXVII	+.254	-.259	+.241	-.328	+.217		
XXVIII	-.254	+.259	-.241	+.328	-.217		
XXIX	-.242	+.257	-.257	+.242	-.321	+.321	
XXX	-.259	+.240	-.322	+.304			
XXXI	+.259	-.240	+.322	-.304			

Notes:

a) Orbital 7

b) Orbital 8

TABLE II-XIV: Pi Orbital Net Charges (<u>Omega Technique</u>) for B-N Rings

Molecule Number	Net Charges (in Electrons) for Atomic Orbitals 1	2	3	4	5	6	
XVII	−.143	−.143	+.143	+.143			
XVIII	−.175	+.175					
XIX	−.201	+.201					
XX	−.197	+.197					
XXI	+.110	−.265	+.154				
XXII	+.106	−.280	+.174				
XXIII	+.106	−.278	+.172				
XXIV	−.200	+.202	−.190	+.247	−.251	+.192	−.203 (a) +.200 (b)
XXV	+.202	−.200	+.209	−.220			
XXVI	−.202	+.200	−.209	+.219			
XXVII	+.200	−.203	+.191	−.263	+.176		
XXVIII	−.199	+.202	−.188	+.256	−.171		
XXIX	−.189	+.202	−.202	+.192	−.254	+.249	
XXX	−.204	+.190	−.255	+.236			
XXI	+.203	−.188	+.250	−.235			

Notes:

a) Orbital 7

b) Orbital 8

TABLE II-XV: Pi Bonding Energy Data (Huckel Method) for B-N Rings

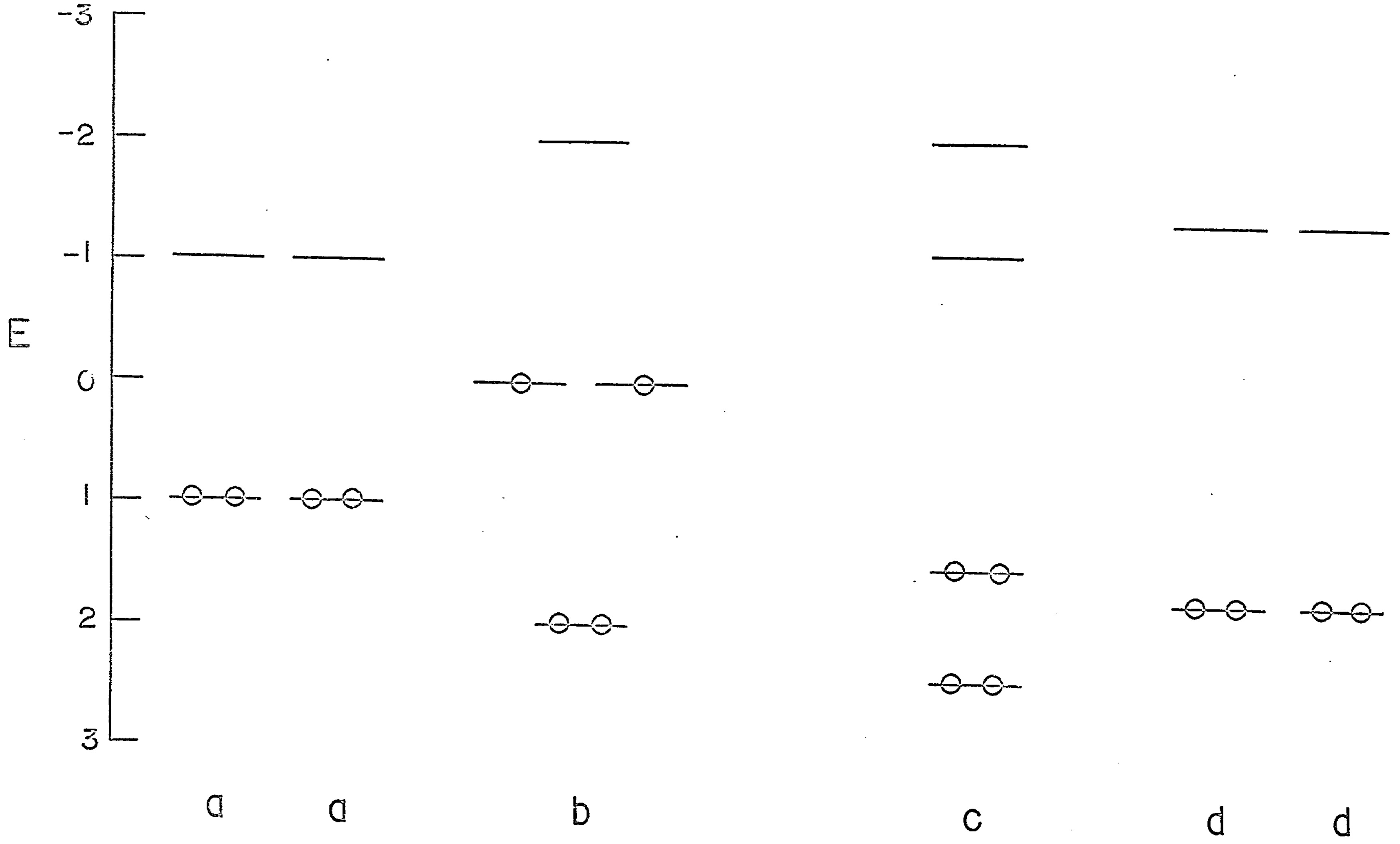
Molecule Number	Total Pi Bonding Energy (in β^{o})	Resonance Energy (in β^{o})	Bonding Energy per Pi Atomic Orbital (in β^{o})
XVII	1.125	0.000	0.28
XVIII	1.841	0.716	0.46
XIX	2.965	1.278	0.49
XX	3.918	1.669	0.49
XXI	2.754	1.629	0.46
XXII	4.269	3.144	0.47
XXIII	5.673	3.424	0.47
XXIV	6.276	2.902	0.52
XXV	6.033	2.659	0.50
XXVI	6.033	2.659	0.50
XXVII	6.758	3.384	0.52
XXVIII	6.758	3.384	0.52
XXIX	5.289	2.477	0.53
XXX	7.125	3.753	0.55
XXI	7.125	3.753	0.55

Figure II-6:

PI ELECTRON ENERGY LEVELS (HUCKEL METHOD) FOR "CC" AND "BN" CYCLOBUTADIENE

Note:

Note:	a	represents isolated C=C.
	b	represents "CC" Cyclobutadiene.
	c	represents "BN" Cyclobutadiene.
	d	represents isolated B-N.


-3
-2
-1
E
0
1
2
3
a
a
b
c
d
d

the sigma electron structure of the molecules is destabilized by the strain associated with 90° (rather than 120°) bond angles within the ring. As a result, such four-membered ring systems are difficult to synthesize. Some derivatives of the $(BN)_2$ and $(BS)_2$ rings have been prepared; a discussion of these derivatives will be given later. Molecular orbital calculations for the four-membered ring in which the two B-N units are joined by B-B and N-N bonds are also listed in Tables II-XI to II-XV (Structure XVII). According to the Huckel method results, there is no pi bonding energy increase when two B-N units are joined in this manner.

Conjugated six-membered rings are common in both carbon and boron chemistry. The best known $(BX)_3$ ring is borazine (Figure II-5, structure XIXa). The borazine ring is completely planar, the N-B-N and B-N-B bond angles are close to 120°, and all the B-N bonds have equal length (48). An extensive set of borazine derivatives are known (48). The conjugated six-membered ring systems $(BO)_3$ and $(BS)_3$ are also known, although the parent compounds boroxine $(B_3H_3O_3)$ and borthiin $(B_3H_3S_3)$ have not yet been isolated (47,68).

The Huckel calculations for $(BN)_3$ listed in Table II-XV indicate that this pi system is $1.28\beta^0$, or 75%, more stable than three isolated B-N units. In comparison, the Huckel pi energy increases by only 33% in going from three carbon-carbon double bonds to benzene (24). The pi energy levels for $(BN)_3$ are similar to those in benzene, since two doubly-degenerate pairs of MOs are obtained, and both the highest unoccupied orbital and the lowest unoccupied orbital are non-degenerate.

Eight-membered conjugated rings are rare in boron chemistry. Some derivatives of $(BN)_4$ have been synthesized recently, however (69,70). The Huckel calculations for $(BN)_4$ (XX, Table XV) predict a pi bonding energy increase of $1.67\beta^{o}$ for the ring relative to four isolated B-N units. This pi energy increase of 74% over a non-conjugated $(BN)_4$ ring is evidently insufficient to overcome the steric and strain effects associated with a planar eight-membered ring, since the $(BN)_4$ derivatives which have been synthesized have been found to be non-planar (70).

The trends in bond orders and net p_{π} orbital charges for the series BN, $(BN)_2$, $(BN)_3$, and $(BN)_4$ can be summarized as follows:

B-N Bond Orders:

$$BN > (BN)_3 > (BN)_4 > (BN)_2$$

Net Charges on B and N:

$$(BN)_3 > (BN)_4 > (BN)_2 > BN \;.$$

The same trends are given by all three calculation methods used[☆] (Tables II-VI, II-IX, II-XI, II-XII, II-XIII, II-XIV).

Rings with Exocyclic Substituents

A number of derivatives of the $(BX)_m$ ring systems have been prepared in which atoms having lone-pairs of electrons are substituted at each boron atom. Molecular orbital calculations are reported herein for the prototypes of such systems. The particular molecules considered are the $(BN)_2$, $(BN)_3$, and $(BN)_4$ monocyclic rings in which an exocyclic nitrogen atom is bonded to each boron atom in the ring. These systems will be termed $(NBN)_2$, $(NBN)_3$, and $(NBN)_4$ respectively, and are illustrated as structures XXI, XXII, and XXIII of Figure II-4.

[☆] Pople method calculations were not done for $(BN)_4$.

The B-N bond orders for these systems are listed in Tables II-VI, II-XI, and II-XII. In each case, the exocyclic B-N bond order is greater than the bond orders within the ring. The difference between the two types of bond orders is greatest for the four-membered ring, the differences being 0.097, 0.081, and 0.147, by the Huckel, omega, and Pople methods respectively, and the difference is least for the six-membered rings, the differences being 0.040, 0.046, and 0.041 respectively. Since the exocyclic bond orders in $(NBN)_m$ are greater than those within the ring, and since the latter are lower than those for the unsubstituted rings $(BN)_m$, the pi bonding within all the $(BN)_m$ rings is appreciably decreased by the presence of "lone-pair" atoms at each boron atom.

According to the Huckel method calculations, the total pi bonding energy is greatly increased when exocyclic nitrogen atoms are substituted at each boron atom. The increase in pi bonding energy of $(BN)_2$, $(BN)_3$, and $(BN)_4$ when $(NBN)_2$, $(NBN)_3$, and $(NBN)_4$ are formed is $0.92\beta^o$, $1.30\beta^o$, and $1.76\beta^o$ respectively (Table II-XV). All these increases are slightly larger than the "resonance" energies of the unsubstituted rings.

Two compounds of the $(BX)_2$ ring type have been synthesized, but since exocyclic substituents with lone pairs of electrons are present at the boron atoms in both of these compounds, these rings should be considered to be of the $(XBX)_2$ type. Lappert and Majumdar (71) have reported the preparation of the $(NBN)_2$ derivative illustrated as structure XXIa of Figure II-5. The infrared spectrum of this compound was interpreted in terms of cis and trans isomers of the molecule (71). The existence of cis and trans isomers indicates restricted rotation about the exocyclic B-N bonds (71). On the basis of the evidence for restricted rotation, Lappert and Majumdar concluded that the pi bonding within the molecule is mainly exocyclic (71). This conclusion is in agreement with the molecular orbital calculations discussed above for $(NBN)_2$. The second $(XBX)_2$ system which has been prepared is the $(SBS)_2$ derivative illustrated as structure XXIb of Figure II-5. This compound was prepared by Wiberg and Sturm (72). Apparently no molecules with the unsubstituted $(BX)_2$ pi system have been prepared to date.

