A Semi-empirical MO Theory of σ Electron Systems.* I. General Theory

By Hidekazu HAMANO**

(Received March 10, 1964)

Most of the theoretical work on organic molecules that has been reported so far is connected with π electron systems; relatively little is known about the electronic states of the σ electrons. However, recent progress in experimental techniques such as nuclear magnetic resonance, nuclear quadrupole resonance, and electron spin resonance has made it desirable to obtain some more theoretical information about the electronic states of the σ electrons in organic molecules. The present paper constitutes an attempt in this direction.

It is obvious that any theoretical description of the σ electrons in organic molecules will be of an approximate nature. We plan to base our discussion on the SCF LCAO MO method as developed by Roothaan,1) a method which has been successfully applied to small molecules. However, we will be forced to introduce some additional approximations, since a straightforward application of Roothaan's theory is not feasible for large organic molecules.

Let us consider a molecule with a closed-shell ground state. It is assumed that each doubly-occupied SCF LCAO MO may, in principle, be associated with either a lone pair or a localized σ bond, though in Roothaan's complete treatment each SCF LCAO

---

* This work was supported by a grant from the U. S. Army Research Office (Durham) and the National Science Foundation to the University of Pennsylvania.

** On leave of absence from Tokyo Gakugei University, Tokyo, Japan.

MO should, in principle, be represented as a linear combination of all available atomic orbitals in the molecule. In a first approximation we represent the SCF LCAO MO's that are associated with lone pairs or σ bonds as linear combinations of the corresponding atomic orbitals on the atoms. If we substitute the MO into the analogue of the Roothaan equations1) and then solve them, we may anticipate one solution for each lone pair and two solutions for each bond; the solution with the lower energy will be called the bonding orbital, and the other solution, the anti-bonding orbital. In the following pages the expression "*to a first approximation*" refers to the above calculation. The first-order treatment is considerably less accurate than a complete SCF LCAO MO calculation would have been, but we may use its results as a starting point for a second-order treatment which will give results that are of an accuracy comparable with that of the solutions of the complete SCF LCAO MO calculations.

It is possible to construct molecular orbitals as linear combinations of the lone-pair, bonding and anti-bonding orbitals obtained above. This approach might be called the LCBO MO method (with molecular orbitals represented as linear combinations of bond or lone-pair orbitals). The coefficients in these linear combinations are unknown, but it may be assumed that in each case there is a major contribution from a lone-pair or a bonding orbital and that the coefficients of the anti-bonding orbitals are significantly smaller. Therefore, they may be determined by means of a perturbation method. In the following remarks we will use the expression "*to a second approximation*" as referring to the results of this perturbation treatment.

We will be forced to introduce some semi-empirical features into the theory, especially in connection with estimating the non-diagonal elements of the matrix that represent the interaction between different bonds or lone pairs, since a non-empirical evaluation of these quantities would be very tedious. This semi-empirical procedure supplies a convenient tool for dealing with large organic molecules.

The general theory will be developed in this paper; applications and some further details will be discussed in subsequent papers.

I. First Order Theory.—*General Considerations.*—In developing our theory we will basically follow Roothaan's method.1) However, we will replace Roothaan's LCAO approximation by the LCBO approach. We will also consider a molecule with a closed-shell ground state. The inner electrons may be taken as being adequately represented by means of the inner-shell atomic orbitals; hence, only the valence electrons need to be taken into account.

The molecular $2N$-electron ground state wave function is represented as an antisymmetrized product of molecular spin orbitals:

$$\Phi=\{(2N!)\}^{-1/2}\sum_{\mathbf{P}}\boldsymbol{P}\delta_{\mathbf{P}} \times\{\prod_{\mathrm{i}}\psi_{\mathrm{i}}(2i-1)\psi_{\mathrm{i}}(2i)\alpha(2i-1)\beta(2i)\} \tag{1}$$

where the ψ_{i} are suitable molecular orbitals, which are represented as LCAO in Roothaan's theory.1) We may also write the MO as linear combinations of orbitals that are localized in specific bonds or lone pairs such as those proposed by Edmiston and Ruedenberg2) or Lennard-Jones,3) which are obtained by means of a unitary transformation. We will go one step further and take the orbitals as bond or lone-pair orbitals themselves. The validity of this procedure is not immediately obvious, however, and so it may be useful to clarify its theoretical basis and the relation between the LCAO and LCBO approximations.

We may represent the bond orbitals as linear combinations of valence atomic orbitals (LCVAO):

$$\varphi_{\mathrm{p}}=a_{\mathrm{p}}(\mathrm{A,p})+b_{\mathrm{p}}(\mathrm{B,p}) \tag{2}$$

where $\mathrm{A,p}$ and $\mathrm{B,p}$ are the valence AO of both atoms respectively, and each φ_{p} is normalized. The valence AO $(\mathrm{A,p})$, $(\mathrm{B,p})$ and lone-pair orbitals φ_{f} may be represented as linear combinations of the AO on the corresponding atoms:

$$\mathrm{A,p}=\sum_{\lambda}d_{\lambda}^{\mathrm{p}}\chi_{\lambda}^{\mathrm{A}}, \qquad \cdot\ \varphi_{\mathrm{f}}=\sum_{\mu}d_{\mu}^{\mathrm{f}}\chi_{\mu}^{\mathrm{A}} \tag{3}$$

where $\chi_{\lambda}^{\mathrm{A}}$ is the λth AO of atom A and d_{λ}^{p} is its coefficient in the pth bond orbital. This set of hybridized AO's belonging to the same atom may be taken as orthonormal and equivalent. Each bond orbital, φ_{p}, may be supposed to be obtained by solving an equation for bond p. Usually two different solutions are obtained, a bonding orbital, φ_{p}^{+} and an anti-bonding orbital, φ_{p}^{-}; they are orthogonal to one another. In this way, we may replace a set of atomic orbitals by an equivalent set of valence orbitals and also replace the paired valence AO $(\mathrm{A,p})$ and $(\mathrm{B,p})$ by the bonding φ_{p}^{+} and anti-bonding

---

1) C. C. J. Roothaan, *Revs. Mod. Phys.*, **23**, 69 (1951).

2) C. Edmiston and K. Ruedenberg, ibid., **35**, 457 (1963); see also, S. F. Boys, ibid., **32**, 296 (1960).

