I - INTRODUCTION

The purpose of this project was three-fold: to understand in detail the complete neglect of differential overlap (CNDO) approximate molecular orbital theory of Pople, Santry, and Segal[1] as well as the intermediate neglect of differential overlap (INDO) theory of Pople, Beveridge, and Dobosh;[2] to adapt a computer program of these theories to the computer facilities available to Sweet Briar and in so doing to gain an insight into algorithmic solutions to quantum chemical problems; and to apply the modified program to a simple problem, a comparison of the effects of chlorine and fluorine on the σ and π electron densities in a series of substituted acetylenes and ethylenes.

II - THEORETICAL

Quantum mechanical theory has been developed to the extent that the Schroedinger equation for any hypothetical or real two-body system can be solved exactly. (An example of a two-body system would be a system with one electron and one nucleus.) A problem with more than one electron around one nucleus, and, in the more complicated cases, more than one nucleus, presents insurmountable difficulties in the exact solution of the Schroedinger equation due to the increased complexity of the Hamiltonian and concurrently of the partial differential equation which must be solved. The time-independent Schroedinger equation for the hydrogen atom, for example, is

$$\left\{-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{r}\right\}\Psi(1)=E\Psi(1) \tag{1}$$

where $\hbar$ is Planck's constant/2π, m is the mass of the electron, $\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$, Ze is the charge of the nucleus (Z=1 for hydrogen), e is the unit of electronic charge and r the distance between the electron and the nucleus. In this expression the first term represents the quantum mechanical operator for the kinetic energy of the system while the second is the potential energy of the electron in the field of the nucleus. Though this equation is a partial differential equation of the second degree with three variables it can be solved by separation of variables as discussed in most quantum mechanics textbooks.[3]

In contrast to the above soluble differential equation is the Schroedinger equation for the many-electron, many center problem which must include the interactions between all the electrons and between the electrons and nuclei. The Hamiltonian for

such a system is given by

$$(2)\ H^{total}(1,2,\ldots N;1,2,\ldots n) = -\frac{\hbar^2}{2}\sum_{A}^{N} M_A^{-1}\nabla_A^2 + \sum_{A<B} e^2 Z_A Z_B r_{AB}^{-1} - \frac{\hbar^2}{2m}\sum_{p}^{n}\nabla_p^2 - \sum_{A}\sum_{p} e^2 Z_A r_{Ap}^{-1} + \sum_{p<q} e^2 r_{pq}^{-1}$$

In the above expression M_A = the mass of nucleus A, m and e are electronic mass and charge, $Z_A e$ is the charge of nucleus A, and r_{ij} is the distance between electron i and electron j. (Note that capital subscripts refer to nuclei and subscripts in the lower case to electrons.) Inspection of the Hamiltonian reveals that kinetic energy terms for all the nuclei and electrons are included as well as the potential energy due to the interaction of each particle with all other particles of the system.

The Schroedinger equation for a system with n particles and N nuclei thus becomes a partial differential equation of 3N + 3n variables, each variable being described by three cartesian coordinates.

$$(3)\ H^{total}(1,2,\ldots,N;1,2,\ldots,n)\,\Psi(1,2,\ldots N;1,2,\ldots n) = E\,\Psi(1,2,\ldots N;1,2,\ldots n)$$

This equation cannot be solved exactly.

Though solutions to the Schroedinger equation for the H atom are of great theoretical interest, there has been a continuous effort among chemists to extend the practical application of the equation to more complicated systems through scientifically sound and meaningful approximations. A recent approximation developed by Pople, Santry and Segal is the complete neglect of differential overlap (CNDO) theory;[1] the intermediate neglect of differential overlap (INDO) theory of Pople, Beveridge, and Dobosh[2] is derived from the CNDO framework.

The CNDO method indirectly utilizes several general approximations which are common to many approximate molecular orbital theories as well as specific approximations which make it unique. One such general approximation is the Born-Oppenheimer approximation which states that the nuclei of a system can be considered stationary relative to the motion of the electrons in their fields. In reality the nuclei of a system are in motion as are the electrons. The mass of any nucleus is so much greater than the mass of an electron that its velocity can be neglected when compared with the much greater velocity of an electron. In the case of the hydrogen nucleus, for example, where this approximation introduces the greatest amount of error, the mass of the nucleus is over 1800 times that of the electron; thus even here the error is small. This assumption reduces the complexity of the problem considerably; one must calculate only n wavefunctions and energies corresponding to the n electrons in motion around N stationary nuclei. The Hamiltonian of equation (3) becomes

$$(4)\quad H^{elec} = \frac{-\hbar^2}{2m}\sum_p \nabla_p^2 - \sum_A \sum_p e^2 Z_A r_{Ap}^{-1} + \sum_{p<q} e^2 r_{pq}^{-1}$$

and the Schroedinger equation

$$(5)\quad H^{elec}(1,2,\ldots,n)\,\psi^{elec}(1,2,\ldots,n) = \varepsilon\,\Psi(1,2,\ldots n)$$

It is important to note here that due to the Born-Oppenheimer approximation only the electronic energy eigenvalues are calculated. In order to include the internuclear repulsion one must add

$$(6)\quad \sum_{A<B} e^2 Z_A Z_B r_{AB}^{-1}$$

with $Z_A e$ the charge on nucleus A, $Z_B e$ the charge on nucleus B and r_{AB} the internuclear distance. The expression for the total energy of a system using the Born-Oppenheimer approximation is therefore

$$(7) \quad E^{total} = E^{elec} + \sum_{A<B} e^2 Z_A Z_B r_{AB}^{-1}$$

Molecular orbital theory is chiefly concerned with the wavefunctions which describe the motion of electrons with respect to the nuclei, as this motion results in the phenomenon of a covalent chemical bond between two or more nuclei. The Born-Oppenheimer approximation's focus on electronic wavefunctions is viable if this is kept in mind, and this approximation thus can be considered "scientifically sound."