Both the $(BX)_3$ and $(XBX)_3$ pi systems are well known in boron chemistry. A large number of derivatives of borazine, $B_3H_3N_3H_3$, have been prepared. In many of these derivatives, the substituent groups at boron are "lone-pair" atoms such as nitrogen (48,73). Derivatives of the boroxine, $(BO)_3$, and the borthiin, $(BS)_3$, rings are also well known, and many of these derivatives have exocyclic "lone-pair" atoms bonded to the boron atoms (74,75,76).

Turner and Warne (69,70) have prepared several compounds which contain the eight-membered $(BN)_4$ ring. All of these compounds have either halogen atoms (Cl, Br) or pseudohalogen groups (such as -NCS) attached to the boron atoms in the ring (70). The structure of the ring system in one $(ClBN)_4$ derivative has been studied (70). The $(BN)_4$ ring is tub-shaped rather than planar, and the B-N bonds alternate in length around the ring (70). The structure of the $(ClBN)_4$ derivative indicates that the conjugated networks in $(XBX)_4$ molecules are best considered to be composed of four XBX units, with only very weak conjugation between separate XBX units. Although the Huckel pi bonding energy of $5.67\beta^{o}$ for $(NBN)_4$ is appreciably greater than that of $4.16\beta^{o}$ for four NBN units, the pi energy difference is evidently insufficient to overcome the steric and strain effects associated with a planar eight-membered ring.

Fused Ring Systems

In organic chemistry, a large number of conjugated systems are known which can be considered to be the result of a fusion between two or more benzene rings. Several examples of molecules containing fused borazine rings have also been prepared, and molecular orbital calculations on systems of this type are reported as structures XXIV to XXXI in Tables II-XI to II-XV. The simplest examples of this type of B-N conjugated system are the boron-nitrogen analogues of biphenyl, with two borazine molecules joined by a B-N, a B-B, or an N-N bond (Structures XXIV, XXV, and XXVI of Figure II-4). The first two members of the series, to be denoted BN - biphenyl (B-N) and BN - biphenyl (B-B), have been prepared (77,78,79). Higher polymeric units of borazine rings joined by B-N bonds are also known (77). The mobile bond order of the B-N linkage joining the two borazine rings in BN - biphenyl (B-N) is smaller than those within the rings (Tables II-XI and II-XII), and the increase in pi bonding energy when the two borazine rings are joined in this manner is $0.35\beta^{o}$, which corresponds to a 6% gain in pi bond energy (Table II-XV). The B-B and N-N bond orders in BN - biphenyl (B-B) and BN - biphenyl (N-N) are very small, 0.12 in the Huckel approximation, and the gain in pi bond energy is only about 2% of that for two isolated borazine rings. Since the percentage increase in pi bond energy in biphenyl relative to two benzene ring is of about the same magnitude as in the boron-nitrogen rings, and since this increase in pi energy in the case of biphenyl is insufficient to overcome steric effects between the rings since the two benzene rings are not coplanar (66), the two borazine rings in the BN - biphenyl molecules are probably not coplanar.

Molecular orbital calculations are also reported in the tables for molecules in which two borazine rings are bonded together by means of an intermediate (exocyclic) nitrogen or boron atom (Structures XXVII and XVIII of Figure II-4). The pi bond energy increase for such systems relative to that of two isolated borazine rings is $0.83\beta^{o}$, which is greater than the corresponding increase ($0.35\beta^{o}$) when the two rings are joined without the intermediate atom. Some molecules are known in which the pi electron structure XXVII could be present. For example, Wagner and Bradford (77) have synthesized the compound illustrated as structure XXVIIa in Figure II-5. Higher polymers of this system, in which substituted borazine rings are joined together by intermediate oxygen atoms, are also known (77).

The boron-nitrogen analogue of naphthalene (structure XXIX of Figure II-IV) has also been prepared (78, 80). The resonance energy for BN - naphthalene, $2.48\beta^{o}$, is almost double that found for a single borazine ring (Table II-XV). The mobile bond orders for BN - naphthalene are not all identical, but the minor variations found within the ring parallel the corresponding trend of bond orders in naphthalene. In particular, the bond common to both rings is the weakest link in the molecule in both naphthalene (24) and its boron-nitrogen analogue (XXIX, Tables II-XI and II-XII).

Theoretically, it is possible to have a boron-nitrogen ring structure in which an N-B-N or B-N-B unit is joined to BN - naphthalene to create a symmetric, conjugated system containing three rings (structures XXX and XXXI of Figure II-4). The Huckel method pi bonding energy for both such structures is $7.13\beta^{o}$, which corresponds to an increase of $0.80\beta^{o}$ over the two component systems mentioned above (Table II-XV). Although molecules of this type have not as yet been prepared, the Huckel calculations on these networks and on BN - naphthalene show that there is a substantial increase in conjugation energy associated with joining small boron-nitrogen pi electron networks together to give polymers in which a large number of six-membered rings are present. The upper limit to such conjugation is found in the well-known "graphite" form of boron nitride (53).

IONIZATION POTENTIALS

According to Koopman's theorem, the ionization potential of a molecule is approximately given by the energy of the highest occupied molecular orbital (1). If it is assumed that the highest occupied molecular orbital in the B-X systems is an orbital of pi character, then the double-occupied energy level of least bonding character calculated by the Huckel, omega, and Pople schemes given an indication of the ionization potential expected for each B-X system. The energies of the highest occupied orbital in the B-N chains and rings illustrated in Figures II-3 and II-4 are given in Table II-XVI. The energy levels are reported relative to the Coulomb integrals for a doubly-occupied, non-bonded nitrogen p_{π} orbital (except for the Pople results).

In all the pi networks in which there are more nitrogen atoms than boron atoms, the highest occupied molecular orbital is non-bonding according to the Huckel method, with an energy equal to the Coulomb integral of nitrogen. All the Huckel method ionization potentials for such systems are reported as zero in Table II-XVI, and the corresponding ionization potentials for these networks predicted by the omega and Pople methods are approximately $0.2\beta^{o}$ to $0.4\beta^{o}$, and 11.7 - 12.4 e.v. respectively. The predicted ionization potentials of systems with an equal number of boron and nitrogen atoms, or with an excess of boron atoms, are all equal to, or larger than, the values above. In general, there is reasonably good agreement between the trend of ionization potentials predicted by the three molecular orbital methods.

The ionization potential of the unsubstituted borazine molecule has been found experimentally to be 10.3 ± 0.2 e.v. (81). This value is about 3.1 e.v. less than that predicted by the Pople method.

TABLE II-XVI: Energy of Highest Occupied Pi Molecular Orbital in B-N Chains and Rings

Molecule Number	Energy[a] of the Highest Occupied Molecular Orbital		
	Huckel Method (in β^o)	Omega Technique (in β^o)	Pople Method (in e.v.)
I	0.281	0.531	13.37
II	0.000	0.232	12.00
III	0.519	0.894	
IV	0.000	0.199	11.76
V	0.730	1.184	
VI	0.114	0.381	12.73 (b)
VII	-0.512	-0.254	
VIII	0.218	0.515	
IX	0.000	0.253	
X	0.281	0.660	
XI	0.000	0.282	
XII	0.000	0.204	
XIII	0.060	0.349	
XIV	0.000	0.303	
XV	0.171	0.550	
XVI	0.037	0.340	
XVII	-0.619	-0.369	
XVIII	0.000	0.345	12.35

TABLE II-XVI continued

Molecule	Energy[a] of the Highest Occupied Molecular Orbital		
Number	Huckel Method (in β^o)	Omega Technique (in β^o)	Pople Method (in e.v.)
XIX	0.281	0.635	13.43
XX	0.000	0.389	
XXI	0.000	0.235	11.65
XXII	0.000	0.234	11.73
XXIII	0.000	0.234	
XXIV	0.146	0.531	
XXV	0.235	0.607	
XXVI	-0.358	-0.014	
XXVII	0.000	0.368	
XXVIII	0.281	0.639	
XXIX	0.114	0.479	
XXX	0.000	0.376	
XXXI	0.281	0.655	

Notes:

a) Huckel and omega method ionization potentials are reported relative to the Coulomb integral of "neutral" nitrogen, $\alpha^o + 1.5\ \beta^o$. Positive ionization potentials listed represent orbitals more stable than this value.

b) cis isomer

CONCLUSIONS

The molecular orbital calculations for boron-nitrogen chains and rings discussed above, together with the experimental properties cited for these systems, have indicated that many of the known characteristics of organic molecules with carbon-carbon double bonds are present in conjugated B-X systems. In some instances, these characteristics are displayed to a lesser extent in the inorganic systems as compared to the organic. For example, the alternation of bond lengths in even-membered B-X chains of alternating B and X atoms should be less pronounced than in the corresponding carbon-carbon chains. In addition, the greater pi energy stability of conjugated monocyclic ring systems with $4n + 2$ pi electrons relative to those with $4n$ electrons is much less evident in rings with alternating B and N atoms than it is with carbon-carbon rings.

On the other hand, there are some characteristics which are more pronounced in the B-N networks than in the organic molecules. The _relative_ increase in pi bonding energy for systems of B-N units connected by boron-nitrogen bonds is greater than the corresponding increase in the carbon-carbon systems. Secondly, the pi bonding in ring systems with extra nitrogen atoms bonded to each boron is mainly _exocyclic_ in nature, in contrast to that in aromatic hydrocarbon systems in which exocyclic, highly electronegative atoms do not substantially contribute to the pi bonding.

Finally, the molecular orbital calculations have established that the pi bonding between the atoms in a B-B or N-N linkage is very slight, and will probably not be sufficient to induce restricted rotation about these bonds.

The trends in the molecular orbital parameters (bond order, charge density, ionization potential) calculated for the boron-nitrogen conjugated systems by the three different molecular orbital methods are all quite similar, and for this reason the three techniques appear to be equally applicable to the types of networks considered.

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APPENDIX II: COMPUTER PROGRAMME FOR HUCKEL AND OMEGA METHODS MOLECULAR ORBITAL CALCULATIONS

The Fortran IV language computer programme used to execute the Huckel method and omega technique molecular orbital calculations on the boron-nitrogen systems is composed of five parts--one main programme and four subroutines. The "SOURCE LISTING" of the main programme "HUCKEL-OMEGA" is illustrated in Figure II-7.

The input data required for the molecular orbital calculations is read in by statements ISN 2-17 of the main programme. For each molecule, one "header" card is required on which is punched the case number (NCASE), the number of pi orbitals (N), the number of pi electrons (NE), and the value of the variable KK. If KK is zero, only Huckel method results are calculated, whereas if KK $>$ 0, both Huckel and omega calculations will be performed. For each pi atomic orbital to be considered, an additional card of data (ISN 12) is required, which lists the atomic number (IZ) of the atom involved, the pi core charge of the orbital (G (I,I)) and the values to be given to the off-diagonal Hamiltonian matrix elements G (I,J)

$$G\ (I,J) \ = \ k_{ij} \qquad\qquad (I \neq J)$$

At this point in the programme, the subroutine COULMB is called (ISN 20), the listing for which is given in Figure II-8. The subroutine COULMB assigns Coulomb integral parameters HU(I), corresponding to h_u of the molecular orbital equations, to each orbital based upon its core charge and the atomic number of the corresponding atom.