3) J. Lennard-Jones, *Proc. Roy. Soc.*, **A198**, 1, 14 (1949). He called these orbitals "*equivalent orbitals.*"

φ_p^- orbitals. We may thus represent the MO's as linear combinations of bond or lone-pair orbitals instead of the LCAO approximation:

$$\psi_i = \sum_p c_{ip}\varphi_p \tag{4}$$

The variational procedure for minimizing the total energy of the molecule then leads to the following equation:

$$\boldsymbol{L}\boldsymbol{c}_i = \varepsilon_i \boldsymbol{S}\boldsymbol{c}_i \tag{5}$$

where $\boldsymbol{L}$ is the set of LCBO SCF Hamiltonian matrix elements which are given by:

$$\begin{aligned}\boldsymbol{L}_{pq}^{+-} &= \langle \varphi_p^+ | \boldsymbol{H} | \varphi_q^- \rangle \\ &+ \sum_i [2\langle \psi_i(1)\varphi_p^+(2) | r_{12}^{-1} | \psi_i(1)\varphi_q^-(2)\rangle \\ &- \langle \psi_i(1)\varphi_p^+(2) | r_{12}^{-1} | \varphi_q^-(1)\psi_i(2)\rangle], \text{ etc.}\end{aligned} \tag{6}$$

The $\boldsymbol{H}$ is the Hamiltonian for the electrons in the combined potential field of the nuclei and inner-shell electrons. The column vectors, $\boldsymbol{c}_i$ represent the coefficients of the BO in the ith MO, ε_i is the eigenvalue of the MO, and $\boldsymbol{S}$ is an overlap matrix with elements $S_{pq}^{+-} = \langle \varphi_p^+ | \varphi_q^- \rangle$, etc. Equation 5 is the secular equation for the SCF LCBO MO.

It would, however, be as difficult as in the LCAO approach to obtain a reliable solution of Eq. 5 from *ab initio* calculations; we therefore wish to solve the equation by introducing the following approach. The matrix elements, S_{pq}^{+-}, are usually smaller than the S_{pq}^{++} or S_{pq}^{--} since the signs of the coefficients, a_p or b_p, of the valence AO in the bond orbital defined by Eq. 2 are different for the bonding and anti-bonding orbitals, and since the overlap integrals between unpaired valence AO's are generally small (they are zero for the AO on the same atom). Since the delocalization of the σ electrons is considered to be small, we may also assume that the $\boldsymbol{L}_{pq}^{+-}$ are relatively small. They may be considered as small perturbations. We will discuss this in greater detail in the second order theory described in Section II. In the first order treatment these smaller terms may, therefore, be neglected. Equations 4 and 5 are then reduced to:

$$\psi_i^+ = \sum_p c_{ip}^+ \varphi_p^+, \qquad \psi_i^- = \sum_p c_{ip}^- \varphi_p^- \tag{7}$$

$$\boldsymbol{L}^+ \boldsymbol{c}_i^+ = \varepsilon_i^+ \boldsymbol{S}^+ \boldsymbol{c}_i^+, \qquad \boldsymbol{L}^- \boldsymbol{c}_i^- = \varepsilon_i^- \boldsymbol{S}^- \boldsymbol{c}_i^- \tag{8}$$

where the plus and minus signs refer to quantities connected with the φ_p^+ and φ_p^- respectively. In this approximation, the ψ_i^+ and ψ_k^- are determined from two independent sets of equations, representing the occupied and unoccupied MO respectively in the molecular ground state. We will only discuss the equations for the occupied orbitals, since the other equations are in every way equivalent. For the sake of brevity, we will omit the plus sign in the following remarks.

The non-orthogonality between the different BO's will cause some complications in the subsequent discussion; it is, therefore, convenient to introduce, according to Löwdin,[4] the following orthogonalized BO (OBO):

$$\varphi^\circ = \varphi(\boldsymbol{1} + \boldsymbol{S}^\circ)^{-1/2} \tag{9}$$

where $\boldsymbol{1}$ is a unit matrix and $\boldsymbol{S}^\circ$ is an overlap matrix with the elements:

$$S_{pq}^\circ = S_{pq} - \delta_{pq}, \quad \delta_{pq} = \begin{cases} 1 & (p=q) \\ 0 & (p \neq q) \end{cases} \tag{10}$$

Equations 7 and 8 may, then, be written as:

$$\psi_i = \sum_p c_{ip}^\circ \varphi_p^\circ \tag{11}$$

$$\boldsymbol{L}\boldsymbol{c}_i^\circ = \varepsilon_i \boldsymbol{c}_i^\circ \tag{12}$$

where

$$\boldsymbol{c}^\circ = (\boldsymbol{1} + \boldsymbol{S}^\circ)^{1/2} \boldsymbol{c}$$

Since the matrix $\boldsymbol{c}^\circ$ is unitary, the molecular wave function, Φ°, and the electronic energy, W_e°, of the ground state may be written as:

$$\begin{aligned}\Phi^\circ &= \{(2N)!\}^{-1/2} \sum_{\mathbf{P}} \boldsymbol{P}\delta_{\mathbf{P}} \\ &\times \{\prod_p \varphi_p^\circ(2p-1)\varphi_p^\circ(2p)\alpha(2p-1)\beta(2p)\}\end{aligned} \tag{13}$$

$$W_e^\circ = \sum_p \overline{W}_p = \sum_p [2\overline{H}_p + \sum_q (2\overline{J}_{pq} - \overline{K}_{pq})] \tag{14}$$

where the summation is to be performed over all the OBO's. The $\overline{H}_p$, $\overline{J}_{pq}$ and $\overline{K}_{pq}$ are core, Coulomb, and exchange integrals respectively with regard to OBO.

It would be a tedious procedure to use the OBO to perform calculations on large molecules. Fortunately, the overlap integrals between different BO's are usually much smaller than those between directly-bonded AO's. The possible consequences of the non-orthogonality of these orbitals have been discussed by Löwdin,[4] by means of OBO instead of non-orthogonal BO. They may, therefore, be neglected. In this approximation, the

---

[4] P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).