A second fundamental approximation utilized in approximate molecular orbital theories is the orbital approximation. The underlying assumption of this approximation is that a satisfactory many-electron molecular orbital wavefunction Ψ can be constructed from a product of functions ϕ_i, each of which depends on the coordinates of one electron only.

$$(8) \quad \Psi(1,2,\ldots,n) = \phi(1)\,\phi(2)\,\phi_3(3)\cdots\phi_n(n)$$

(The parenthetical numbers in equation 8 refer to electronic coordinates.) By definition each function ϕ_i is known as an orbital, in the case of an atom, an atomic orbital and in the case of a molecule, a molecular orbital. As Pople and Beveridge point out,[4] if the true Hamiltonian could be constructed as a sum of operators depending only on the coordinates of one electron, then a separation of variables approach could yield exact solutions to the

Schroedinger equation for the system. This, as has been shown, however, is not the case (see equation (3)), and the assumption that the molecular wavefunction is of the above form introduces an approximation and some degree of error.

As well as these general approximations, a specific theoretical framework - the variational method - is used in the CNDO and other approximate molecular orbital methods as a general approach to the solution of the complex problem. This method is based on the variational theorem which, according to Dewar,[5] states that "the expectation value of H for an arbitrary well-behaved function Ψ is not less than the lowest eigenvalue E_0 of H" where the expectation value E is given by

$$(9) \qquad E = \frac{\int \Psi^{*} H \Psi \, d\tau}{\int \Psi^{*} \Psi \, d\tau}$$

For proof of this theorem the reader may refer to *Molecular Quantum Mechanics* by P. W. Atkins[6] as well as other quantum chemistry texts. If one applied the variational method to a completely flexible wavefunction with an infinite number of variable parameters one could obtain all the correct wavefunctions and eigenvalues for the Hamiltonian. Such an application is not feasible for mathematical as well as practical reasons, however, but the approach can be applied to incompletely flexible functions which can be varied and minimized with respect to only a given few parameters. The set of functions thus obtained are approximations to the true wavefunctions, and the energies corresponding to the Ψ_i are functions of the variable parameters. The variation theorem, then, provides a method for adjusting the variable parameters of some arbitrary trial wavefunction to opti-

mize the correspondence of that wavefunction to the true wavefunction. (For example, if E(k) is found to be an eigenvalue of some arbitrary wavefunction $\Psi(k)$, the variation method calls for minimization of E(k) with respect to k ($\partial/\partial k\, E(k)=0$) and a solution for the minimum value of k. Substitution of the minimum value of k into E(k) will yield E_{min}, and substitution of the minimum value of k into $\Psi(k)$ will, according to the variational theorem, give the best approximate wavefunction using the given parameter.) A convenient choice of eigenfunctions in the variational method is often a set of functions which are linear combinations of atomic orbitals. (LCAO).

$$(10) \qquad \Psi_i = \sum_{\mu} c_{\mu i}\, \phi_\mu$$

where ϕ_μ are atomic orbitals and $c_{\mu i}$ are weighting coefficients. A further requirement imposed by the LCAO approximation is that the molecular orbitals be orthonormal. That is,

$$(11) \qquad \sum_{\mu\nu} c^*_{\mu i}\, c_{\nu j}\, S_{\mu\nu} = \delta_{ij}$$

where δ_{ij} is the Kronecker delta and $S_{\mu\nu}$ is the overlap integral

$$(12) \qquad S_{\mu\nu} = \int \phi_\mu(1)\, \phi_\nu(1)\, d\tau.$$

The above brief discussion of some of the important general approximations and the methods used in approximate molecular orbital theories leads to a more rigorous analysis of the CNDO and INDO methods. The following formulations of these theories will deal with closed-shell systems only.

As well as being based on the above general approximations, the CNDO method is a simplification of the LCAO approach to the

Hartree-Fock, self-consistent field (SCF) method. The LCAO/SCF approach leads to Roothaans algebraic equations.

The Hartree-Fock equations are

$$(13) \quad F\psi_i = \varepsilon_i \psi_i \qquad i = 1, n$$

where

$$(14) \quad F = \left[H^{core} + \sum_j (2J_i - K_j)\right]$$

$$(15) \quad J_i(1) = \int \psi_i^*(2) \frac{1}{r_{12}} \psi_i(2)\, d\tau_2$$

and

$$(16) \quad K_j(1)\,\psi_i(1) = \left[\int \psi_j^*(2) \frac{1}{r_{12}} \psi_i(2)\, d\tau_2\right] \psi_j(1)$$

In the above equations H^{core} refers to the Hamiltonian of an electron in the field of a bare nucleus and r_{12} to the interelectronic distance. The eigenvalues of the above Hamiltonian F are

$$(17) \quad \varepsilon_i = H_{ii}^{core} + \sum_j (2J_{ij} - K_{ij})$$

where

$$(18) \quad J_{ij} = \iint \psi_i^*(1)\,\psi_j^*(2) \frac{1}{r_{12}} \psi_i(1)\,\psi_j(2)\, d\tau_1\, d\tau_2$$

and

$$(19) \quad K_{ij} = \iint \psi_i^*(1)\,\psi_j^*(2) \frac{1}{r_{12}} \psi_j(1)\,\psi_i(2)\, d\tau_1\, d\tau_2$$