The next step in the main programme is to assign initial charge densities in the QA(I) and P(I,I) matrices (ISN 21-22). P is used to store

Figure II-7:

FORTRAN IV SOURCE LISTING FOR THE

"HUCKEL-OMEGA" MAIN COMPUTER PROGRAMME

```
 ISN        SOURCE STATEMENT

   0 $IBFTC MAIN
     C         BAIRD-WHITEHEAD OMEGA TECHNIQUE    APRIL/66
     C         PROGRAMMED BY N.C.BAIRD      FORTRAN IV
     C         COULMB,SORT2,COULSN,(EVALUE) SUBROUTINES REQUIRED
     C         G(I,I) IS THE CORE CHARGE FOR I)G(I,J) IS THE BETA FOR THE
     C         PAIR I,J.NE IS THE NUMBER OF PI ELECTRONS.
     C         IF KK IS ZERO,ONLY HUCKEL RESULTS PRINTED OUT.
     C         Z IS THE ATOMIC NUMBER.N IS THE TOTAL NO. OF ATOMIC ORBITA
   1           DIMENSION H(50,50),C(50,50),P(50,50),G(50,50),IZ(50),HU(50
              1 ,QA(50)
   2         1 READ(5,2)NCASE,N,NE,KK
   7         2 FORMAT(4I3)
  10           DO 3 I=1,N
  11           READ(5,4)IZ(I),(G(I,J),J=I,N)
  16         4 FORMAT(I4,19F4.2/20F4.2)
  17           CALL COULMB(IZ,G,I,HU)
  20           QA(I)=G(I,I)
  21         3 P(I,I)=G(I,I)
  23           NIT=0
     C         CALCULATION OF HAMILTONIAN
  24         5 NIT=NIT+1
  25           DO 6 I=1,N
  26           IF(IZ(I).GT.10)GOTO7
  31           H(I,I)=HU(I)+(G(I,I)-P(I,I))*(0.45*HU(I)+1.30)
  32           GOTO6
  33         7 H(I,I)=HU(I)+(G(I,I)-P(I,I))*(0.42*HU(I)+0.86)
  34         6 CONTINUE
  36           NN=N-1
  37           DO 8 I=1,NN
  40           II=I+1
  41           DO 9 J=II,N
  42           H(I,J)=G(I,J)
  43         9 H(J,I)=G(I,J)
  45         8 CONTINUE
  47           CALL EVALUE(H,50,50,C,50,50,N,0.0001,1)
  50           CALL SORT2(H,C,N)
  51           CALL COULSN(C,P,N,NE)
  52           DO 10 I=1,N
  53           IF(ABS(P(I,I)-QA(I)).GT.0.0001)GOTO11
  56        10 CONTINUE
  60           IF(NIT.EQ.1)GOTO17
  63           GOTO12
  64        11 IF(NIT.GT.20)GOTO16
  67           JJ=2*(NIT/2)
  70           IF(JJ.EQ.NIT)GOTO13
  73           DO 14 I=1,N
  74        14 QA(I)=P(I,I)
  76           IF(NIT.EQ.1)GOTO17
 101           GOTO5
 102        13 DO 15 I=1,N
 103           P(I,I)=0.5*(P(I,I)+QA(I))
 104        15 QA(I)=P(I,I)
 106           GOTO5
 107        17 WRITE(6,18)NCASE,N,NE
 110        18 FORMAT(1H1,12HRESULTS CASE,I8,30X,2I8)
```

```
ISN        SOURCE STATEMENT

111           WRITE(6,19)
112        19 FORMAT(1H0,12HINPUT MATRIX)
113           DO 20 I=1,N
114        20 WRITE(6,21)IZ(I),(G(I,J),J=I,N)
122        21 FORMAT(1H ,I6,15X,25F4.1/1H ,25F4.1)
123           WRITE(6,22)NCASE
124        22 FORMAT(1H0,19HHUCKEL RESULTS CASE,I8)
125           GOTO23
126        16 WRITE(6,24)
127        24 FORMAT(1H0,14HNO CONVERGENCE)
130           GOTO1
131        12 WRITE(6,25)NCASE
132        25 FORMAT(1H0,18HOMEGA RESULTS CASE,I8)
133        23 DO 26 I=1,N
134        26 WRITE(6,32)H(I,I)
136        32 FORMAT(1H ,F10.4)
137           DO 27 I=1,N
140        27 WRITE(6,28)(C(I,J),J=1,N)
146           WRITE(6,29)NCASE
147        29 FORMAT(1H1,13HP MATRIX CASE,I8)
150           DO 30 I=1,N
151        30 WRITE(6,28)(P(I,J),J=1,N)
157        28 FORMAT(1H0,15F8.4/1H ,15F8.4)
160           IF(NIT.EQ.1.AND.KK.GT.0)GOTO5
163           GOTO1
164           END
```

Figure II-8:

FORTRAN IV SOURCE LISTING FOR

THE "COULMB" SUBROUTINE

```
      ISN          SOURCE STATEMENT

        0 $IBFTC COULMB
        1          SUBROUTINE COULMB(IZ,G,I,HU)
        2          DIMENSION IZ(50),G(50,50),HU(50)
           C       THIS SUBROUTINE ASSIGNS THE HUCKEL HU TO ATOM
        3          IF(IZ(I).EQ.5)HU(I)=-1.1
        6          IF(IZ(I).EQ.6)HU(I)=0.0
       11          IF(IZ(I).EQ.9)HU(I)=3.0
       14          IF(IZ(I).EQ.13)HU(I)=-0.9
       17          IF(IZ(I).EQ.14)HU(I)=0.0
       22          IF(IZ(I).EQ.17)HU(I)=1.8
       25          IF(ABS(G(I,I)-2.0).LT.0.01)GOTO1
       30          IF(IZ(I).EQ.7)HU(I)=0.6
       33          IF(IZ(I).EQ.8)HU(I)=1.0
       36          IF(IZ(I).EQ.15)HU(I)=0.2
       41          IF(IZ(I).EQ.16)HU(I)=0.4
       44          RETURN
       45        1 IF(IZ(I).EQ.7)HU(I)=1.5
       50          IF(IZ(I).EQ.8)HU(I)=2.1
       53          IF(IZ(I).EQ.15)HU(I)=1.1
       56          IF(IZ(I).EQ.16)HU(I)=1.3
       61          RETURN
       62          END
```

the bond order-charge density matrix, whereas the charge densities of the previous iteration are stored in the QA matrix. The variable NIT (ISN 24, 25) keeps track of the iteration number.

The Hamiltonian matrix H elements are calculated next by means of ISN 25-44. The diagonal elements are defined by the formulae in equations 68 and 69 of Part II. 1. Note that when NIT = 1, all G (I,I) = P (I,I), so that the Hamiltonian matrix elements are those of the Huckel method.

The second subroutine, EVALUE, which solves the secular equations for the eigenvalues H(I,I) and the eigenvectors C, is called at this point. This subroutine is of a very general nature, and is available as a library subroutine at the McGill University Computer Centre.

After the eigenvalues and eigenvectors have been calculated, the subroutine SORT2 is called (ISN 51) which sorts the eigenvalues and the corresponding eigenvectors into the order of decreasing energetic stability. The listing of the SORT2 subroutine is given in Figure II-9.

In order to calculate the total Huckel pi energy of the system being considered, a variable EPI is defined, and the one-electron energies of the doubly-occupied molecular orbitals are summed together to give EPI (ISN 52-56).

The bond order-charge density matrix P is calculated according to the formula given in equation 25 of Part II. 1 by means of the subroutine COULSN (ISN 57). This subroutine, devised by J. M. Sichel (43), is illustrated in Figure II-10.

The calculated orbital electronic charge densities, P (I,I), are checked against those of the previous iteration, QA(I) in order to establish whether a self-consistent field has been achieved (ISN 60-64). If a self-consistent field has not been obtained, the operation of the programme is

Figure II-9:

FORTRAN IV SOURCE LISTING FOR

THE "SORT2" SUBROUTINE

```
         ISN        SOURCE STATEMENT

           0 $IBFTC SORT2
           1          SUBROUTINE SORT2(E,C,N)
             C        PLACES EIGENVALUES AND EIGENVECTORS IN ORDER OF
           2          DIMENSION E(50,50)    ,C(50,50)
           3          DO 56 I=2,N
           4          JA=I-1
           5          DO 56 J=1,JA
           6          IF(E(I,I).LE.E(J,J))GO TO 56
          11          ET=E(I,I)
          12          E(I,I)=E(J,J)
          13          E(J,J)=ET
          14          DO 57 K=1,N
          15          CT=C(K,I)
          16          C(K,I)=C(K,J)
          17       57 C(K,J)=CT
          21       56 CONTINUE
          24          RETURN
          25          END
```

Figure II-10:

FORTRAN IV SOURCE LISTING FOR

THE "COULSN" SUBROUTINE

```
      ISN        SOURCE STATEMENT

        0 $IBFTC COULSN
        1          SUBROUTINE COULSN(C,P,N,NE)
           C       COMPUTE COULSON CHARGE DENSITY-BOND ORDER MATRIX
           C       ONLY UPPER HALF AND DIAGONAL NEEDED
        2          DIMENSION  C(50,50),P(50,50)
        3          NOC=NE/2
        4          DO 60 L=1,N
        5          DO 60 K=1,L
        6          P(K,L)=0.
        7          DO 61 I=1,NOC
       10       61 P(K,L)=P(K,L)+C(K,I)*C(L,I)
       12          P(K,L)=2.*P(K,L)
       13       60 P(L,K)=P(K,L)
       16          RETURN
       17          END
```

returned to ISN 25 and the calculations repeated. In order to achieve a self-consistent field with a minimum number of iterations, the charge densities P (I,I) (to be used in the calculation of the Hamiltonian matrix elements) are averaged over P (I,I) and QA (I) when the parameter NIT is even (ISN 76, 110-114). If NIT is odd, no averaging is used (ISN 76-104). In both cases, the matrix elements P (I,I) are stored as QA (I) so that the charge density distribution of the next iteration may be checked for self-consistency. If a self-consistent field of charges has been attained (i.e. each element of the matrices P (I,I) and QA (I) do not differ by more than ±0.0001 electron), or if the value of NIT is 1, the molecular orbital calculation results are printed out by means of the statement numbers ISN 115 to 165. A typical print-out from this programme is given in Figure II-11 for the $(BN)_3$ system. On the first page, the input matrices IZ (I) and G (I, J) are given, along with the Huckel method energy levels, total pi energy, and the Huckel method coefficient matrix C. On the second page of results, the Huckel method bond order matrix, P, is printed out, together with the omega technique energy levels and coefficient matrix C. On the final page of print-out for each molecule, the P matrix calculated by the omega technique is given.

The print-out section of the main programme is designed such that if NIT = 1, the Huckel method results are printed out, and then the operation of the program returns to ISN 25 to continue the calculations if the parameter KK is not equal to zero (ISN 166). After the omega technique parameters have been printed out, the next molecule is considered by returning the operation of the programme to ISN 2 (ISN 171).

Figure II-11:

COMPUTER PRINT-OUT FROM THE "HUCKEL-OMEGA" PROGRAMME

FOR THE $(BN)_3$ Pi ELECTRON SYSTEM

```
RESULTS CASE        6                                               6

INPUT MATRIX
      5                 0.0 0.9 0.0 0.0 0.0 0.9
      7                 2.0 0.9 0.0 0.0 0.0
      5                 0.0 0.9 0.0 0.0
      7                 2.0 0.9 0.0
      5                 0.0 0.9
      7                 2.0

HUCKEL RESULTS CASE      6E PI=  11.96527
    2.4204
    1.7811
    1.7811
   -1.3811
   -1.3811
   -2.0204

  0.2628 -0.2111  0.1213 -0.3885 -0.6756  0.5141

  0.5141 -0.6741 -0.3911  0.2435  0.0004 -0.2628

  0.2628  0.0005 -0.2435 -0.3908  0.6743  0.5141

  0.5141  0.6757 -0.3883 -0.1214 -0.2110 -0.2628

  0.2628  0.2106  0.1222  0.7794  0.0013  0.5141

  0.5141 -0.0016  0.7794 -0.1221  0.2106 -0.2628
```

```
P MATRIX CASE        6

   0.2567  0.4600  0.0789 -0.1092  0.0789  0.4600

   0.4600  1.7433  0.4600 -0.0789 -0.1092 -0.0789

   0.0789  0.4600  0.2567  0.4600  0.0789 -0.1092

  -0.1092 -0.0789  0.4600  1.7433  0.4600 -0.0789

   0.0789 -0.1092  0.0789  0.4600  0.2567  0.4600

   0.4600 -0.0789 -0.1092 -0.0789  0.4600  1.7433

OMEGA RESULTS CASE      6E PI=   13.96514
     2.7121
     2.1352
     2.1352
    -1.5002
    -1.5002
    -2.0771

   0.2382  0.1043 -0.1812 -0.3941 -0.6838  0.5259

   0.5259 -0.3954 -0.6831  0.2091  0.0002 -0.2382

   0.2382 -0.2091  0.0002 -0.3951  0.6832  0.5259

   0.5259 -0.3938  0.6840 -0.1044 -0.1812 -0.2382

   0.2382  0.1048  0.1810  0.7893  0.0006  0.5259

   0.5259  0.7893 -0.0009 -0.1047  0.1810 -0.2382
```

```
P MATRIX CASE        6

  0.2010   0.4156   0.0698 -0.0795  0.0698   0.4156

  0.4156   1.7990   0.4156 -0.0698 -0.0795 -0.0698

  0.0698   0.4156   0.2009  0.4156  0.0698 -0.0795

 -0.0795  -0.0698   0.4156  1.7990  0.4156 -0.0698

  0.0698  -0.0795   0.0698  0.4156  0.2009  0.4156

  0.4156  -0.0698  -0.0795 -0.0698  0.4156  1.7990
```

A list of the symbols used in this programme is given in Table II-XVII.