OBO's are reduced to the corresponding BO's. Equations 12, 13 and 14 may be rewritten as:

$$\boldsymbol{L}\boldsymbol{c}_{\mathrm{i}}=\varepsilon_{\mathrm{i}}\boldsymbol{c}_{\mathrm{i}} \tag{15}$$

$$\begin{aligned}\Phi^{\circ}=&\{(2N)!\}^{-1/2}\sum_{\boldsymbol{P}}\boldsymbol{P}\delta_{\boldsymbol{P}}\\ &\times\{\prod_{\mathrm{p}}\varphi_{\mathrm{p}}(2p-1)\varphi_{\mathrm{p}}(2p)\alpha(2p-1)\beta(2p)\}\end{aligned} \tag{16}$$

$$W_{\mathrm{e}}^{\circ}=2\sum_{\mathrm{p}}H_{\mathrm{p}}+\sum_{\mathrm{pq}}(2J_{\mathrm{pq}}-K_{\mathrm{pq}}) \tag{17}$$

Equations 16 and 17 show that the quantities in terms of the MO's may, instead, be expressed in terms of BO's in the first order treatment. Therefore, we may use the BO's instead of the MO's as a basis for the discussion of the first order theory. The method for determining the BO's will be discussed in the next subsection.

SCF Bond Orbital Approach. — Let us now proceed to determine the explicit form of the BO's which are represented by the variational function of Eqs. 2 and 3. Since we wish to make use of the SCF procedure, our method may be called the "*SCF BO approach.*"

Most σ electron systems of organic molecules contain some heteropolar bonds. It may be convenient to introduce the bond polarity parameter proposed by Mulliken:[5]

$$\begin{aligned}Q_{\mathrm{p}}=Q_{\mathrm{p}}^{\mathrm{A}}=b_{\mathrm{p}}^{2}-a_{\mathrm{p}}^{2}=&(b_{\mathrm{p}}^{2}+a_{\mathrm{p}}b_{\mathrm{p}}S_{\mathrm{p}})\\ &-(a_{\mathrm{p}}^{2}+a_{\mathrm{p}}b_{\mathrm{p}}S_{\mathrm{p}})=-Q_{\mathrm{p}}^{\mathrm{B}}\end{aligned} \tag{18}$$

where

$$S_{\mathrm{p}}=\langle\mathrm{A,p}|\mathrm{B,p}\rangle$$

The numerical evaluation of the various integrals involving atomic orbitals would be quite tedious. If we neglect the differential overlap between valence AO's in different BO's, we may simplify matters by making use of Mulliken's approximation:[5]

$$\begin{aligned}&(\mathrm{A,p:B,p})\\ &\sim 1/2S_{\mathrm{p}}[(\mathrm{A,p:A,p})+(\mathrm{B,p:B,p})]\end{aligned} \tag{19}$$

Nevertheless, the exchange integrals between the valence AO's on the same atom belonging to adjacent bonds or lone pairs need not necessarily be negligible; they have to be explicitly taken into account. Equation 17 may then be rewritten as:

$$\begin{aligned}W_{\mathrm{e}}^{\circ}=&\sum_{\mathrm{R,p}}(1-Q_{\mathrm{p}}^{\mathrm{R}})H_{\mathrm{R,p}}+2\sum_{\mathrm{p}}F_{\mathrm{p}}\gamma_{\mathrm{p}}\\ &+1/4\sum_{\mathrm{R,pU,p}}(1-Q_{\mathrm{p}}^{\mathrm{R}})(1-Q_{\mathrm{p}}^{\mathrm{U}})J_{\mathrm{R,pU,p}}\\ &+1/2\sum_{\mathrm{R,pT,q}}(1-Q_{\mathrm{p}}^{\mathrm{R}})(1-Q_{\mathrm{q}}^{\mathrm{T}})(J_{\mathrm{R,pT,q}}\\ &-1/2\delta_{\mathrm{R,pT,q}}K_{\mathrm{R,pT,q}})+2\sum_{\mathrm{f}}H_{\mathrm{f}}\\ &+2\sum_{\mathrm{fg}}(J_{\mathrm{fg}}-1/2\delta_{\mathrm{fg}}K_{\mathrm{fg}})\\ &+\sum_{\mathrm{fR,p}}(1-Q_{\mathrm{p}}^{\mathrm{R}})(J_{\mathrm{fR,p}}-1/2\delta_{\mathrm{fR,p}}K_{\mathrm{fR,p}})\end{aligned} \tag{20}$$

where

$$F_{\mathrm{p}}=2a_{\mathrm{p}}b_{\mathrm{p}}=[-S_{\mathrm{p}}+\{1-(1-S_{\mathrm{p}}^{2})Q_{\mathrm{p}}^{2}\}^{1/2}]/(1-S_{\mathrm{p}}^{2}) \tag{21}$$

$$\gamma_{\mathrm{p}}=H_{\mathrm{A,pB,p}}-1/2S_{\mathrm{p}}(H_{\mathrm{A,p}}+H_{\mathrm{B,p}}) \tag{22}$$

and where the R, p, U, p, etc., stand for the valence AO (A, p), (B, p), etc.; f and g refer to lone pair orbitals; $\delta_{\mathrm{R,pT,q}}$, etc., are taken as unity if the R, p and T, q are the valence AO's of the same atom in different bonds, otherwise they are zero.

The variational procedure leads to the following simultaneous equation:

$$\partial W_{\mathrm{e}}^{\circ}/\partial Q_{\mathrm{p}}=0 \tag{23}$$

$$\partial W_{\mathrm{e}}^{\circ}/\partial d_{\lambda}=0,\ \text{etc.} \tag{24}$$

In general, the explicit solutions of Eq. 24 may complicate the discussion; they correspond to the information on the atomic valence state. We may assume that the solutions of Eq. 24 have already been obtained implicitly and that they may then be inserted into Eq. 23. This does not mean that a calculation of the valence states of atoms in molecules is not important—their significance has already been emphasized by Moffitt[6-8]—, but only that it would be beyond the scope of this paper to discuss them here. Equation 23 may now be written as:

$$\begin{aligned}&(H_{\mathrm{B,p}}-H_{\mathrm{A,p}})-2Q_{\mathrm{p}}M_{\mathrm{p}}\gamma_{\mathrm{p}}+1/2(J_{\mathrm{B,pB,p}}\\ &-J_{\mathrm{A,pA,p}})+Q_{\mathrm{p}}[1/2(J_{\mathrm{A,pA,p}}+J_{\mathrm{B,pB,p}})\\ &-J_{\mathrm{A,pB,p}}]+\sum_{\mathrm{T,q}\neq\mathrm{p}}(1-Q_{\mathrm{q}}^{\mathrm{T}})[(J_{\mathrm{B,pT,q}}\\ &-1/2\delta_{\mathrm{B,pT,q}}K_{\mathrm{B,pT,q}})-(J_{\mathrm{A,pT,q}}-1/2\delta_{\mathrm{A,pT,q}}\cdot\\ &K_{\mathrm{A,pT,q}})]+2\sum_{\mathrm{f}}[(J_{\mathrm{B,pf}}-1/2\delta_{\mathrm{B,pf}}K_{\mathrm{B,pf}})\\ &-(J_{\mathrm{A,pf}}-1/2\delta_{\mathrm{A,pf}}K_{\mathrm{A,pf}})]=0\end{aligned} \tag{25}$$

where;

$$\begin{aligned}M_{\mathrm{p}}=&[1-(1-S_{\mathrm{p}}^{2})Q_{\mathrm{p}}^{2}]^{-1/2}=1+1/2(1-S_{\mathrm{p}}^{2})Q_{\mathrm{p}}^{2}\\ &+3/8(1-S_{\mathrm{p}}^{2})^{2}Q_{\mathrm{p}}^{4}+\cdots\cdots\end{aligned} \tag{26}$$

Since we are now considering electron pair bonds, even the small values of the polarity parameters may be of interest. By expanding M_{p} as above and by taking only the zeroth and first powers of Q_{p}, we obtain for Eq. 25:

---

5) R. S. Mulliken, ibid., **46**, 497, 675 (1949).

6) W. Moffitt, *Proc. Roy. Soc.*, **A202**, 534 (1950).

7) W. Moffitt, ibid., **A210**, 245 (1951).

8) W. Moffitt, *Reports Prog. Phys.*, **17**, 173 (1954).

$$Q_\mathrm{p}=K_\mathrm{p}[(\chi_\mathrm{B,p}-\chi_\mathrm{A,p}) + \sum_{\substack{\mathrm{T,q}\\(\mathrm{q}\neq\mathrm{p})}} Q_\mathrm{p}^\mathrm{T}\{(J_\mathrm{B,pT,q}-1/2\delta_\mathrm{B,pT,q}K_\mathrm{B,pT,q}) - (J_\mathrm{A,pT,q}-1/2\delta_\mathrm{A,pT,q}K_\mathrm{A,pT,q})\}] \tag{27}$$

where ;

$$K_\mathrm{p}=[1/2(J_\mathrm{A,pA,p}+J_\mathrm{B,pB,p})-J_\mathrm{A,pB,p}-2\gamma_\mathrm{p}]^{-1} \tag{28}$$

$$\chi_\mathrm{U,p}=\chi_\mathrm{U,p}^\circ+\chi'_\mathrm{U,p} \tag{29}$$

$$\chi_\mathrm{U,p}^\circ=-\varepsilon_\mathrm{U,pU,p}^\circ-1/2J_\mathrm{U,pU,p}^\circ \tag{30}$$

$$\chi'_\mathrm{U,p}=-H'_\mathrm{U,p}-\sum_{\substack{\mathrm{T,q}\\(\mathrm{q}\neq\mathrm{p})}} J'_\mathrm{U,pT,q}-2\sum_\mathrm{f} J'_\mathrm{U,pf} \tag{31}$$

$$\varepsilon_\mathrm{U,pU,p}^\circ=H_\mathrm{U,p}^\circ+\sum_{\substack{\mathrm{T,q}\\(\mathrm{q}\neq\mathrm{p})}}(J_\mathrm{U,pT,q}^\circ-1/2K_\mathrm{U,pT,q}^\circ) +2\sum_\mathrm{f}(J_\mathrm{U,pf}^\circ-1/2K_\mathrm{U,pf}^\circ) \tag{32}$$

The superscripts small circle and prime refer to the corresponding one-center and two-center integrals respectively under the conditions $H_\mathrm{U,p}^\circ+H'_\mathrm{U,p}=H_\mathrm{U,p}$, etc. $\varepsilon_\mathrm{U,pU,p}^\circ$ is the Hartree-Fock energy parameter associated with U, p in the valence state of the atom U and generally not an eigenvalue of the hybridized AO. The $\chi_\mathrm{U,p}$, $\chi_\mathrm{U,p}^\circ$, and $\chi'_\mathrm{U,p}$ may be defined as the "*intramolecular electronegativity of the atom U for the bond p,*" "*the electronegativity of the atom U for the bond p,*" *and* "*the induced electronegativity of the atom U for the bond p,*" respectively; the second quantity is specific for the atom and is equivalent to the electronegativity scale defined by Moffitt;[9] the third quantity consequently also the first, depend on the interaction energy with the other atoms. We may approximate the $\chi_\mathrm{U,p}^\circ$ as:

$$\chi_\mathrm{U,p}^\circ\sim1/2(I_\mathrm{U,p}+E_\mathrm{U,p}) \tag{33}$$

where the approximations $-\varepsilon_\mathrm{U,pU,p}^\circ\sim I_\mathrm{U,p}$, $J_\mathrm{U,pU,p}^\circ\sim I_\mathrm{U,p}-E_\mathrm{U,p}$ are used; the $I_\mathrm{U,p}$ and $E_\mathrm{U,p}$ are the corresponding ionization potential and electron affinity respectively. This definition of electronegativity agrees with the one given by Mulliken.[10]

We may also give a different definition of the electronegativity scale without changing our conclusions. If we add the quantity $J_\mathrm{A,pB,p}$ to the $-\chi'_\mathrm{A,p}$ and $-\chi'_\mathrm{B,p}$ respectively, we obtain the quantities $\varepsilon'_\mathrm{A,pA,p}=-\chi'_\mathrm{A,p}+J_\mathrm{A,pB,p}$, etc., which are the neutral penetration energies and which are usually small. From these quantities, a different electronegativity scale may be defined:

$$\chi_\mathrm{U,p}=-\varepsilon_\mathrm{U,pU,p}-1/2J_\mathrm{U,pU,p} \tag{34}$$

where

$$\varepsilon_\mathrm{U,pU,p}=\varepsilon_\mathrm{U,pU,p}^\circ+\varepsilon'_\mathrm{U,pU,p} \tag{35}$$

Equation 34 corresponds to the generalized definition of Moffitt's electronegativity scale.[9] This procedure causes no changes in the results of Eq. 27, because we have $\chi'_\mathrm{B,p}-\chi'_\mathrm{A,p}=\varepsilon'_\mathrm{A,pA,p}-\varepsilon'_\mathrm{B,pB,p}$. These quantities are generally very small; they become important only if the quantity $(\chi_\mathrm{B,p}^\circ-\chi_\mathrm{A,p}^\circ)$ is zero or very small, because the order of the magnitude of $(\chi'_\mathrm{B,p}-\chi'_\mathrm{A,p})$ may then become compatible with $(\chi_\mathrm{B,p}^\circ-\chi_\mathrm{A,p}^\circ)$. This effect may, therefore be called the "*homopolar inductive effect or the quantum-mechanical inductive effect;*" it depends on the position of the bond in the molecule, but not on the polarities of the other bonds.