J_{ij} and K_{ij} are known as "coulomb" and "exchange" integrals respectively. J_{ij} represents the repulsion between electron 1 in orbital ψ_i and electron 2 in orbital ψ_j when the electrons are moving independently of each other. (Note that $\psi_i^*\psi_i$ and $\psi_j^*\psi_j$ by definition each represent a charge distribution, the probability of finding an electron in a given position.) Similarly the exchange integral K_{ij} has the physical interpretation that it represents the reduction in electron repulsion between two electrons in different

orbitals with parallel spins.[7]

If the molecular orbitals Ψ_i are approximated as linear combinations of atomic orbitals, Roothaans equations are obtained. Substitution of the LCAO expansion of equation (10) into the Hartree-Fock equations yields

$$(20) \quad \sum_{\nu} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{\nu i} = 0$$

where

$$(21) \quad F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \tfrac{1}{2} (\mu\lambda|\nu\sigma) \right]$$

$$(22) \quad H_{\mu\nu} = \int \phi_\mu(1) H^{core} \phi_\nu(1) \, d\tau_1$$

$$(23) \quad P_{\lambda\sigma} = 2 \sum_{i}^{occ} c^{*}_{\lambda i} c_{\sigma i}$$

and

$$(24) \quad (\mu\nu|\lambda\sigma) = \int \phi_\mu(1) \phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda(2) \phi_\sigma(2) \, d\tau_1 \, d\tau_2$$

The quantity $(\mu\nu|\lambda\sigma)$ is known as an electron interaction integral; electron (1) is assumed to be on the left-hand side of the operator and electron (2) on the right-hand side.

The equations (20) may be written in matrix form and transformed to the form of a standard eigenvalue problem. If this is done the elements ε_i will be roots of the secular determinant

$$(25) \quad |F_{\mu\nu} - \varepsilon S_{\mu\nu}| = 0$$

and each element ε_i will be an energy eigenvalue of the molecular orbital Ψ_i. In equation (21) $H_{\mu\nu}$ is the expectation value for the core Hamiltonian interacting with electron (1) in atomic orbital ϕ_μ and electron (1) in atomic orbital ϕ_ν. (Note that suffixes μ and ν refer to molecular orbital Ψ_i, and λ and σ to molecular orbi-

tal Ψ_j.) In equation (23) $P_{\lambda\sigma}$ is summed over the occupied molecular orbitals only, and the matrix composed of the elements $P_{\lambda\sigma}$ is referred to as the density matrix.

The series of steps used in solving the secular determinant in equation (25) is equivalent to that used in the more approximate CNDO approach. An initial set of linear expansion coefficients is assumed from which is determined an initial density matrix (see equation (23). A first guess at the matrix elements $F_{\mu\nu}$ can then be made. After diagonalization a new set of coefficients is computed, and the process is repeated until a comparison of old and new values of the coefficients or some other chosen parameter is within a specified tolerance limit.

The LCAO/SCF method can be applied without modification to simple systems, but computational limitations have resulted in the growth of more approximate self-consistent field methods which seek to avoid the evaluation of many of the electron repulsion integrals, most of which actually have values near zero when calculated. Pople proposed the combinations of the zero differential overlap (ZDO) approximation[8] with a semiempirical determination of other parameters for the π electrons of aromatic systems.[9] The ZDO approach is based on systematic neglect of the overlap of certain pairs of electrons in different orbitals. According to this approximation

$$(26)\quad (\mu\nu|\lambda\sigma) = (\mu\mu|\lambda\lambda)\,\delta_{\mu\nu}\,\delta_{\lambda\sigma}$$

where δ_{ij} is the Kronecker delta. Further, the corresponding overlap integrals

$$(27)\quad S_{\mu\nu} = \int \phi_\mu(1)\,\phi_\nu(1)\,d\tau$$

are neglected in the normalization of the molecular orbitals.

It is important to note, however, that the core integrals

$$(28)\qquad H_{\mu\nu} = \int \phi_\mu(1)\, H^{core}\, \phi_\nu(1)\, d\tau_1$$

involving an overlap distribution are not neglected by this method; the terms have a possible effect on bonding.

Thus while not ignoring all such interactions as does the Huckel method, the ZDO treatment is not as rigorous as the above complete LCAO/SCF approach. Pople, Santry, and Segal's formulation of CNDO theory[1] signifies a significant advance in approximate molecular orbital theory in that the ZDO approximation is extended to a system involving all valence electrons rather than just the π electrons of the molecule, the inner electrons being treated as part of a rigid, non-polarizable core.

Pople, Santry, and Segal[1] as well as Pople and Beveridge[10] discuss the importance of maintaining invariance with respect to certain transformations of the set of basis functions ϕ_μ at all levels of application of the ZDO approximation. These transformations are (1) transformations mixing orbitals of the same principle and azimuthal quantum numbers n and l (a mixing of $2p_x$ and $2p_y$ orbitals, for example) and (2) transformations mixing any atomic orbitals on the same atom (hybridization of orbitals, for example.) The LCAO/SCF method will lead to the same wavefunctions and properties regardless of these transformations; any approximation to the method, however, might remove this invariance.