In all, molecular orbital calculations for thirty-one B-N conjugated networks were executed by this programme. A listing of the computer output and the input data sheets for these systems is available (82).

TABLE II-XVII: Symbols Used in the "Huckel-Omega" Computer Programme and Associated Subroutines

Symbol	Definition
H(I, J)	Hamiltonian Matrix Elements (F_{II}, F_{IJ})
C(I, J)	Molecular Orbital Coefficient Matrix Elements
P(I, J)	Bond Order and Charge Density Matrix P_{IJ}
G(I, I)	G(I, I) are the "core charges" for orbital I.
G(I, J)	G(I, J) when $I \neq J$ are the "resonance integrals" parameters k_{IJ}
IZ (I)	Atomic Number of Atom with AO I.
HU (I)	Huckel Method h_u value, for orbital I.
QA (I)	Electron Densities for AO I from previous iteration.
KK	Control Parameter (see text)
N	Total number of pi atomic orbitals.
NE	" " " " " electrons.
NCASE	Case number of molecule considered.
NOC	Total Number of doubly-occupied molecular orbitals.
NIT	Iteration number.
EPI	Pi energy for system.
ET	Temporary storage parameter
CT	" " "

CLAIMS TO ORIGINAL RESEARCH

PART I

1. The relationship between the electronegativity equalization method for calculating electron density distributions in molecules and the method of molecular orbitals was derived and discussed. The formulae relating the ionic character and ionic resonance energy of a two-centre bond to the difference in electronegativity between the centres were found to be similar in form, whether the formulae were derived from electronegativity equalization considerations, from LCAO molecular orbital theory, or from empirical correlations.
2. A "molecular orbital" bond electronegativity function was proposed. Methods by which bond electronegativity functions could be extended to include interatomic terms were outlined. General formulae for the equilibrated electronegativity, orbital charge density, and extra ionic resonance energy were derived for electronegativity equalization methods in which the electronegativity was assumed to be linearly dependent on electron density.
3. Hinze, Whitehead and Jaffe's method for calculating group electronegativities was simplified and extended so that the electron density distributions in saturated molecules could be calculated in a simple manner. The parameters of the bond electronegativity function, which were required for such self-consistent field electronegativity equalization calculations, were evaluated for a number of atoms.
4. The ionic characters for several diatomic molecules, and for a number of "isolated" bonds, were calculated by electronegativity equalization, and the results compared to bond polarities obtained by other theoretical methods.

5. Self-consistent field electron densities were calculated by the bond electronegativity equalization method for some saturated hydrocarbons and saturated alkane derivatives of nitrogen and oxygen.

6. The B.E.E. method electron densities were discussed with reference to the relative inductive effects of alkyl groups and hydrogen atoms, the variation in group electronegativity with molecular environment, the transmission of electronic effects through carbon-carbon bonds, the inductive stabilization of hydrocarbon ions, and the inductive effects induced in an alkane by nitrogen and oxygen atom substitution. Correlations were established between the hydrogen and carbon atom charge densities and the ^{1}H and ^{13}C N.M.R. chemical shifts in some alkanes and saturated alcohols.

PART II

1. Two approximate methods, both based on Pople's procedure, for the calculation of the molecular orbitals in pi-electron networks were proposed.
2. The "Coulomb integrals" in the approximate methods were shown to be related to the Coulomb integrals for the simple Huckel method and the "omega technique," and to the "molecular orbital" bond electronegativity function proposed in Part I.
3. Coulomb integral parameters for the p_{π} atomic orbitals of several atoms were calculated.
4. The extent to which the omega technique improves the Coulomb integrals of the Huckel method toward the values calculated by Pople's method was analyzed by considering molecular orbital calculations for a typical pi electron network.
5. Net orbital charges, bonding energies, ionization potentials, and bond orders between bonded atoms were calculated for the ground states of 31 boron-nitrogen pi electron networks by the simple Huckel and omega technique methods, and were calculated for 8 B-N pi networks by Pople's method.
6. The molecular orbital results for the boron-nitrogen systems were discussed with reference to the structure, stability, occurrence, and spectra of molecules in which boron-nitrogen, boron-oxygen, boron-sulphur or boron-halogen pi networks could be present.

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Ionic Character

By

N. C. Baird and M. A. Whitehead

The concept of ionic character in σ and π bond systems is considered in the light of recent definitions of orbital electronegativity [*6*, *14*].

Le caractère ionique des liaisons σ et π est discuté en tenant compte des définitions récentes de l'électronégativité des orbitales.

Das Konzept des ionischen Charakters in σ und π Bindungen wird im Lichte neuerer Definitionen von Orbitalelektronegativitäten diskutiert.

Hinze, Whitehead and Jaffe [*6*] used the Principle of the Equalization of Orbital Electronegativities [*1*, *6*, *7*, *12*] for two atomic orbitals forming a covalent σ bond to define the ionic character of the bond as

$$i = \left| \frac{\chi_A^0 - \chi_B^0}{2\,(c_A + c_B)} \right| \tag{1}$$

in which χ^0 represents the atomic orbital electronegativity of the atom prior to bonding. c_A and c_B are constants.

The orbital electronegativities are expressed as a linear function of the number of electrons n in an orbital. Thus for the bonding atomic orbital of atom A:

$$\chi_A^0 = b_A + 2 c_A n_A \tag{2}$$

and likewise for atom B.

This applies to the formation of a covalent σ bond, a co-ordinate covalent σ bond and a π bond [*5*]. The energy of an orbital j, occupied by n_j electrons is given by [*5*, *6*, *7*].

$$E\,(n_j) = a + b n_j + c n_j^2 . \tag{3}$$

The orbital electronegativity defined by:

$$\chi_j^0 = \frac{\partial E}{\partial n_j} = b + 2\,c n_j \tag{4}$$

is a property of the atom before bond formation, and hence can only have $n_j = 0$, 1 or 2. The combination of $n_j^A = 0$ and $n_j^B = 2$ defines a co-ordinate σ bond, and $n_j^A = 1$ with $n_j^B = 1$ a normal covalent σ bond. In the case of π bonded systems both n_j^A and n_j^B can be 0, 1 or 2 independently.

The two electrons in the bond, formed by the overlap of two atomic orbitals, must be in equilibrium and each electron sees the same potential, χ, on atoms A and B. Thus the equilibrium occupation numbers n_A^* and n_B^* [*2*, *6*, *9*] are defined from

$$\chi^*(n_A^*) = \chi^*(n_B^*) \,. \tag{5}$$

The sum of n_A^* and n_B^* is 2 for a σ bond (covalent or co-ordinate) but may be 1, 2, 3 or 4 for a π bond.

Thus a plot of $\chi_A(n_A)$ against n_A and similarly for n_B gives Fig. 1, where the intersection of the two lines gives the equilibrium values n_A^* and n_B^*.

The case where n_A varies from 0 to 2 as n_B goes from 2 to 0 is the normal σ covalent or co-ordinate bond [6]. The dotted lines for n_A equal to 3 or 4 are of course hypothetical since the Pauli Principle would be violated, and in all actual cases the lines are found to cross where neither n_A nor n_B actually exceeds 2.

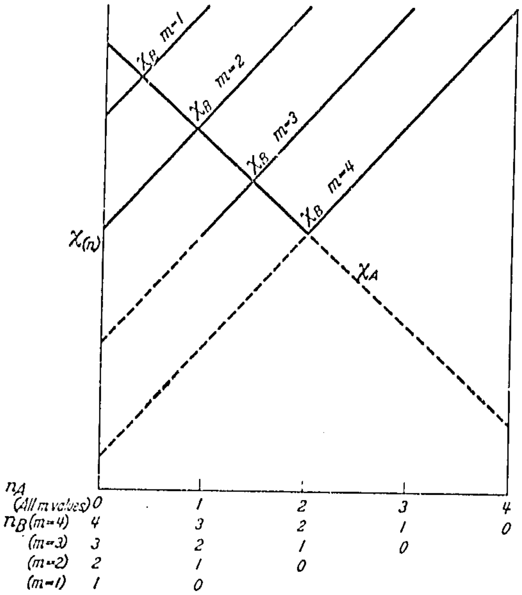

Fig. 1. The electronegativities of atoms A and B in an AB bond as a function of n_A and n_B. The lines are designated by m where $m = n_A + n_B$. The significance of the parameters is discussed in the text

Since ionic character is the amount by which transfer of charge must occur to equalize the orbital electronegativities,

$$i = | n_A^* - n_A | = | n_B^* - n_B | \tag{6}$$

which is the ionic character for a σ or π bond depending on the values of the n^* and n. Since the electronegativities are equal [equ. (5)], then

$$b_A + 2c_A n_A = b_B + 2c_B n_B \tag{7}$$

and n_A and n_B are related by

$$n_A + n_B = m \tag{8}$$

where m can have all possible values of one through four. In a π bond system with $n_A = n_B = 0$ there is of course no bond; with $n_A = n_B = 2$ the σ bond electronegativity changes result in equalization of the p electronegativities such that the two p orbitals retain two electrons each; but for all other combinations of n_A and n_B, π ionic bond character occurs. Combining equations 7 and 8

$$b_A + 2c_A n_A = b_B + 2c_B (m - n_A)$$

from which the occupation number for orbital A may be found to be

$$n_A = \frac{b_B - b_A + 2c_B m}{2(c_A + c_B)} \,. \tag{9}$$

The ionic character is given by $| n_A^* - n_A |$. Substituting for n_A,

$$i = \left| \frac{(b_A + 2c_A n_A^*) - (b_B + 2c_B [m - n_A^*])}{2(c_A + c_B)} \right| . \tag{10}$$

The equilibrium values for n_A^* can vary from 0 to 2 and m from 1 to 4. In all possible combinations of n_A^* and m this equation reduces to

$$i = \left| \frac{\chi_A^0 - \chi_B^0}{2(c_A + c_B)} \right| \tag{11}$$

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ionic characters calculated with the correct values of $|c_A + c_B|$ are therefore substantially lower than those using $i_\sigma = 1/2\,|\chi_A - \chi_B|$ which is the equation resulting from equation (1) with $|c_A + c_B| = 1$, and identical with that due to GORDY [3]. A comparison between the values of i_σ calculated from equation (1) with c_A and c_B from Tab. 1, and other assessments of i_σ for diatomic molecules is shown in Tab. 3. The values of χ used by PAULING [9] and HANNAY and SMYTH [4] are naturally PAULING's original *atomic* electronegativities and not the orbital electronegativities used in this paper. The results obtained by the above theory (Tab. 3) are in marked disagreement with those calculated with the same, or

Table 1

b and c values for the valence state orbitals of the monovalent atoms in σ bond formation

The orbital being considered has no superscript designation of its occupation since occupation numbers of 0, 1 and 2 are used to calculate I_v and E_v (see reference [5]).