The K_p's are considered to be specific for the bond p, because the γ_p's are not supposed to depend on the adjacent atoms or bonds, as follows from their definition. They are also defined as:

$$K_\mathrm{p}=\partial Q_\mathrm{p}/\partial(\chi_\mathrm{B,p}-\chi_\mathrm{A,p}) \tag{36}$$

This suggests that the K_p may be called the "*auto-polarizability of the bond p*"; that is, the K_p measures the change of Q_p when the electronegativity difference is changed. The K_p may be approximated by:

$$K_\mathrm{p}\sim[1/2\{I_\mathrm{A,p}-E_\mathrm{B,p}) + (I_\mathrm{B,p}-E_\mathrm{A,p})\}-J_\mathrm{A,pB,p}-2\gamma_\mathrm{p}]^{-1} \tag{37}$$

The first term is the average energy of the ion pairs $\mathrm{A^+B^-}$ and $\mathrm{A^-B^+}$ at infinite distances, and the second and third terms correspond to the average values of the Coulomb attraction and exchange repulsion energies of these ion pairs respectively. To a good approximation, therefore, K_p is regarded as an inverse of the average energy of the ion pairs $\mathrm{A^+B^-}$ and $\mathrm{A^-B^+}$ at the equilibrium distance of bond p. We may conclude that the mobilities of the electrons in the bond decrease with an increase in the average energy of these two ion pairs. The sign of K_p is always positive, because the second and third terms of Eq. 28 have opposite signs and their sum—which corresponds to the interaction energy between atoms A and B—is small compared with the first term, which is always

---

[9] W. Moffitt, *Proc. Roy. Soc.*, **A202**, 548 (1950).
[10] R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).

positive. This is important for the interpretation of the empirical rules, as will be shown later.

Now we wish to introduce the following inductive parameter:

$$\begin{aligned}\Pi_{\mathrm{pq}}=K_{\mathrm{p}}[&(J_{\mathrm{B,pA,q}}-1/2\delta_{\mathrm{B,pA,q}}K_{\mathrm{B,pA,q}})\\ &-(J_{\mathrm{A,pA,q}}-1/2\delta_{\mathrm{A,pA,q}}K_{\mathrm{A,pA,q}})\\ &-(J_{\mathrm{B,pB,q}}-1/2\delta_{\mathrm{B,pB,q}}K_{\mathrm{B,pB,q}})\\ &+(J_{\mathrm{A,pB,q}}-1/2\delta_{\mathrm{A,pB,q}}K_{\mathrm{A,pB,q}})]\\ \equiv{}&\delta_{\mathbf{P}+\mathbf{P}'}\Pi_{\mathbf{P}(\mathrm{B,pA,p})\mathbf{P}'(\mathrm{A,qB,q})}\\ &(\mathrm{q}\neq\mathrm{p}) \qquad (38)\end{aligned}$$

where **P** and **P′** are the operators which represent the permutations of the orders of B, p, A, p, etc., and where $\delta_{\mathbf{P}+\mathbf{P}'}$ is unity when $(\mathbf{P}+\mathbf{P}')$ is even, and otherwise minus unity. Equation 27 may now be simplified as:

$$Q_{\mathrm{p}}=Q_{\mathrm{p}}^{\circ}+Q_{\mathrm{p}}' \qquad (39)$$

where

$$Q_{\mathrm{p}}^{\circ}=K_{\mathrm{p}}(\chi_{\mathrm{B,p}}-\chi_{\mathrm{A,p}}) \qquad (40)$$

$$Q_{\mathrm{p}}'=\sum_{\mathrm{q}\neq\mathrm{p}}\Pi_{\mathrm{pq}}Q_{\mathrm{q}} \qquad (41)$$

It follows from these equations that the bond polarity, Q_{p}, consists of the following two parts: 1) Q_{p}°, the specific bond polarity of the bond p, which is determined by the electronegativity difference if we neglect the small homopolar inductive effect, and 2) Q_{p}', the induced bond polarity, which is induced by the polarity of the other bonds. These equations also give another definition of Π_{pq}:

$$\Pi_{\mathrm{pq}}=\partial Q_{\mathrm{p}}/\partial Q_{\mathrm{q}} \qquad (42)$$

This means that Π_{pq} is a measure of the change in Q_{p} when Q_{q} is changed; it may be defined as the "*mutual polarizability of the bond p to the bond q*" for p≠q. For p=q, the quantity Π_{pp} is always unity and may be defined as the "*self-polarizability of the bond p*." The Π_{pq}'s have the following additional properties:

$$\Pi_{\mathrm{pq}}/\Pi_{\mathrm{qp}}=K_{\mathrm{p}}/K_{\mathrm{q}},\ 0<|\Pi_{\mathrm{pq}}|<1\ \ (\mathrm{q}\neq\mathrm{p}) \qquad (43)$$

So far we have considered one specified bond p only. Equations 27 and 39, however, are in principle simultaneous equation. We will proceed to derive their explicit solutions. we obtain the explicit solution of Eq. 27 as:

$$\overline{Q}_{\mathrm{p}}=\Delta_{\mathrm{p}}/\Delta_{\mathrm{n}},\quad (p=1,2,3,\ldots\ldots,n) \qquad (44)$$

where;

$$\Delta_{\mathrm{n}}=\det\{2\delta_{\mathrm{pq}}-\Pi_{\mathrm{pq}}\} \qquad (45)$$

which is a determinant of n rows and columns; Δ_{p} is obtained from Δ_{n} by replacing the pth column of Δ_{n} by the column $(Q_1^{\circ}, Q_2^{\circ}, Q_3^{\circ}, \ldots\ldots, Q_{\mathrm{n}}^{\circ})$; n and p denote the total number of bonds in the molecule and the pth bond respectively and $\overline{Q}_{\mathrm{p}}$ stands for the corresponding SCF value of Q_{p}.