Because the ZDO approximation is applied to atomic orbitals only, the differential overlap $\phi_\mu\phi_\nu$ may be monotomic (atomic orbitals centered on the same atom) or diatomic (atomic orbitals centered on different atoms.) In the case of a monotomic overlap

$\phi_\mu \phi_\nu$ on the same atom, the simple rotation of axis transformation such as transformation (1) may lead to variant results unless this possibility is considered in the development of the theory.

In the CNDO method in particular the ZDO approximation is used for all products of different atomic orbitals $\phi_\mu \phi_\nu$. To restore invariance under all transformations a further approximation is added to those of the ZDO approximation - that the electron interaction integrals which remain depend only on the atoms A and B to which the orbitals ϕ_μ and ϕ_ν belong and not on the type of orbital.

$$(29) \quad (\mu\mu|\nu\nu) = \gamma_{AB} \quad \left\{ \begin{array}{l} \text{all } \mu \text{ on atom A} \\ \text{all } \nu \text{ on atom B} \end{array} \right\}$$

γ_{AB} physically measures an average repulsion between an electron in one of the valence orbitals of atom A and an electron in one of the valence orbitals of atom B.

If the atomic orbitals of the basis set are transformed into orbitals which themselves are linear combinations of the original atomic orbitals,

$$(30) \quad \phi'_\alpha = \sum_\mu^A t_{\mu\alpha} \phi_\mu$$

$$(31) \quad \phi'_\beta = \sum_\nu^A t_{\nu\beta} \phi_\nu$$

$$(32) \quad \phi'_\gamma = \sum_\lambda^B t_{\lambda\gamma} \phi_\lambda$$

$$(33) \quad \phi'_\delta = \sum_\sigma^B t_{\sigma\delta} \phi_\sigma$$

then it can be shown that equation (29) restores invariance. The electron interaction interaction $(\mu\nu|\lambda\sigma)$ becomes

$$(34) \quad (\alpha\beta|\gamma\delta) = \gamma_{AB}\, \delta_{\gamma\delta}\, \delta_{\alpha\beta}$$

based on the orthonormality of the transformation matrices t. (In equation (34) δ_{ij} is the Kronecker delta.) These transformations thus do not cause equation (29) to vary.

Application of the ZDO approximation to the elements of the Fock Hamiltonian matrix of equation (21) gives

$$(35)\quad F_{\mu\mu} = H_{\mu\mu} + \sum_{\lambda} P_{\lambda\lambda}\left[(\mu\mu|\lambda\lambda) - \tfrac{1}{2}(\mu\lambda|\mu\lambda)\right]$$

$$= H_{\mu\mu} - \tfrac{1}{2} P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\lambda} P_{\lambda\lambda}(\mu\mu|\lambda\lambda)$$

For the case in which $\mu \neq \nu$

$$(36)\quad F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}(\mu\mu|\nu\nu)$$

Adding the further approximations of equation (29), the diagonal Fock matrix elements become

$$(37)\quad F_{\mu\mu} = H_{\mu\mu} - \tfrac{1}{2} P_{\mu\mu}\gamma_{AA} + \sum_{B} P_{BB}\gamma_{AB} \qquad (\phi_\mu \text{ on } A)$$

and the elements for which $\mu \neq \nu$ become

$$(38)\quad F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}\gamma_{AB}$$

In equation (37) the population matrix P_{BB} is the total electron density on atom B.

$$(39)\quad P_{BB} = \sum_{\lambda}^{B} P_{\lambda\lambda}$$

The core Hamiltonian operator, which consists of the potential due to the nucleus and the inner non-valence shells, is also modified according to the approximations proposed. If

$$(40)\quad H = -\tfrac{1}{2}\nabla^2 - \sum_{B} V_B$$

where $-V_B$ is the core potential of atom B, the diagonal elements

elements $H_{\mu\mu}$ of the Hamiltonian may be thought of as a sum of one-center and two-center terms. (A one-center term is a term involving only one atom, while a two-center term involves interatomic interaction between two atoms.) These diagonal elements represent the interaction of an electron in ϕ_μ centered on atom A with the core of A as well as with the cores of other atoms. Separating into one and two-center contributions

$$(41)\quad H_{\mu\mu} = U_{\mu\mu} - \sum_{B\neq A} \langle \mu | V_B | \mu \rangle \quad (\phi_\mu \text{ on } A)$$

where

$$(42)\quad U_{\mu\mu} = \langle \mu | -\tfrac{1}{2}\nabla^2 - V_A | \mu \rangle$$

$$(43)\quad \langle \mu | V_B | \mu \rangle = \int \phi_\mu V_B \phi_\mu \, d\tau$$

and

$$(44)\quad \langle \mu | -\tfrac{1}{2}\nabla^2 - V_A | \mu \rangle = \int \phi_\mu (-\tfrac{1}{2}\nabla^2 - V_A) \phi_\mu \, d\tau$$

According to equation (44) $U_{\mu\mu}$ is a one-center term, and since ϕ_μ is on atom A, the integral represents the interaction of an electron in orbital ϕ_μ with its own core potential. The second term of equation (41) relates the potentials of all other atoms B to the electron in orbital ϕ_μ on atom A; it is the two-center contribution to the core Hamiltonian element $H_{\mu\mu}$.