Atom	Valence state	Ionization Potential I_v (e.v.)	Electron Affinity E_v (e.v.)	b* (e.v.)	c* (e.v.)
H	s	13.60	0.75	20.02	−6.42
Li	s	5.39	0.82	7.67	−2.28
Na	s	5.14	0.47	7.47	−2.33
F	$s^2\,p^2\,p^2\,p$	20.86	3.50	29.54	−8.68
Cl	$s^2\,p^2\,p^2\,p$	15.08	3.73	20.75	−5.67
Br	$s^2\,p^2\,p^2\,p$	13.10	3.70	17.80	−4.70
I	$s^2\,p^2\,p^2\,p$	12.67	3.52	17.25	−4.57

* Mulliken Scale

Table 2

b and c values for the valence state orbitals of selected atoms forming π bonds

The orbital being considered has no superscript designation of its occupation since occupation numbers of 0, 1 and 2 are used to calculate I_v and E_v (see reference [5]). *di* is a *sp* hybridized orbital and *tr* a sp^2 hybrid orbital while π designates the *p* orbital used in π bonding independent of its occupation number. In Be and B the π orbital is empty, in C and $N^{(1)}$ singly occupied and in $N^{(2)}$, F and Cl doubly occupied in the atom.

Atom	Valence state	Ionization Potential I_v (e.v.)	Electron Affinity E_v (e.v.)	b* (e.v.)	c* (e.v.)
Be^-	$di^1di^1\pi$	+0.16	−0.9~~0~~5	+.71 ~~−0.25~~	−0.5~~8~~6
B^-	$tr^1tr^1tr^1\pi$	+1.06	−5.32	+4.25 ~~−1.07~~	−3.19
C	$di^1di^1\pi^1\pi$	+11.19	+0.10	+16.73	−5.54
C	$tr^1tr^1tr^1\pi$	+11.16	+0.03	+16.72	−5.56
$N^{(1)}$	$tr^2tr^1tr^1\pi$	+14.12	+1.78	+20.29	−6.17
$N^{+(2)}$	$tr^1tr^1tr^1\pi$	+28.71	+11.95	+37.09	−8.38
F^+	$s^2p^2p^1\pi$	+39.67	+18.11	+50.45	−10.78
Cl^+	$s^2p^2p^1\pi$	+26.36	+13.38	+32.86	−6.49

* Mulliken Scale

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Molecule

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HCl
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HI
FCl
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factor necessary to correct for the fact that the value of $1/[2\,|c_A + c_B|]$ is not a constant, and that the χ^0_{hybrids} used in equation (11) differ from compound to compound, neither of which is taken into account explicitly in equation (16). Thus the method of Hannay and Smyth is almost equivalent to ours for the diatomic molecules considered.

The present approach has the advantage that changes in the electronegativity of the bonding orbital of an atom in different molecules (such as carbon in ethane, ethylene and acetylene) can be accounted for, since χ, b and c can all be calculated for any normal valence states (*s*, *p*, *di*, *tr* and *te*) for the atoms under consideration, and for all intermediate hybridizations, readily estimated [*6*]. Whereas the Pauling χ are only valid for atoms whose bonding orbitals are of exactly the same hybridized character as in the molecules from whose dissociation energy the χ were derived.

The second advantage is that equation (11) is applicable to polyatomic and π-bonded systems. Hinze et al. [*6*] demonstrated that the effects of the groups A, B and C upon the electronegativity of the bonding orbital of atom R in ABCR-can be taken into account and equation (13) applied. The technique of handling polyatomic molecules has been generalized and simplified and the results for these together with π bonded systems will be given in the next paper. In general, it is concluded that the factor $|c_A + c_B|$ varies from molecule to molecule, substantiating previous qualitative arguments [*1*, *6*, *8*] that there can be no unique curve relating ionic character to electronegativity difference.

We wish to acknowledge financial support from the National Research Council of Canada. One of us (N.C.B.) thanks the council for the award of a studentship.

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Group Orbital Electronegativities

By

M. A. Whitehead, N. C. Baird and M. Kaplansky

The Self-consistent Group Orbital and Bond Electronegativity (SGOBE) method [4] for calculating the orbital charge distributions in polyatomic molecules is reviewed, and a simplification described. The charge distributions for several polyatomic molecules are calculated. The chemical significance of the results is discussed.

Es wird ein Überblick über die SGOBE-Methode zur Berechnung von Ladungsverteilungen in Molekülen gegeben und eine Vereinfachung dazu beschrieben. Die Ladungsverteilung einiger mehratomiger Moleküle wird berechnet und die chemische Bedeutung diskutiert.

La méthode auto-cohérente des orbitaux de groupe et électronégativités des liaisons (SGOBE) pour calculer la distribution de charge orbitale des atomes dans les molécules polyatomiques est résumée, et une simplification de la méthode SGOBE est décrite. Les distributions de charge de plusieurs molécules polyatomiques sont calculées, et la signification des résultats est discutée.

Introduction

Attempts have been made to extend the Atomic Electronegativity Concept (AEC) to organic and inorganic radicals. Estimates have been made [8] of the Effective Atomic Electronegativity of radicals, $\chi_{\mathrm{eff}}^{\mathrm{At}}$, by means of empirical relationships between $\chi_{\mathrm{eff}}^{\mathrm{At}}$ and (I) infrared stretching frequencies, (II) thermochemical data, (III) chemical reactivity, (IV) nuclear magnetic resonance chemical shifts, and (V) nuclear quadrupole resonance frequencies.

In this paper a simplification of the SGOBE method [4] is described. The electron charge distributions of atomic orbitals in molecules, and the orbital effective electronegativity χ_{eff} of radicals present in polyatomic molecules, are calculated using the Electronegativity Equalization Principle [9].

Throughout this paper all electronegativities are *Orbital Electronegativities*; no such concept as Atomic Electronegativities is used.

Background

1. The orbital electronegativity of orbital j on atom A is given by χ_j^{A}. It is related to the charge of orbital j, n_j^{A} by [4]

$$\chi_j^{\mathrm{A}}(n_j^{\mathrm{A}}) = b_j^{\mathrm{A}} + 2\,c_j^{\mathrm{A}}\,n_j^{\mathrm{A}} \qquad (1)$$

where b_j^{A} and c_j^{A} are parameters dependent on the atom A, its valence state, and the electron configuration of all the other orbitals on atom A.

2. The effective occupation number, integral or non-integral, of an atomic orbital is designated "charge".

3. The parameters b_j^{A} and c_j^{A} can be calculated [1] from the ionization potential and electron affinity of orbital j, I_{vj}^{A} and E_{vj}^{A}, using

$$b_j^{\mathrm{A}} = \frac{1}{2}\,(3\,I_{vj}^{\mathrm{A}} - E_{vj}^{\mathrm{A}}) \tag{2}$$

and

$$c_j^{\mathrm{A}} = \frac{1}{2}\,(E_{vj}^{\mathrm{A}} - I_{vj}^{\mathrm{A}})\ . \tag{3}$$

4. The modified principle of orbital Electronegativity Equalization [4] states that since two electrons forming a chemical bond are in equilibrium, the potential at each electron from the atomic cores A and B must be equal. Eq. (1) defines this potential. If χ^{X} represents the equilibrium electronegativity of the orbital of atom X, the principle requires that

$$\chi_{\mathrm{equ}}^{\mathrm{A}} = \chi_{\mathrm{equ}}^{\mathrm{B}}\ . \tag{4}$$

The total charge of the molecular orbital is 2. If the orbitals forming the bond are j of A and k of B, and the asterisk denotes equilibrium values,

$$n_j^{\mathrm{A}*} + n_k^{\mathrm{B}*} = 2$$

whence the ionic character of the bond i_{jk}^{AB} is given by

$$i_{jk}^{\mathrm{AB}} = |\,n_j^{\mathrm{A}*} - 1\,| = \left|\frac{\Delta\chi_{jk}^{\mathrm{AB}}}{2\,(c_j^{\mathrm{A}} + c_k^{\mathrm{B}})}\right|\ . \tag{5}$$

$\Delta\,\chi_{jk}^{\mathrm{AB}}$ is the orbital electronegativity difference $|\,\chi_j^{\mathrm{A}} - \chi_k^{\mathrm{B}}\,|$ for the condition $n_j^{\mathrm{A}} = n_k^{\mathrm{B}} = 1$, that is the free atomic condition before bond formation. The principle is equivalent to minimizing the energy of the molecular orbital, expressed as a sum of the atomic orbital energies.

5. The use of eq. (5) is complicated when orbital j is on a polyvalent atom, the other orbitals of which may or may not be bonded. A tetravalent carbon atom in the tetrahedral valence state (te^4), has four bonding orbitals 1, 2, 3 and 4. The parameters b_1 and c_1 are calculated from eqs. (2) and (3) using values of I_{v1} and E_{v1} for the case

$$n_2 = n_3 = n_4 = 1\ . \tag{6}$$

Usually each of the bonds formed by orbitals 2, 3 and 4 will be polar, and eq. (6) will not hold. Thus before eq. (1) can be applied to calculations, the parameters b_1 and c_1 must be corrected for n_2, n_3 and n_4 differing from unity. This will be considered below.

Theory

The energy changes which occur when electrons are added to an orbital are effected by the character and charge of every other valency orbital of the atom, and if the energy of an orbital is expressed by [4]

$$E\,(n_j) = a_j + b_j\,n_j + c_j\,n_j^2 \tag{7}$$

then the parameters a_j, b_j and c_j are dependent on the nuclear charge Z, on the charge and hybridization characters of all the other orbitals of the atom, and on the hybridization character of j. The dependence of the parameters, and of I_{vj} and E_{vj}, upon the charge of each of the valence state orbitals is given in Tab. 1 for carbon in the tetrahedral state. (All energy data is from reference 3.) The values of I_{vj} and E_{vj} show that they depend mainly on the total charge, n_T, of the three

---

n_K	n_l
0	0
1	0
1	1
2	0
1	1
2	1
1	1
0	2
1	2
2	2

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The dotted curves in Figs. 1 and 2 show how well eqs. (8) and (9) reproduce the variation of E_{vj} and I_{vj} with n_T, especially in the area of interest. The parameters for several atoms in their valence states are listed in Tab. 2. Thus I_{vj}, E_{vj}, b_j and c_j can be calculated when n_k, n_l and n_m differ from unity, and hence the electronegativity of j. This value of χ_j is the effective orbital electronegativity of the radical, χ_j^{R}.

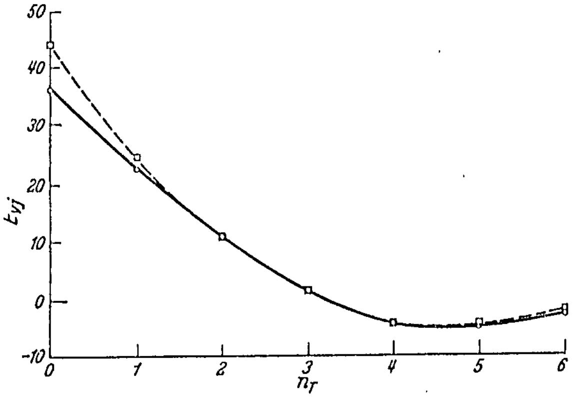

Fig. 2. E_{vj} represents the electron affinity of te_j, and $n_T = n_k + n_l + n_m$. The solid curve represents that given by the calculations of HINZE et al.; the dotted curve represents the results from eq. (8). The parameters of (8) δ, ε and ζ were evaluated from the HINZE data for $n_T = 2$, 3 and 4

This method is analogous to the SGOBE method [4], which required E (n_j) versus n_j curves to be plotted, extrapolation of these curves to the point of interest, estimation of E ($n_j + 1$), E (n_j) and E ($n_j - 1$) from the curves, and calculation of E_{vj}, I_{vj}, b_j and c_j from the energy terms. A tetravalent carbon atom requires the plotting of twenty separate curves to cover all possible cases [4]. The method developed above simplifies the calculations of the SGOBE method for finding b_j and c_j. The validity of the assumptions and approximations can be seen from the values of $\chi_{\mathrm{eff}}^{\mathrm{R}}$ calculated for the radicals CH_3, CH_2Cl, $CHCl_2$ and CCl_3 in the hydrides RH. Using a pure p bonding orbital on the chlorine atom, they differ from the SGOBE results by 0%, 0%, 0.7% and 1.3% respectively.