Let us now define the following quantity:

$$\overline{\Pi}_{\mathrm{pq}}=(-1)^{\mathrm{p+q}}\Delta_{\mathrm{n}}^{\mathrm{pq}}/\Delta_{\mathrm{n}}=\partial\overline{Q}_{\mathrm{p}}/\partial Q_{\mathrm{q}}^{\circ} \qquad (46)$$

where $\Delta_{\mathrm{n}}^{\mathrm{pq}}$ is the determinant obtained by striking out from Δ_{n} the pth column and qth row. $\overline{\Pi}_{\mathrm{pq}}(p\neq q)$ may be called the "*SCF mutual polarizability of the bond p to the bond q*" corresponding to Π_{pq}, and $\overline{\Pi}_{\mathrm{pp}}$, "*SCF self-polarizability of the bond p*" corresponding to Π_{pp}. These definitions allow us to rewrite:

$$\overline{\boldsymbol{Q}}=\overline{\boldsymbol{\Pi}}\boldsymbol{Q}^{\circ} \qquad (47)$$

where $\overline{\boldsymbol{Q}}$ and $\boldsymbol{Q}^{\circ}$ are column vectors whose components are given by Eqs. 44 and 40 respectively, and where $\overline{\boldsymbol{\Pi}}$ is a matrix with components that are given by Eq. 46. That is, these components are combined by the relation $Q_{\mathrm{p}}=\sum_{\mathrm{q}}\overline{\Pi}_{\mathrm{pq}}Q_{\mathrm{q}}^{\circ}$.

We have so far considered only the case where the bond polarities are small. In general, the quantity K_{p} may formally be written as:

$$\begin{aligned}K_{\mathrm{p}}=[&1/2(J_{\mathrm{A,pA,p}}+J_{\mathrm{B,pB,p}})\\ &-J_{\mathrm{A,pB,p}}-2M_{\mathrm{p}}\gamma_{\mathrm{p}}]^{-1} \qquad (48)\end{aligned}$$

Apparently we obtain the general theory if we replace γ_{p} by $M_{\mathrm{p}}\gamma_{\mathrm{p}}$, as is indicated by Eq. 28. The extreme values for M_{p} are reached for $|Q_{\mathrm{p}}|=0$ (pure homopolar bond) as $M_{\mathrm{p}}=1$ and for $|Q_{\mathrm{p}}|=1$ (pure ionic bond) as $M_{\mathrm{p}}=|S_{\mathrm{p}}|^{-1}$. Since, in the interval $0\leq|Q_{\mathrm{p}}|\leq 1$, M_{p} is a monotonous and single-value function of Q_{p}, it will have all the values between 1 and $|S_{\mathrm{p}}|^{-1}$. If Q_{p} is no longer small with respect to unity, it is necessary to solve Eq. 47 by means of an SCF procedure and by considering the explicit dependence of M_{p} on Q_{p}. This may become a very cumbersome problem. Since, in general, $\overline{Q}_{\mathrm{p}}$ will not be very different from Q_{p}°, we may take to a first approximation the M_{p} value which corresponds to Q_{p}°. This will not affect the values of K_{p} very much.11) The K_{p} may then be defined specifically for the bond p, and we may follow the the preceding argument just as it is.

---

11) Since the S_{p} values for σ bonds are usually around 0.5, M_{p} can only take values from 1 to 2. Therefore this may be a satisfactory approximation.

The SCF bond polarities, $\overline{Q}_p$, thus obtained enable us to determine the coefficients, a_p and b_p, of the valence AO as:

$$a_p^2 = 1/2(1-\overline{Q}_p - F_pS_p), \text{ and}$$

$$b_p^2 = 1/2(1+\overline{Q}_p - F_pS_p) \tag{49}$$

The corresponding values, $\overline{Q}_p^-$, for the anti-bonding orbital of the bond p may similarly be derived if it is borne in mind that $\overline{Q}_p^- = -\overline{Q}_p^+$ as a result of the orthogonality between the bonding and anti-bonding orbitals of the bond p.

We are now in a position to solve the secular equation 15 by taking the SCF BO as a basis. We will then be able to determine the first order SCF LCBO MO's and their eigenvalues. The method will be described in Section III in connection with the semi-empirical approach.

II. Second Order Theory.—In the first order treatment we neglected the interactions between bonding and anti-bonding orbitals. We will now proceed to a more accurate treatment in which these interactions are explicitly considered. Since they are usually small, they may be treated as perturbations. We may then take the above sets of the SCF LCBO MO's and their eigenvalues as a basis for developing the second order theory.

The overlap integrals between the bonding and anti-bonding orbitals may be neglected even in this higher approximation, as has been discussed above. By making use of first and second order perturbation theories, we easily obtain the following perturbed MO's ψ_i, their eigenvalues, ε_i, and also the molecular electronic energy, W_e:

$$\psi_i = \psi_i^+ - \sum_k [\beta_{ik}^{+-}/(\varepsilon_k^- - \varepsilon_i^+)]\,\psi_k^- \tag{50}$$

$$\varepsilon_i = \varepsilon_i^+ - \sum_k (\beta_{ik}^{+-})^2/(\varepsilon_k^- - \varepsilon_i^+) \tag{51}$$

$$W_e = W_e^\circ - \sum_{ik} (\beta_{ik}^{+-})^2/(\varepsilon_k^- - \varepsilon_i^+) \tag{52}$$

where β_{ik}^{+-} is the component of the Hamiltonian matrix that represents the interactions between occupied and unoccupied MO's in a first order theory. The occupied MO's and their eigenvalues in the ground state only are described here. The corresponding quantities for unoccupied MO's are obtained in a similar fashion.

Since all the BO's are represented as linear combinations of the AO's, the LCBO MO's may finally be reduced to the LCAO's. These LCAO MO's may then be considered to be good approximations of Roothaan's SCF LCAO MO's. The localized MO's obtained from these MO's by means of a unitary transformation are now not strictly localized in the specific bonds or lone pairs, whereas in the first order theory the orbitals have been the BO's themselves. Therefore, the second order theory includes a consideration of the delocalization of bond or lone pair electrons, which is generally taken to be small for σ-electron systems. In our theory the delocalization is described in terms of the electron transfer from bonding to antibonding orbitals on different bonds.