The off-diagonal terms deal with two different atomic orbitals ϕ_μ or ϕ_ν which may both be on atom A or which may be on different atoms. When ϕ_μ and ϕ_ν are both on atom A

$$(45)\quad H_{\mu\nu} = U_{\mu\nu} - \sum_{B(\neq A)} \langle \mu | V_B | \nu \rangle \quad (\phi_\mu, \phi_\nu \text{ on atom } A)$$

Because the choice of a hybrid basis set (not s, p, d functions) leads to non-zero $U_{\mu\nu}$ elements in equation (45), the CNDO method is restricted to the use of s, p, d functions. This choice for a

basis set causes $U_{\mu\nu}$ to be zero by symmetry. The second term in equation (45) represents the interactions of the charge distribution $\phi_\mu\phi_\nu$ with the cores of other atoms B. These terms lead to a further approximation which is consistent with the ZDO approximation, that these interactions are set equal to zero unless $\phi_\mu=\phi_\nu$, in which case they are considered equal for all valence orbitals on A. No differentiation is made between types of orbitals based on quantum numbers. This approximation allows invariance to be maintained. According to these added approximations

$$(46) \quad \langle \mu | V_B | \nu \rangle = 0$$

$$(47) \quad \langle \mu | V_B | \mu \rangle = V_{AB}$$

$$(48) \quad H_{\mu\mu} = U_{\mu\mu} - \sum_{B(\neq A)} V_{AB} \qquad (\mu \text{ on atom } A)$$

and

$$(49) \quad H_{\mu\nu} = 0 \qquad (\mu \neq \nu,\ \phi_\mu, \phi_\nu \text{ on atom } A)$$

The remaining matrix elements $H_{\mu\nu}$ to be considered are the elements dealing with atomic orbitals ϕ_μ and ϕ_ν on different atoms A and B. Neglecting three-center terms, the CNDO method assumes that $H_{\mu\nu}$ is dependent only on the potential of the two atoms in question and not on the potentials of any other atoms. The term $H_{\mu\nu}$ thus deals with the effect of two electrostatic fields on the energy levels of an electron and is referred to as the "resonance integral" $\beta_{\mu\nu}$. In this case

$$(50) \quad H_{\mu\nu} = \langle \mu | -\tfrac{1}{2}\nabla^2 - V_A - V_B | \nu \rangle = \beta_{\mu\nu}$$

The final approximation of the CNDO method deals with the

estimation of a value for the resonance integral,

$$(51) \quad H_{\mu\nu} = \beta_{\mu\nu} = \beta^{0}_{AB} S_{\mu\nu}$$

where $S_{\mu\nu}$ is the overlap integral. This approximation formulates $\beta_{\mu\nu}$ in terms of a known integral $S_{\mu\nu}$ (one which has already been calculated) and an empirical parameter β^{0}_{AB} which is adjusted to achieve the best energy values for a given system. In order to maintain invariance, however, the parameter β^{0}_{AB} must be the same for all orbitals on the two atoms in question. It can be dependent on interatomic distance, however.

The approximations thus employed by the CNDO method are

(a) the zero differential overlap approximation

$$(52) \quad (\mu\nu|\lambda\sigma) = (\mu\mu|\nu\nu)\,\delta_{\mu\nu}\,\delta_{\lambda\sigma}$$

which also calls for the neglect of the overlap integral $S_{\mu\nu}$ in the normalization of the molecular orbitals and sets $S_{\mu\nu} = 0$ unless $\mu = \nu$

(b) the averaging of the electron interaction integral between ϕ_{μ} on A and ϕ_{λ} on B

$$(53) \quad (\mu\mu|\lambda\lambda) = \gamma_{AB} \qquad \begin{Bmatrix} \phi_{\mu} & \text{on} & A \\ \phi_{\lambda} & \text{on} & B \end{Bmatrix}$$

(c) the approximation of the interaction of $\phi_{\mu}\phi_{\nu}$ with other cores as zero if $\phi_{\mu} \neq \phi_{\nu}$ and V_{AB} if $\phi_{\mu} = \phi_{\nu}$

$$(54) \quad \langle \mu | V_B | \nu \rangle = 0$$

$$(55) \quad \langle \mu | V_B | \mu \rangle = V_{AB}$$

and lastly

(d) the approximation of resonance integrals through use of a proportionality factor

$$(56) \quad H_{\mu\nu} = \beta^{0}_{AB} S_{\mu\nu} \qquad (\phi_{\mu} \text{ on } A,\ \phi_{\nu} \text{ on } B)$$

The final Fock matrix elements reduce to

$$(57)\quad F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \tfrac{1}{2} P_{\mu\mu})\gamma_{AA} + \sum_{B\neq A} (P_{BB}\gamma_{AB} - V_{AB})$$

$$(58)\quad F_{\mu\nu} = \overset{\circ}{\beta}_{AB} S_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}\gamma_{AB} \qquad (\mu \neq \nu)$$

where ϕ_μ is on A and ϕ_ν on B. If ϕ_μ and ϕ_ν are both on the same atom A

$$(59)\quad F_{\mu\nu} = -\tfrac{1}{2} P_{\mu\nu}\gamma_{AA}$$

The diagonal elements $F_{\mu\mu}$ may be written

$$(60)\quad F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \tfrac{1}{2} P_{\mu\mu})\gamma_{AA} + \sum_{B(\neq A)} [-Q_B\gamma_{AB} + (Z_B\gamma_{AB} - V_{AB}$$

where Q_B is the net charge on atom B.

$$(61)\quad Q_B = Z_B - P_{BB}$$

The quantity $Z_B\gamma_{AB} - V_{AB}$ is known as a penetration integral and is the difference between the potentials due to the valence electrons and the core of atom B.