The total charge n_T can be the sum of the n from one or more orbitals; one can consider the dependence of I_{vj} and E_{vj} upon only some of the n_T, keeping the rest constant; thus $n_T = \sum_{i=1}^{1,2\text{ or }3} n_i$. Different values of the parameters

Table 2. *The parameters of the I_{vj} and E_{vj} equations*

Element	Valence State	α*	β*	γ*	δ*	ε*	ζ*
C	*te*	57.067	−17.240	1.029	39.020	−18.245	1.895
Si	*te*	32.822	− 6.779	−0.075	26.566	− 8.873	0.315
N	*te*	100.067	−28.174	1.972	64.500	−21.895	1.702
	sppp	48.229	−21.101	1.977	29.017	−19.921	2.902
O	*te*	120.724	−23.124	0.801	92.759	−23.248	1.184
	sppp	78.883	−26.033	1.833	48.034	−19.444	1.367
S	*te*	109.407	−26.980	1.640	45.930	− 7.440	−0.159
	sppp	49.893	−15.385	0.962	28.008	− 8.351	−0.064
B	*te*	34.841	−15.663	1.715	14.157	− 6.236	−0.039
C	*trtrtrπ*	56.622	−19.110	1.319	44.465	−20.880	2.169

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* The α, β and γ are parameters of the I_{vj} eq. (8) and the δ, ε and ζ belong to the eq. (9) for E_{vj}. In the case of the te valence states the parameters were calculated for te_j where $n_T = n_k + n_l + n_m$; in the *sppp* valence state the parameters are for p_j where $n_T = n_k^p + n_l^p$, and n_m^s assumed a lone pair s orbital; in *trtrtrπ* the parameters are for π_j and $n_T = n_k^{tr} + n_l^{tr} + n_m^{tr}$

α_j, β_j etc. will be obtained depend
n_T.

Eqs. (8) and (9) are subject to
must have the same hybridization
represents an s orbital, the value
from that for $n_k = 0$, $n_l = n_m = 1$
$n_k + n_l + n_m$, since to express I_{vj} (
find the value of I_{vj} (or E_{vj}) for n

$$I_{vj}^{(1)} \text{ for } n_k = n_l = 1$$

$$I_{vj}^{(2)} \text{ for } n_k = n_m =$$

which generate two different para
the p electron in orbital j different
for the *sppp* valence states of seve

Expressing E_{vj} and I_{vj} in the
Principle of Electronegativity E
charge distributions in molecules
be illustrated by an example such as CH_3NH_2, in which all the carbon and nitrogen bonding orbitals are tetrahedral, and the hydrogen orbitals are atomic 1s orbitals. The atomic orbital charges are denoted by n_A, n_B etc. as in Fig. 3. An iterative computer program is used to calculate the equilibrium charge distribution for which the bond electronegativities χ_{equ} of the two orbitals forming the bond are equal:

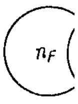

Fig. 3.

1. The charge n_A is chosen t
calculated from

2. The nitrogen orbital electr
tronegativity in the NH bond

The $\chi_{\mathrm{equ}}^{\mathrm{A}}$ for hydrogen is calculat
from a previous paper [1].

3. Substituting eqs. (8) and (9)
tion of $n_T^{(1)}$:

$$b_B = (1.5\,\alpha_B - 0.5\,\delta_B) + (1.5$$

$$c_B = 0.5\,(\delta_B - \alpha_B) + 0.5\,(n_T^{(1)})\,(\varepsilon_B - \beta_B) + 0.5\,(n_T^{(1)})^2\,(\zeta_B - \gamma_B) \qquad \text{(IV)}$$

where $n_T^{(1)} = n_B^{(1)} + n_C$.

Since n_B and $\chi_{\text{equ}}^{\text{B}}$ are known, $n_T^{(1)}$, can be calculated from III.

4. In a symmetrical molecule, such as the above, $n_{\text{B}}^{(1)} = n_B$ hence

$$n_{\text{C}} = n_T^{(1)} - n_{\text{B}} \,. \qquad \text{(V)}$$

The first bond of the molecule is now fully analysed on the basis of the initial choice of n_A. Consider next the CN bond.

5. I_{v_c} and E_{v_c} are evaluated in terms of the known $n_T^{(2)}$, defined by

$$n_T^{(2)} = 2\,n_B \qquad \text{(VI)}$$

and used to give b_C, c_C and $\chi_{\text{equ}}^{\text{C}}$.

6. The remaining steps are the same as sections (3) and (4) above, and yield $n_T^{(3)}$. Since

$$n_T^{(3)} = 3\,n_E$$

then n_E is found.

7. n_F is found from $n_E + n_F = 2$.

8. $\chi_{\text{equ}}^{\text{E}}$ is found by the procedure used to find $\chi_{\text{equ}}^{\text{C}}$.

9. $\chi_{\text{equ}}^{\text{F}}$ is evaluated with b_F and c_F from the published [*1*] values for hydrogen.

10. If $\chi_{\text{equ}}^{\text{E}} \neq \chi_{\text{equ}}^{\text{F}}$ the original choice of n_A is incorrect: a new value of n_A is chosen using the fact that if $\chi_{\text{equ}}^{\text{F}} > \chi_{\text{equ}}^{\text{E}}$, then the new value of n_A must be less than the starting choice of n_A, and vice versa.

11. When $|\chi_{\text{equ}}^{\text{E}} - \chi_{\text{equ}}^{\text{F}}| < 0.001$ the molecular charge distribution is self consistent, and the iterations cease. This programme was written in Fortran IV for the McGill IBM 7040 computer.

Results

The charge distributions of several organic molecules are given in Tab. 3—5.

In chlorine containing compounds, no *a priori* assumption of the hybridization present in the chlorine bonding orbital can be made. Combining the present method with nuclear quadrupole resonance theory and data [*12*] gives an estimate of the amount of *s*-*p* hybridization in the chlorine bonding orbital, since ϱ, the ratio of the nuclear quadrupole coupling constant of a chlorine atom in a molecule to that of a free chlorine atom, is related to

(I) the ionic character $i = |n_{Cl} - 1|$ of the C-Cl bond.

(II) the extent of *s* and *d* hybridization of the chlorine bonding orbital — *s* and *d* respectively

and (III) the extent of π electron transfer from the chlorine p_π orbitals to the carbon p_π orbitals.

The relation is

$$\varrho = (1 - s + d - i - \pi) + i\,(s + d) \qquad (10)$$

In the aliphatic chlorides both π and d are assumed [*12*] to be very small giving

$$\varrho = (1 - i)\,(1 - s) \qquad (11)$$

Since ϱ is known and i and s are related, this equation is soluble. The parameters of the electronegativity eq. (1) have been calculated for several hybridizations of the chlorine orbital [*1*], and the electron charge distributions of the alkyl halides and ionic character i of the C-Cl bond, were solved for each hybridization. A plot of i versus s is a straight line (Fig. 4, Curve [*1*]).

Table 3. *Charge di*

Compound
$HO^{A}—H$
$HS^{A}—H$
$H_2N^{A}—H$
$H_3\,Si^{A}—H$
$H_3\,C^{A}—H$
$H_3C—{}^{B}C^{A}—H_3$
$H_3\,CC_C—{}^{B}C^{A}—H_3$ H_2
$H_3—{}^{C}C—{}^{B}N^{A}—H$
$H_3—{}^{C}C—{}^{B}O^{A}—H$
$H_3—{}^{C}C—{}^{B}S^{A}—H$
$(CH_3)_3\,C—{}^{B}C^{A}—$
$HC{\equiv}C^{A}—H$
 $^{A}—H$

Table 4. *The* ^{13}C

Molecule
CCl_4
$CHCl_3$
CH_2Cl_2
CH_3Cl
CH_4
CH_3CH_3
$(\dot{C}H_3)_2CH_2$
$(CH_3)_2\dot{C}H_2$
$\dot{C}H_3CH_2Cl$
$CH_3\dot{C}H_2Cl$

The dotted ca

[a] Lauterbur,

[b] Holm, C. H.

[c] Spiesecke, I

Table 5. *The hybridization of the chlorine bonding orbital and the charge distributions in several alkyl chlorides*

Molecule	s_{Cl}	n_{Cl}	n_H	$\varrho_{Cl^{35}}$
CCl_4	0.201	1.073		0.7406[a]
$CHCl_3$	0.203	1.124	0.843	0.6981[a]
CH_2Cl_2	0.204	1.176	0.888	0.6559[a]
CH_3Cl	0.197	1.228	0.936	0.6207[a]
CH_4			0.985	
CH_3CH_3			0.982	
CH_2ClCH_2Cl	0.199	1.217	0.923	0.6262[b]
$CHCl_2CHCl_2$	0.194	1.147	0.870	0.6873[c]
CCl_3CCl_3	0.189	1.087		0.7413[a]

	S_{Cl}	n_A	n_B	n_C	n_D	$\varrho_{Cl^{35}}$
$H_3{}^D{-}C{-}{}^C\overset{Cl_A}{\overset{\vert}{C}}{-}{}^BH_2$	0.215	1.240	0.926	1.079	0.968	0.5960[c]
$H_3{}^D{-}C{-}{}^C\underset{Cl_2}{\underset{{}_A\vert}{C}}{-}{}^BH$	0.210	1.183	0.890	1.133	0.955	0.6453[b]
$H_{3D}{-}C{-}{}_CC{-}{}_ACl_3$	0.204	1.131		1.193	0.943	0.6914[b]

---

[a] Livingston, R.: J. Physic. Chem. 57, 496 (1953).
[b] Livingston, R.: J. chem. Physics 20, 1170 (1952).
[c] Hooper, H. O., and P. J. Bray: J. chem. Physics 33, 335 (1960).

A second plot of i versus s can be made from eq. (11), and this is a curve; the two curves cross at a unique i and s for the system. This value of s is then used to determine the charge distributions of the remaining orbitals. Charge distributions and orbital hybridizations for some alkyl halides are given in Tab. 5.

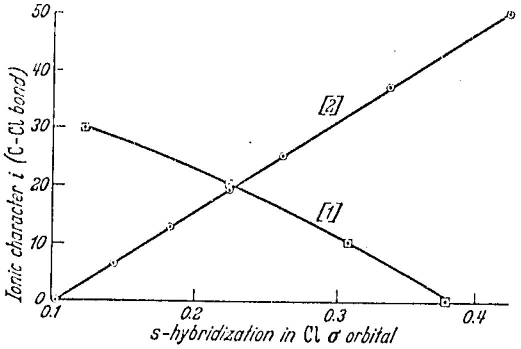

Fig. 4. Plots of ionic character, i versus the amount of s-hybridization in the chlorine σ orbitals. [1] is calculated from nuclear quadrupole resonance data and $\varrho = (1 - i)\,(1 - s)$ where $i = |n_{Cl} - 1|$. [2] is calculated from the electronegativity equation

$$\chi_j^A = b_j^A + 2\,c_j^A\,n_j^A$$

with various assumed hybridizations. Where the curves [1] and [2] cross the i and s values are unique; the charge distributions are calculated using these values of i and s

Hydrocarbons

The charge distributions of the hydrocarbons (Tab. 3) indicate that the polarity of the C-H bond is 2%, 7% and 12%, for aliphatic, ethylenic and acetylenic carbon atoms respectively; in each case the carbon atom bears a small negative charge relative to the free atom, agreeing with the experimental evidence of increased acidity in this series.