III. Semi-empirical Approach.—Le us now set out to solve Eq. 15, which is the secular equation in the first order theory. By making use of the results obtained in Section I, we can easily estimate the values of the diagonal elements, L_{pp}, of the SCF LCBO Hamiltonian matrix. Since within the present approximation the matrix $\boldsymbol{c}$ is unitary, the L_{pp}^{++} may be rewritten as:

$$\begin{aligned} L_{pp}^{++} &= H_p + \sum_q (2J_{pq} - K_{pq}) \\ &= -1/2(\chi_{A,p} + \chi_{B,p}) + 1/2J_{A,pB,p} \\ &\quad + 1/4\overline{Q}_p(J_{B,pB,p} + J_{A,pA,p}) - 1/2 \sum_{\substack{T,q \\ (q\neq p)}} \overline{Q}_q^T \cdot \\ &\quad [(J_{A,pT,q} - 1/2\delta_{A,pT,q}K_{A,pT,q}) \\ &\quad + (J_{B,pT,q} - 1/2\delta_{B,pT,q}K_{B,pT,q})] \\ &\quad + (F_p + M_p\overline{Q}_p^2)\gamma_p \end{aligned} \tag{53}$$

and, for lone pairs:

$$L_{ff}^{++} = -\chi_{ff} - \sum_{R,p} \overline{Q}_p^R (J_{fR,p} - 1/2\delta_{fR,p}K_{fR,p}) \tag{54}$$

where:

$$\begin{aligned} \chi_{ff} &= -H_f - 2\sum_g (J_{fg} - 1/2\delta_{fg}K_{fg}) \\ &\quad - \sum_{R,p} (J_{fR,p} - 1/2\delta_{fR,p}K_{fR,p}) \end{aligned} \tag{55}$$

$\chi_{A,p}$, etc. are defined by Eq. 29. The corresponding L_{pp}^{--} values for the anti-bonding orbital of the bond p are similarly derived. However, we do not obtain the values for the non-diagonal elements, $L_{pq}(p\neq q)$, in this way because these quantities are not considered in the treatment described in Section I. Non-empirical calculations of these quantities are usually very tedious, especially for the large organic molecules that we wish to consider. Furthermore, even if Eq. 15 were solved, we would find the same difficulty in estimating the β_{pq}^{+-}, which will appear in the calculation of β_{ik}^{+-} in the second order theory. Therefore, we wish to propose the following semi-empirical method:

1) The values of $\alpha_{pp}(\equiv L_{pp}$ including $L_{pp}^{--})$, etc. are determined non-empirically from Eq. 53 or 54.

2) The values of $\beta_{pq}^{++}(\equiv L_{pq}^{++})$, etc. are taken as empirical parameters, and Eq. 15 is then solved.

3) The values of β_{pq}^{+-} are also taken as empirical parameters. These assumptions enable us to perform perturbation calculations.

4) The results of the calculations are used to estimate the values of β_{pq}^{++}, β_{pq}^{+-}, etc., from the observed ionization potentials, spectroscopic data, etc.

The present semi-empirical method for σ-electron systems is very similar to the method developed by Pariser and Parr[12] for π-electron systems, as may be seen from our procedure for determining the α and β values. Since it is a relatively simple method, we expect it to be applicable to calculations of many properties of complex molecules.

IV. Inductive and Resonance Effects.—The concepts of "*inductive effect*" and "*resonance effect*," both of which are related to electron migration, have proved to be useful in organic chemistry. The inductive effect was originally defined as a classical electrostatic effect.[12,13] Even though several theoretical studies[13-18] of the inductive effect have been reported, we feel that its theoretical foundation has not yet been properly established. Therefore, we will try to discuss it on the basis of our theory.

In general, the inductive parameters, Π_{pq}, which were defined by Eq. 38 will be especially large if p and q are two adjacent bonds. If the adjacent bonds, p and q, are chosen in such a way that the A, p and A, q are AO's of the same atom, A, the sign of Π_{pq} should be negative and, therefore, Q_p and Q_q should have opposite signs, because the second term in the brackets of Eq. 38 is then dominant and K_p is positive. The intra-bond charge transfer in bonds p and q should, therefore, follow the direction of the arrows in Fig. 1. When this theorem is applied to the adjacent bonds of large molecules, for example, to the mono-substituted *n*-hydrocarbons, $C_mH_{2m+1}X$, the intra-bond electron transfers should follow the arrows in Fig. 2, since we take X to be more electronegative than the carbon. This conclusion agrees with that of the classical treatment[13] of the inductive effect. Equation 41 may thus be regarded as a quantum-mechanical representation of the inductive effect. The similarity between classical and quantum-mechanical results is confirmed by an inspection of the brackets of Eq. 38, which correspond to Coulomb interactions between the (A, p), (B, p), (A, q) and (B, q) if we take the (A, p) and (B, q) to be positive point charges and the (A, q) and (B, p) to be negative point charges or vice versa. It has thus been shown that the procedure for determining the bond polarity in the first order theory corresponds to a consideration of the inductive effect. Hereafter we will use the term "*inductive effect*" in this sense. The application of the inductive effect will be described in the second paper of this series.

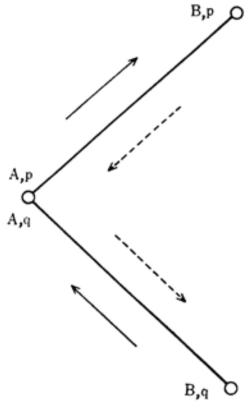
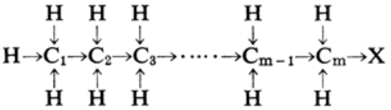


Fig. 1. Intra-bond charge transfers in the adjacent bonds p and q caused by the inductive effect.



$$\begin{array}{ccccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & & & \mathrm{H} & & \mathrm{H} & & \\ & & \downarrow & & \downarrow & & \downarrow & & & & \downarrow & & \downarrow & & \\ \mathrm{H} & \rightarrow & \mathrm{C}_1 & \rightarrow & \mathrm{C}_2 & \rightarrow & \mathrm{C}_3 & \rightarrow \cdots\cdots \rightarrow & & & \mathrm{C}_{m-1} & \rightarrow & \mathrm{C}_m & \rightarrow & \mathrm{X} \\ & & \uparrow & & \uparrow & & \uparrow & & & & \uparrow & & \uparrow & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

Fig. 2. Intra-bond charge transfers in the $C_mH_{2m+1}X$ molecule caused by the inductive effect.