After developing the CNDO theory, Pople and Segal follow with a discussion of possible methods for calculation and choice of parameters.[11] The original formulation is known as the CNDO/1 parameterization. They since have proposed a second and more successful method, the CNDO/2 parameterization.[12] As well as choosing a basis set, in the CNDO method one must empirically determine or otherwise specify values for the overlap integral $S_{\mu\nu}$, the core Hamiltonian elements $U_{\mu\mu}$, V_{AB}, the electron-repulsion integrals γ_{AB} and the bonding parameters $\overset{\circ}{\beta}_{AB}$.

A logical choice of basis functions would seem to be the hydrogenic wavefunctions. These wavefunctions, however, are expressed as products of an angular and a radial part, the latter

of which is mathematically complex and necessitates the evaluation of difficult integrals. For this reason the atomic orbitals in the CNDO method are chosen to be combinations of the spherical harmonics $Y_{lm}(\theta,\phi)$(the angular hydrogenic solution) and Slater functions[13] radial-like functions which are less complex than the true radial hydrogenic solutions. Slater functions are nodeless with an orbital exponent ζ which is determined by application of an empirical set of rules, Slater's rules. (In the CNDO approximation the exponent for hydrogen, however, is given a value of 1.2 instead of 2.6, the value determined by Slater's rules; 1.2 is more in accord with the best value for the constant according to the LCAO calculation for the hydrogen molecule.) The CNDO/1 parameterization was originally formulated only for molecules composed of atoms H through F.

The overlap integral $S_{\mu\nu}$ is generally calculated in the following way: the overlap integral may be written

$$(62)\quad S_{ab} = \int \Omega_{ab}(1)\,d\tau$$

where Ω_{ab} is a charge distribution function and is a product of any two Slater-type-orbitals (STO) χ_a and χ_b which are themselves specified by principle, azimuthal and magnetic quantum numbers (n, l, m).

$$(63)\quad \Omega_{ab}(1) = \chi_a(1)\,\chi_b(1) \qquad \left\{ \begin{matrix} \chi_a \text{ on atom } A \\ \chi_b \text{ on atom } B \end{matrix} \right\}$$

If χ_a and χ_b are on the same atom,

$$(64)\quad \begin{matrix} S_{ab} = 0 & \chi_a \neq \chi_b \\ S_{ab} = 1 & \chi_a = \chi_b \end{matrix}$$

The charge distribution $\Omega_{ab}(1)$ is written as a product of the analytical form of the STO's in spherical coordinates. If

$$(65)\ \chi_a(r,\theta,\phi) = N_a r^{n_a-1} \exp(-\zeta_a r)\, Y_{\ell_a m}(\theta,\phi)$$

$\Omega_{ab}(1)$ becomes

$$(66)\ \Omega_{ab}(1) = N_a N_b\, r_A^{n_a-1}\, r_B^{n_b-1} \exp(-\zeta_a r_A - \zeta_b r_B)$$
$$\times\ \Theta_{\ell_a m}(\cos\theta_A)\ \Theta_{\ell_b m}(\cos\theta_B)\ \Phi_m^2(\phi)$$

(The functions $\Theta_{\ell_a m}(\cos\theta_A)\Phi_m(\phi)$ are the real normalized shperical harmonics $Y_\ell^m(\theta,\phi)$.) $\Omega_{ab}(1)$ is transformed to elliptical coordinates and the integration is carried out over ϕ. The result of this integration is the reduced overlap integral, an expression involving one or more basic two-center integrals which is subsequently integrated over the μ and v coordinates to yield the value for the overlap integral.

The electron repulsion integral γ_{AB} is calculated as a two-center integral involving valence s functions.

$$(67)\ \gamma_{AB} = \iint s_A^2(1)\ \frac{1}{r_{12}}\ s_B^2(2)\ d\tau_1\, d\tau_2$$

Using Slater s functions

$$(68)\ \gamma(n_a,n_b,\zeta_a,\zeta_b,R) = \iint \Omega_{aa}(1)\ \frac{1}{r_{12}}\ \Omega_{bb}(2)\ d\tau_1\, d\tau_2$$

where R is the distance between atom A and atom B, and $\Omega_{aa}(1)$ and $\Omega_{bb}(2)$ are the products of Slater s functions and represent charge distributions. The operator $\frac{1}{r_{12}}$ is developed according to a given expansion, and the coulomb integral rearranged accordingly,

$$(69)\ \gamma(n_a,n_b,\zeta_a,\zeta_b,R) = \int \Omega_{aa}(1)\ I(n_b,\zeta_b,1)\ d\tau_1$$

where I is the potential of electron 2 at the position of electron 1.

$$(70)\quad I(n_b, l_b, 1) = \int \frac{1}{r_>} \Omega_{bb}(2)\, d\tau_2$$

In equation (70) $\frac{1}{r_>}$ is the final form of the operator $\frac{1}{r_{12}}$ based on the development according to the expansion. $r_>$ represents the greater value between r_1 and r_2 where r_1 and r_2 are the radii arrived at in the expansion and transformation to spherical polar coordinates.

The two-center coulomb integral is then solved in two steps, the first being an evaluation of the potential $I(n_b, l_b, 1)$ by integration of equation (70) over spherical polar coordinates centered on b and the second a multiplication of the results of the first step by $\Omega_{aa}(1)$ and integration over the coordinates of electron 2 in elliptical coordinates. The second integration is done through use of the reduced overlap integral.