This charge, 0.061e in methane, is appreciably smaller than those calculated by Hoffmann [5] using Mulliken's concept of gross atomic populations. In this approach the charge resid-

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The same hybridizations were assumed to hold for the methyl derivatives of these hydrides. The order of the R-H bond polarities for both the hydrides and their methyl derivatives is the same as that derived from the AEC using Pauling's electronegativity values [*6*], namely

$$\chi^{\mathrm{R}}_{\mathrm{eff}} \text{ order is } \mathrm{O} > \mathrm{N} > \mathrm{S} > \mathrm{C} > \mathrm{Si} \;.$$

Comparing the polarity of the R-H bonds with the corresponding methyl derivatives, shows that for R, N, O or S replacing hydrogen by a $-CH_3$ group results in a *smaller* positive charge on the hydrogen atom of the R-H bond. This corresponds to the positive inductive effect of the methyl group in organic chemistry [*2*]. The only exception to this effect is in methane, where replacement of -H by $-CH_3$ results in a very small withdrawal of electron density from the hydrogen orbital.

This slight electron-feeding ability is also encountered in the alkyl chlorides (Tab. 4). Thus in CH_3Cl, CH_3CH_2Cl; CH_2Cl_2 and $CH_3CH\,Cl_2$ the bond polarity of the CH bond illustrates this effect. The SGOBE method's prediction this effect shows that it overcomes the defects of previous approximate group electronegativity treatments, which usually assume [*13*] that

$$\chi^{\mathrm{At}}_{\mathrm{CH_3}} = \frac{1}{2}\chi^{\mathrm{At}}_{\mathrm{C}} + \frac{1}{6}\left[\chi^{\mathrm{At}}_{\mathrm{H}} + \chi^{\mathrm{At}}_{\mathrm{H}} + \chi^{\mathrm{At}}_{\mathrm{H}}\right]$$

and $\chi^{\mathrm{At}}_{\mathrm{CH_3}} > \chi^{\mathrm{At}}_{\mathrm{H}}$ since $\chi^{\mathrm{At}}_{\mathrm{C}} > \chi^{\mathrm{At}}_{\mathrm{H}}$. This leads to a larger bond polarity in any *polarity* versus *change in electronegativity* relationship, and the $-CH_3$ possesses a negative inductive effect.

General

Although no direct method is available to check these calculated molecular charge distributions, it is possible to correlate them qualitatively with empirical methods, which measure physical properties dependent, in part, on the orbital charges.

a) Molecular Dipole Moments: the paraffin hydrocarbons possess zero, or almost zero, dipole moments [*2*] whether symmetrical or unsymmetrical; this is substantiated by the present results where the charge distributions for atoms in the molecule are finite but small in their difference from the free atomic state; the extended Huckel results are rather difficult to fit into this low dipole moment picture, since the large deviation of orbital charge from unity would yield rather large dipole moments in some unsymmetrical paraffin hydrocarbons.

Similarly in the alkyl chlorides, inorganic halides and methyl derivatives, the charge distributions agree with the current qualitative picture for the molecular dipole moments [*2*]:

1. In all carbon-chlorine bonds the chlorine is more negative and the carbon more positive than in the free atomic case

$$n^{\mathrm{Mol}}_{\mathrm{T}} > n^{\mathrm{At}}_{\mathrm{T}}]_{\mathrm{Cl}} \;; \qquad n^{\mathrm{Mol}}_{\mathrm{T}} < n^{\mathrm{At}}_{\mathrm{T}}]_{\mathrm{C}} \;.$$

2. The charge density on atoms or groups bound to a chlorinated carbon will be drawn slightly toward the positive centre, carbon, resulting in a higher separation of positive and negative charge centres, and increased dipole moment, as in the molecules CH_4 and CH_3Cl where the 1s orbitals of hydrogen have an effective charge of 0.985 and 0.936 respectively; thus in CH_3Cl there is a charge transfer to the central carbon atomic orbitals, from the H 1s orbitals.

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3. The valence
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It can be concluded
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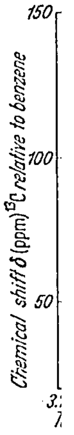

Fig. 5. Plot o
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With such a fixed hybridization of the chlorine bonding orbital, it is possible to predict unknown n.q.r. frequencies for ^{35}Cl in alkyl halides, by assuming $s = 0.2$ and calculating, i_{C-Cl} from the SGOBE method and hence ϱ. Thus the n.q.r. ^{35}Cl frequencies of $CHCl_2CH_2Cl$ are expected to be 35.12 and 36.76 Mcs respectively at 77 °K.

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COULOMB PARAMETERS IN SIMPLE HUCKEL AND OMEGA TECHNIQUE MOLECULAR ORBITAL METHODS[1]

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ABSTRACT

The well-known similarities of the simple Huckel and omega technique molecular orbital procedures for pi electrons to Pople's self-consistent field method are extended by considering systematic approximations to the latter. From the relationships found, Huckel-method Coulomb integrals and omega values for a variety of atoms (Be, B, C, N, O, F, Mg, Al, Si, P, S, Cl, Ge, As, Se, Sn, Sb, Te) are derived. The Huckel and omega Coulomb integrals are shown to be directly related to a recent definition of orbital electronegativity. The ability of the omega techniques to improve upon the Huckel-method charge distributions is discussed by use of an arbitrary but typical example.

INTRODUCTION

Semi-empirical pi-electron molecular orbital methods, using atomic orbitals as a basis set, continue to be extensively employed in discussions of the structure, stability, reactivity, and spectra of conjugated organic molecules. Three such procedures, the Pariser–Parr–Pople method (1–3), the simple Huckel method (4, 5), and the "omega" technique (5, 6), have been widely applied to such problems (3, 5). The evaluation of the necessary secular determinant matrix elements for the latter two methods is usually empirical, although attempts have been made to estimate the Coulomb integrals from electronegativities, atomic spectral data, and the parameters or results of the Pariser–Parr–Pople technique (7).

In the present study, the well-known similarities among the Huckel, omega, and Pariser–Parr–Pople methods will be considered in some detail, and extended. In particular, quantitative relations between the Coulomb parameters of the three techniques will be derived, and these relationships exploited to provide theoretical estimates of the Coulomb integrals for a wide variety of atoms.

THEORY AND DISCUSSION

All the molecular orbital procedures to be discussed consider only the "pi" electrons of conjugated molecules. The one-electron molecular orbitals (MOs) ψ_i for such electrons are approximated as linear combinations of atomic orbitals (AOs) ϕ_u, with coefficients c_{iu} determined by an energy minimization process; thus

$$\psi_i = \sum_u c_{iu}\phi_u. \qquad [1]$$

The total electronic wave function representing the ground state of a closed shell of pi electrons in a conjugated molecule can normally be accurately expressed as a single Slater determinant of the occupied MOs ψ_i. Pople (2, 8) introduced a simplified self-consistent field procedure to deal with such systems. Various systematic approximations were introduced by Pople (neglect of differential overlap, treatment of the sigma electrons

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[2] *Holder of N.R.C. Postgraduate Scholarships 1963–1966.*

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as a non-polarizable core, approximation of certain integrals, etc. (2, 3, 8)) which reduce the elements of the F matrix of the secular determinant.

$$\det |F_{uv} - ES_{uv}| = 0 \tag{2}$$

to the form

$$F_{uu} = U_{uu} + \tfrac{1}{2}P_{uu}\gamma_{uu} + \sum_{w \neq u} (P_{ww} - Z_w)\gamma_{uw} \tag{3}$$

and

$$F_{uv} = H_{uv} - \tfrac{1}{2}P_{uv}\gamma_{uv} \qquad (u \neq v), \tag{4}$$

where the bond-order matrix elements P_{uv} are defined as

$$P_{uv} = 2\sum_i c_{iu}c_{iv}, \tag{5}$$

the summation i being over the occupied MOs only. With the approximation for the overlap integrals S_{uv} that

$$\begin{aligned} S_{uv} = \delta_{uv} &= 1 \quad \text{if } u = v, \\ &= 0 \quad \text{if } u \neq v \end{aligned} \tag{6}$$

the diagonal elements P_{uu} of the bond-order matrix P may be identified with q_u, the total pi-electron charge density in AO u,

$$q_u = P_{uu}. \tag{7}$$

In [3] and [4], the Z_w represent the pi-electron core charge of the atom associated with AO w, and in neutral molecules this is equal to the number of pi electrons (0, 1, or 2) contributed by AO w to the pi system. The γ_{uv} (and γ_{uu}) are the two-electron repulsion integrals

$$\gamma_{uv} = \int\int \phi_u^*(1)\phi_v^*(2)(1/r_{12})\phi_u(1)\phi_v(2)\,d\tau(1)\,d\tau(2). \tag{8}$$

The one-center repulsion integrals of [8], γ_{uu}, are normally approximated as (1, 3, 8)

$$\gamma_{uu} = I_u - A_u, \tag{9}$$

where I_u, A_u are the valence-state ionization potential and electron affinity of AO u.

The core integral U_{uu} is associated with the ionization potential I_u by (3, 9, 10)

$$U_{uu} = -I_u. \tag{10}$$

The core resonance integral H_{uv} is normally obtained empirically.

Substitution of the relations [7], [9], [10] into eq. [3] for F_{uu} gives

$$F_{uu} = -I_u + \tfrac{1}{2}q_u(I_u - A_u) + \sum_{w \neq u} (q_w - Z_w)\gamma_{uw}, \tag{11}$$

which may be rearranged, by use of the core charge Z_u of AO u, to give

$$F_{uu} = [-I_u + \tfrac{1}{2}Z_u(I_u - A_u)] + [\tfrac{1}{2}(q_u - Z_u)(I_u - A_u)] + \left[\sum_{w \neq u} (q_w - Z_w)\gamma_{uw}\right]. \tag{12}$$

This can be shortened to

$$F_{uu} = J(u) + K(u, q_u) + L(u, q_w), \tag{13}$$

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in which J, K, L
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(*c*) For nearest neighbors u and v, F_{uv} can be expressed in terms of $F_{CC'}$, the nearest neighbor F_{uv} for the ground state of benzene, thus

$$F_{uv} = k_{uv}F_{CC'}, \tag{23}$$

where k_{uv} is an empirical constant for the pair u, v.

Since for neutral molecules

$$\sum_{w} (q_w - Z_w) = 0, \tag{24}$$

approximation a would be exact if all the ϵ_{uw} were identical, i.e.

$$\epsilon_{u1} = \epsilon_{u2} = \qquad = \epsilon_{uu} = \epsilon. \tag{25}$$

In this case the equation reduces to

$$\sum_{w} (q_w - Z_w)\epsilon_{uw} = \epsilon\sum_{w} (q_w - Z_w) = 0. \tag{26}$$

The equalities [25] are usually incorrect for real systems; however, the ϵ_{uw} for small ring systems are all of the same order of magnitude. In benzene, for example, Pariser and Parr's (1) empirical γ_{uu}, γ_{uv} integrals give ϵ_{uw} for $u = 1$ of

$$\epsilon_{11} = 5.3 \text{ eV}$$

$$\epsilon_{12} = \epsilon_{16} = 7.3 \text{ eV}$$

$$\epsilon_{13} = \epsilon_{15} = 5.5 \text{ eV}$$

$$\epsilon_{14} = 4.9 \text{ eV}$$

$$\text{i.e. all } \epsilon_{uw} = 6.1 \pm 1.2 \text{ eV}.$$

Approximation b is not a drastic one since in the Pariser–Parr–Pople method, the off-diagonal F_{uv} for non-nearest neighbors are assumed to have $H_{uv} = 0$ (1, 2, 3). The remaining term $-P_{uv}\epsilon_{uv}$, of F_{uv} would be expected to be small in most cases.

The F_{uu} for method A is then simply $J(u)$ of [13], or

$$F_{uu} = -\left[I_u + Z_u\frac{(A_u - I_u)}{2}\right]. \tag{27}$$

The term in square brackets of [27] corresponds exactly to the orbital electronegativity χ_u of the "neutral" AO u using the "molecular orbital" definition of bond electronegativity (11). Three neutral orbital cases are possible, corresponding to vacant, singly occupied, and lone-pair atomic orbitals,

$$F_{uu}\ (Z_u = 0) = -I_u = -\chi_u\ (Z_u = 0), \tag{28}$$

$$F_{uu}\ (Z_u = 1) = -(I_u + A_u)/2 = -\chi_u\ (Z_u = 1), \tag{29}$$

$$F_{uu}\ (Z_u = 2) = -A_u = -\chi_u\ (Z_u = 2). \tag{30}$$

Coulomb integrals have been previously associated with orbital electronegativities for singly occupied ($Z_u = 1$) AOs (3, 12, 13) and the above relations show the association to be a general one.