The significance of the resonance effect for conjugated systems is well established; it is accompanied by a stabilization energy of the molecule which has been called "*resonance energy*" or "*conjugation energy*." On the other hand, for σ-electron systems, this effect is generally taken to be small. In our theory

---

[12] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

[13] K. Higashi, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **57**, 1006 (1936).

[14] L. G. Groves and S. Sugden, *J. Chem. Soc.*, **1937**, 158.

[15] R. P. Smith, T. Ree, J. L. Magee and H. Eyring, *J. Am. Chem. Soc.*, **73**, 2263 (1951).

[16] J. M. Cahill and C. R. Mueller, *J. Chem. Phys.*, **24**, 513 (1956).

[17] C. D. Re, *J. Chem. Soc.*, **1958**, 4031.

[18] S. Maeda, This Bulletin, **31**, 260 (1958).

it has been defined as the delocalization of σ-bond electrons in the second order theory. The resonance energy of molecules is then represented by the second term of Eq. 52. We will use the term "*resonance effect*" in the above sense.

We have thus defined the two effects separately on the basis of reasonable approximations; previous theories did not even distinguish between the two effects. The differences will become more obvious in the following considerations. In the first order theory, the electron density in each BO is equal to two, and the bond order[19] between different BO's is zero in our approximation. The inductive effect may then be defined as an intrabond charge transfer; even then the electron density in each bond or lone pair is still two and the inter-bond orders are zero. On the other hand, the resonance effect corresponds to an inter-bond charge transfer from bonding to anti-bonding orbitals on different bonds.

Discussion

The present semi-empirical MO theory may not be as rigorous as the non-empirical SCF LCAO MO method but at least it makes it possible to deal satisfactorily with large molecules. Essentially based on the Hartree-Fock method, it is obtained by introducing some additional assumptions and approximations. However, it is impossible to avoid the deficiencies inherent in all one-electron methods; this causes the K_p to predict equal probabilities for the two possible ionic structures, A^+B^- and A^-B^+. This defect may be removed by considering the correlation between the paired electrons with opposite spins. This correlation problem has already been discussed by several authors.[20-25]

It may be valuable to compare our approach with previous theoretical work on the subject. Lennard-Jones[13] and his collaborators[26-28] have shown that the usual delocalized MO for saturated molecules may be replaced by a set of equivalent orbitals. However, their determination requires a knowledge of molecular symmetry. Recently Edmiston and Ruedenberg[2] proposed a method for determining more general localized MO's that do not follow from the molecular symmetry. The authors suggest that in a more precise theory each MO may be represented as a linear combination of the above localized orbitals. Although the localized orbitals are sometimes hard to determine, especially for large organic molecules, it is possible to overcome this difficulty by replacing the orbitals by the ordinary bond orbitals; this was done in the LCBO MO theory of Brown.[29] In this treatment the MO's are represented as linear combinations of bonding orbitals only, and the contributions of the anti-bonding orbitals are neglected. It was subsequently pointed out by Dewar and Pettit[30] that the contributions from the anti-bonding orbitals to the molecular energy, though small, are not negligible and that they ought to be taken into account. This delocalization effect of σ-electrons was also accounted for by Mulliken et al.[31] in terms of hyperconjugation.

The practical advantage of our theory is that it is closely connected with familiar chemical concepts such as inductive effect and electronegativity. This makes it possible to explain some previously proposed empirical rules. The details will be described in subsequent papers.

It is worth noting that the definitions of the absolute scale of electronegativity are independent of the different approaches. Our definition agrees with those obtained by Parks and Parr[20] or Oohata,[23] who used different approaches in which the correlation is taken into account; that is, all the results lead to the Moffitt scale.[9] This seems to support the validity of the absolute electronegativity scale. A detailed discussion of the electronegativity will be presented in a subsequent paper.

Summary

A semi-empirical MO theory is proposed for complex saturated molecules. In a first-order treatment, each MO is represented as a localized function that contains only the AO connected with one bond or atom. This enables us to define a set of bonding, anti-bonding and lone-pair orbitals. The molecular wave function is obtained as an anti-symmetrized product of the bonding and lone-pair orbitals.

---

[19] The bond orders between BO are defined in the same way as for AO, the term "*inter-bond bond order*" is sometimes used in this paper.

[20] J. M. Parks and R. G. Parr, *J. Chem. Phys.*, **28**, 335 (1958).

[21] A. C. Hurley, J. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc.*, **A220**, 446 (1953).

[22] K. Oohata, *J. Phys. Soc. Japan*, **15**, 1048 (1960).

[23] K. Oohata, *Prog. Theor. Phys.*, **25**, 215 (1961).

[24] O. Sinanoglu, *J. Chem. Phys.*, **33**, 1212 (1960).

[25] J. M. Foster and S. F. Boys, *Revs. Modern Phys.*, **32**, 300 (1960).

[26] G. G. Hall and J. Lennard-Jones, *Proc. Roy. Soc.*, **A202**, 155 (1950).

[27] J. Lennard-Jones and J. A. Pople, ibid., **A202**, 166 (1950).

[28] J. Lennard-Jones and G. G. Hall, *Discussions Faraday Soc.*, **10**, 18 (1951).

[29] R. D. Brown, *J. Chem. Soc.*, **1953**, 2615.

[30] M. J. S. Dewar and R. Pettit, ibid., **1954**, 1625.

[31] R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

In this approximate theory we discuss the definitions of the electronegativity scale and of the inductive effect; the electronegativity scales proposed by Moffitt and Mulliken are obtained as special cases. In a subsequent, more accurate second-order theory each MO is represented as a linear combination of all bonding, anti-bonding and lone-pair orbitals; this treatment is made by means of the perturbation theory. A semi-empirical approach is developed by taking the interactions between different bonds as empirical parameters. No applications of the general theory are presented here; they will be discussed in subsequent papers.

The author wishes to thank Dr. H. F. Hameka for his stimulating interest and encouragement and Professor R. G. Parr for his reading of the manuscript.

Department of Chemistry
University of Pennsylvania
Philadelphia 4, Pennsylvania, U.S.A.