The third empirically determined value, V_{AB}, representing the interaction of a valence electron of atom A with the core charge of atom B, is calculated through use of a valence s orbital on A and through the assumption that the core charge of atom B is centered at a point in the nucleus rather than dispersed throughout the nucleus and inner shells (as likely is the case).

$$(71)\quad V_{AB} = Z_B \int s_A^2(1) \left(\frac{1}{r_{1B}}\right) d\tau_1$$

Z_B is the core charge of atom B, and r_{1B} is the distance between electron 1 and nucleus B. This integral is handled in the same general way as the overlap integral with s being a Slater s type orbital.

Calculation of the atomic matrix elements of the one-electron core Hamiltonian $U_{\mu\mu}$ is based on observed atomic energy

levels. Applying the CNDO approximations, atoms from Li through F have energies

$$(72)\quad E(X, 2s^m 2p^n) = m\,U_{2s,2s} + n\,U_{2p,2p} + \tfrac{1}{2}(m+n)(m+n-1)\gamma_{AA}$$

where X is the atom in question and γ_{AA} is the CNDO approximation of the electron repulsion integrals. Equation (72) refers to an electronic state, and since degeneracy occurs due to the neglect of exchange integrals in the CNDO method, an average of the energies of all the states having the given configuration is used in calculating the $U_{\mu\mu}$ elements. Further, the $U_{\mu\mu}$ integrals are related to ionization potentials or electron affinities of given states, experimental values of either of the two being used in the determination of $U_{\mu\mu}$. The γ parameters previously determined are also used in this calculation.

Having empirically calculated $U_{\mu\mu}$, the only remaining parameter to be specified is β°_{AB}. β°_{AB} is assumed to be a sum of contributions from atom A and atom B.

$$(73)\quad \beta^{\circ}_{AB} = \tfrac{1}{2}(\beta^{\circ}_{A} + \beta^{\circ}_{B})$$

The values of β°_{A} and β°_{B} are chosen to give the best fit with accurate LCAO/SCF calculations using the valence shell basis set. These values, then, are based on the assumption that the LCAO/SCF calculations are the best calculations obtainable.

With the determination of the parameters $S_{\mu\nu}$, $U_{\mu\mu}$, V_{AB}, γ_{AB} and β°_{AB}, the solution of the problem calls for a cycle of steps similar to that discussed for the LCAO/SCF method. The initial guess of the molecular orbital coefficients is made by setting $F_{\mu\mu}$ equal to the appropriate ionization potentials for the state

being considered and by setting $F_{\mu\nu} = S_{\mu\nu}\beta^{\circ}_{AB}$. The latter is similar to the familiar Hückel approximation in that all off-diagonal elements are set equal to constants, $S_{\mu\nu}\beta^{\circ}_{AB}$. Diagonalization of this extended-Hückel approximation to the Fock matrix yields a set of eigenvectors (the coefficients) and eigenvalues (orbital energies). Electrons are then paired, and the pairs assigned to the molecular orbitals with lowest energies. Using the values of the coefficients, the density matrix is computed, which subsequently is used in the determination of new coefficients. The cycle is thus

(a) an initial guess at the Fock matrix by a Huckel-like approximation

(b) diagonalization of the matrix to yield a set of energies and molecular orbital coefficients

(c) determination of the density matrix $P_{\mu\nu}$ from the coefficients computed in (b)

(d) formation of a new Fock matrix using the density matrix of (c) (see equations (57), (58), and (59))

Steps (b), (c), and (d) are repeated until a given parameter remains within a specified limit, at which time the molecular orbitals determined are declared "self-consistent."

The CNDO/2 parameterization[12] attempts to rectify some of the discrepancies between calculated CNDO/1 molecular properties and corresponding experimentally determined values. When testing the CNDO/1 parameterization Pople and Segal found that it was unsatisfactory if used to estimate equilibrium internuclear bondlengths.[10] For example, the bond length computed for HF was 0.581 Å, well below that experimentally determined, 0.92 Å. As a result, the dissociation energies calculated were also well

off from the experimental data. It was found that the penetration integrals ($Z_B \gamma_{AB} - V_{AB}$) were the source of the problem since they gave rise to bonding energies when there should have been none. The CNDO/2 method accordingly neglects altogether this term by

$$(74) \quad V_{AB} = Z_B \gamma_{AB}$$

Due to equation (74) the penetration integral obviously becomes zero.

The second difference between the CNDO/1 and CNDO/2 theories deals with the computation of $U_{\mu\mu}$. In the CNDO/1 theory ionization potentials were used or, alternatively, electron affinities. The CNDO/2 procedure is to use an average of both ionization potentials and electron affinities to account for the tendency of the atomic orbital to lose and gain electrons. The CNDO/2 alterations of CNDO/1 parameterizations cause equation (57) to become

$$(75) \quad F_{\mu\mu} = -\tfrac{1}{2}(I_\mu + A_\mu) + \left[(P_{AA} - Z_A) - \tfrac{1}{2}(P_{\mu\mu} - 1)\right]\gamma_{AA} + \sum_{B(\neq A)} (P_{BB} - Z_B)\gamma_{AB}$$

where I_μ is the ionization potential of atomic orbital ϕ_μ and A_μ is the electron affinity of the orbital.