Numerical values of the terms $J(u)$, evaluated from the valence-state energy data of Hinze and Jaffe (14) for a variety of atoms which could use p_π AOs in a conjugated network are listed in Table I. The $J(u)$ are in electron volts, whereas in simple Huckel

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Atom	Valence state of core	Z_u
Be	di^1di^1	0
B	$tr^1tr^1tr^1$	0
C	$tr^1tr^1tr^1$	1
N	$tr^2tr^1tr^1$	1
N	$tr^1tr^1tr^1$	2
O	$s^2p^2p^1$	1
O	$s^2p^1p^1$	2
F	$s^2p^2p^1$	2
Mg	di^1di^1	0
Al	$tr^1tr^1tr^1$	0
Si	$tr^1tr^1tr^1$	1
P	$tr^2tr^1tr^1$	1
P	$tr^1tr^1tr^1$	2
S	$s^2p^2p^1$	1
S	$s^2p^1p^1$	2
Cl	$s^2p^2p^1$	2
Ge	$tr^1tr^1tr^1$	1
As	$tr^2tr^1tr^1$	1
Se	$s^2p^2p^1$	1
Sn	$tr^1tr^1tr^1$	1
Sb	$tr^2tr^1tr^1$	1
Te	$s^2p^2p^1$	1

*All energy data and paramet

†All valence state energy data

‡Arbitrarily chosen (see text) a

methods it is conventi Coulomb and resonan expression,

[31]

where J(C) and $F_{CC'}$ From [31]

[32]

which requires the num for the nearest neighb

[33]

For this case, $P_{CC'}$ is becomes

[34]

The core resonance inte of benzene. From the $H_{CC'} = -2.39$ eV; fro obtain -1.75 eV, and -1.92 eV. The observed can be used to derive H above is then -4.82, –

The correspondence between method A and the simple Huckel method can now be demonstrated by showing the one-to-one relation between Huckel h_u values obtained empirically and the h_u calculated by [32] from the valence-state energy data. The only difficulty in such an analysis is the choice of appropriate Huckel h_u to be used. For the purposes of this study, the consistent and widely used "best" values listed by Streitwieser (7*a*) have been adopted. The correlation of these h_u with the term $(J(u) - J(\mathrm{C}))$ is given in Fig. 1. The correlation line is excellent, considering that the "best" h_u are only estimated to within ±0.25.* The slope of the line, -4.2_3 eV, is within the range of the estimates of $F_{\mathrm{CC'}}$ given above.

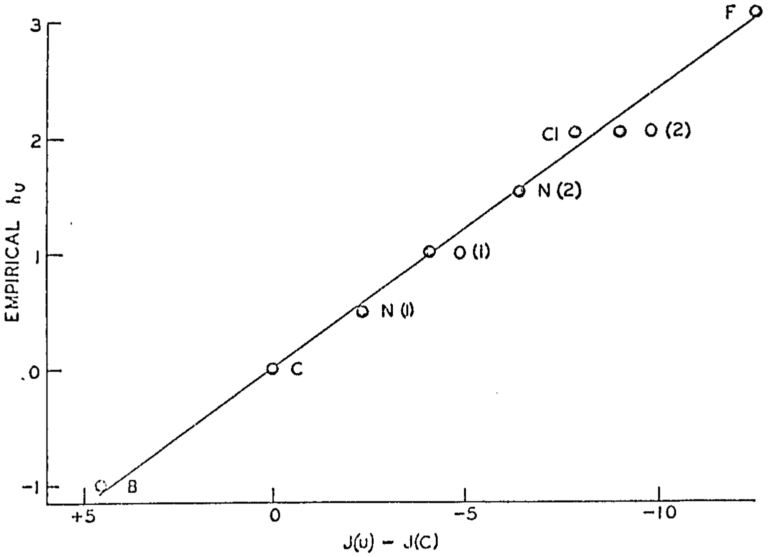

FIG. 1. Plot of $J(u) - J(\mathrm{C})$ against the empirical Huckel h_u. NOTE: The integer in brackets following the atomic symbol represents the core charge Z_u for atoms having more than one value of Z_u listed in Table I.

The quantitative correspondence between the theoretical and empirical h_u gives some insight into the nature of the effective hamiltonian $H_{\mathrm{eff}}{}^0$ of [14]. The $H_{\mathrm{eff}}{}^0$ corresponds to the Pople-method hamiltonian for a molecular charge distribution in which all the pi atomic orbitals are neutral (i.e. all $q_u = Z_u$). From this elucidation, the Huckel h_u for a variety of atoms not considered by Streitwieser may be calculated. These h_u, evaluated using $F_{\mathrm{CC'}} = -4.23$ eV, are listed in Table I.

Certain trends in the h_u are evident:

(I) Atoms of Groups 2 and 3, the p_π AOs of which are normally vacant, have very low h_u, of the order of −1.

(II) Group 4 atoms have h_u close to zero.

(III) Group 5, 6, and 7 atoms display a wide range of h_u depending upon Group, Period, and pi core charge of the atoms, although in general all the h_u are quite high, and for a given atom $h_u (Z_u = 2) > h_u (Z_u = 1)$. The term for sulfur $(Z_u = 2)$ is close to that of nitrogen $(Z_u = 2)$ as anticipated (7*a*).

All the atomic energy terms used in the derivation of the $J(u)$ values in Table I were obtained by assuming that the sigma-bonded AOs of the valence shell were "neutral" (that

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**The excellent correlation obtained may be due in part to the use of atomic and molecular ionization potential data in deriving some Huckel h_u which would have been considered in arriving at the "best" values.*

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[35]

[36]

[37]

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Approximation Metho
Several attempts ha
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(6, 17–20). Streitwiese
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density q_u of the AO

[38]

where ω is an empirica
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expression [13] will be
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The approximation
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[39]

By retaining the definit
becomes

[40]

where

[41]

Equation [40] may be
(see [39]) of eq. [11] giv

[42]

The term of [42] in square brackets represents the molecular-orbital definition of the bond electronegativity function for AO u (11) with charge density q_u. The method B Coulomb integrals are then directly associated with the bond electronegativities of the pi AOs; in method A this association held only for the "neutral" orbital electronegativities. Klopman (13) has previously noted the correspondence between electronegativity and Coulomb integrals in omega-type methods.

By use of the value of $F_{CC'}$ from method A of -4.23 eV, the terms ω_u for various atomic p_π orbitals u may be evaluated (eq. [41]). These parameters are listed in Table I. Empirical values of ω for carbon have ranged from 0.33 to 1.8 (7*a*), but the widely used and "best" value is $\omega_C = 1.4$ (6, 7*a*, 20). The theoretical value of ω_C in Table I is 1.32, in excellent agreement with the empirical result. Although Pritchard and Sumner (19) derived quite different ω_u for different atoms, the ω value for *all* atoms is normally taken to be the same as that for carbon (6). The widely different ω_u's for different atoms (and different Z_u) listed in Table I indicate that this extension is not justified.

Within each Period, there appears to be a good correlation of ω_u with h_u, ω_u generally increasing with atomic number. Within each Group of the Periodic Table, ω_u decreases as the atomic number increases. For atoms with different possible pi core charges Z_u, ω_u for $Z_u = 2$ is greater than that for $Z_u = 1$.

The relation between ω_u and h_u for the first Period atoms (except Be†) is illustrated in Fig. 2. This relation may be expressed as

$$\omega_u = 0.45h_u + 1.3_0. \qquad [43]$$

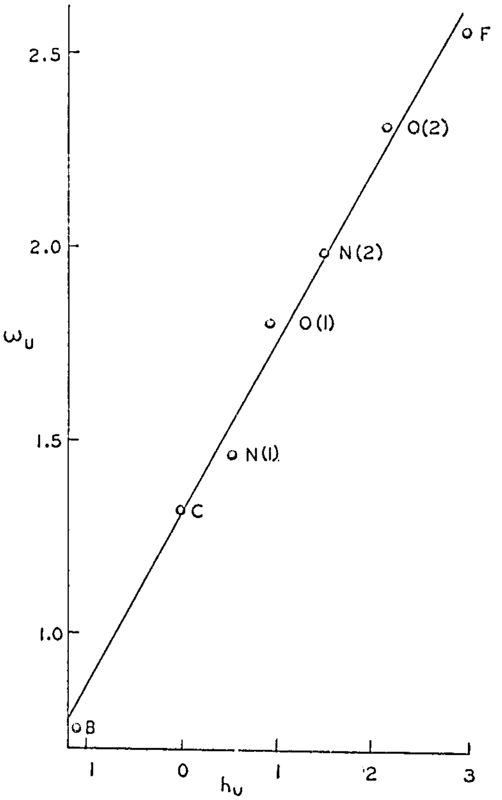

FIG. 2. Plot of ω_u against h_u for atoms of the first Period.

†*The Group 2 elements for the first and second Periods fall significantly off the correlation lines.*

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[44]

for the elements Al
Equations [40], [4

[45]

with

[46]

for the atoms B, C,

[47]

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value of about -2 eV,
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Comparison of the Met

Now that methods
procedures, have been
of each method to Pop

Calculated

Atom number*	Huckel charge ($Z_u - q_u$)
1	−0.3697
2	+0.1452
3	−0.0082
4	+0.0957

*Numbering scheme as in Fig. 3.
†Equivalent to $\omega +$ *all* neighbors.

system was chosen and calculations were performed to establish the extent to which the omega technique improved the Huckel F_{uu} parameters, during the self-consistent field calculations, towards those required by Pople's method.

The example used is a six-membered ring system containing five carbon atoms, each having a p_π AO (with $h_u = 0$), and one conjugating heteroatom, X, with $h_X = 1.0$. The pi system of the molecule is assumed to contain 6 electrons, and all nearest neighbors are assumed to have F_{uv} equal to that of benzene. For simplicity, the geometry of the ring is taken to be identical to that of benzene, and the heteroatom X is assumed to have all γ_{uX} equal to those of the carbon atoms. The values of the latter integrals were taken from Pariser and Parr's paper (1).

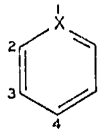

FIG. 3.

The simple Huckel charge distribution based on these assumptions is given in Table II. The ΔF_{uu} listed in the remaining columns of Table II corresponds to the differences between $J(u)$, the simple Huckel F_{uu}, and the F_{uu} for the various methods calculated on the basis of the Huckel charge distribution;

$$\Delta F_{uu} = F_{uu} - J(\mathrm{C}). \tag{48}$$

The ΔF_{uu}'s corresponding to the omega technique (column 4 of Table II) bear little resemblance in sign, magnitude, or relative order for the different atoms to those required by the Pople method (column 7) for the same charge distribution. The correspondence between the omega ΔF_{uu} and the Pople ΔF_{uu} is not substantially improved by adding nearest-neighbor terms (column 5) and first and second nearest-neighbor terms (column 6) to the ΔF_{uu} of the omega technique. The inclusion of the first, or first and second nearest-neighbor terms has been previously suggested (21, 22) as a means of improving the omega technique. The simple Huckel ΔF_{uu}, all zero of course, are actually closer to those of Pople's method than are the ΔF_{uu} of any other of the techniques.

Since the second iteration F_{uu}'s of the omega techniques are not altered from the Huckel F_{uu}'s in even qualitatively the same manner as those in the Pople method, it is difficult to see why the self-consistent field charges of the ω methods represent an improvement over those of the Huckel method. The ω technique will have the effect of "smoothing out" the net excess charges calculated by the Huckel method, but will not necessarily lead to any improvement in the relative *order* of charge densities among the atoms.

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