Aside from modifications in the method for determination of $U_{\mu\mu}$ and the neglect of the penetration integral, the features of the CNDO/2 theory are the same as those of the CNDO/1 theory. In the CNDO/2 method other parameters are calculated as in the CNDO/1 method, and the same self-consistent—type cycle is used to obtain a solution. These two changes, however, improve the success of the calculations with respect to bond lengths and dissociation energies.

The CNDO/1 and CNDO/2 parameterizations were originally proposed for molecules composed of atoms through atomic number 9 (fluorine) with a maximum of 4 basis functions per atom (2s, $2p_x$, $2p_y$, and $2p_z$). The difficulties of extending the theory through the second row of elements (through chlorine) are practical ones. Few accurate LCAO/SCF calculations for heavier atoms are available for comparison of results, and atomic energy levels of the 3d atomic orbitals are also difficult to obtain. Santry and Segal attempt to extend the theory,[14] however, considering first a basis set of five 3d atomic orbitals with the same radial part as the 3s and 3p functions (the spd set) and second, a basis set with more accurate d functions (the spd' set). The latter involves modifications in the CNDO/2 theory but will not be discussed because the former is the basis set for the heavier atoms sodium to chlorine in the computer program to be discussed in the next section.

Calculations using an spd basis set rely on the CNDO/2 parameterization as discussed above with a difference in the method of estimating bonding parameters β°_{AB} .

$$(76) \quad \beta^{\circ}_{AB} = \tfrac{1}{2} K \left(\beta^{\circ}_{A} + \beta^{\circ}_{B} \right)$$

If A is a second-row element and C a first-row element, β°_{A} is approximated by the proportionality relation

$$(77) \quad \beta^{\circ}_{A} = \beta^{\circ}_{C} \, \frac{U_{3s,3s}(A) + U_{3p,3p}(A)}{U_{2s,2s}(C) + U_{2p,2p}(C)}$$

where U refers to the core Hamiltonian elements. The proportionality constant K is set equal to unity if only first row atoms are involved but is given a value of 0.75 if either A or B is a second-

row element. Such a proportionality constant was found to improve the overall estimation of β°_{AB} values and thus of the theory itself.

Following the formulation of the CNDO/2 parameterization, Pople, Beveridge, and Dobosh proposed the intermediate neglect of differential overlap (INDO) method[2] to alleviate problems in the CNDO calculation for open-shell systems. The CNDO method frequently does not account for separation of states arising from the same configuration, nor, in some cases, does it yield spin densities in the σ orbitals of open-shell molecules.[2] Each of these problems is closely related to the neglect of the two-electron exchange integral

$$(78)\quad (\mu\nu|\mu\nu) = \iint \phi_\mu(1)\,\phi_\mu(2)\,\frac{1}{r_{12}}\,\phi_\nu(1)\,\phi_\nu(2)\,d\tau_1\,d\tau_2 \qquad \left\{\begin{matrix}\mu \neq \nu \\ \phi_\mu, \phi_\nu \text{ on } A\end{matrix}\right\}$$

For this reason the INDO method retains monotomic differential overlap in one-center integrals. In this way the elements of the Fock matrix are modified by

$$(79)\quad F_{\mu\mu} = U_{\mu\mu} + \sum_{\lambda\sigma}^{A}\left[P_{\lambda\sigma}(\mu\mu|\lambda\sigma) - \tfrac{1}{2}P_{\lambda\sigma}(\mu\lambda|\mu\sigma)\right] + \sum_{B(\neq A)}(P_{BB} - Z_B)\,\gamma_{AB} \qquad (\mu \text{ on atom } A)$$

$$(80)\quad F_{\mu\nu} = U_{\mu\nu} + \sum_{\lambda\sigma}^{A}\left[P_{\lambda\sigma}(\mu\nu|\lambda\sigma) - \tfrac{1}{2}P_{\lambda\sigma}(\mu\lambda|\nu\sigma)\right. \qquad \left\{\begin{matrix}\mu \neq \nu \\ \phi_\mu, \phi_\nu \text{ on } A\end{matrix}\right\}$$

and

$$(81)\quad F_{\mu\nu} = \tfrac{1}{2}(\beta^{\circ}_A + \beta^{\circ}_B)\,S_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\,\gamma_{AB} \qquad \left\{\begin{matrix}\mu \text{ on } A \\ \nu \text{ on } B\end{matrix}\right\}$$

The above formulation of the INDO Fock matrix elements is based on closed-shell theory since this is the main concern of the entire paper. However, the basic application is to open-shell molecules because in general the CNDO and INDO results are very similar for closed-shell systems.[15] For a sample comparison

of CNDO and INDO calculations on the same molecule, the reader is referred to appendix A.

The INDO theory has not been implemented for molecules containing atoms of the second row. Its use, therefore, is still limited to atoms H through F.

In spite of the above limitations the CNDO and INDO theories have been applied to a wide variety of problems. One obvious area of concentration has been the determination of the equilibrium geometries of molecules through minimization of the total energy. Calculations of this sort involve systematic variation of the molecular coordinates. Through application of either of these theories equilibrium bond angles as well as bond lengths may be determined.

CNDO/2 calculations of equilibrium geometries have been reported for diatomic, AB_2, and AB_3 molecules.[12] Comparison of theoretical results with experimental bond lengths and bond angles is, on the whole, encouraging. Pople and Gordon have continued such calculations and comparisons, using INDO theory and systematically studying molecules containing the atoms H, C, N, O, and F with one or two polyvalent atoms (C, N, or O).[16] If A and B represent polyvalent atoms and X and Y represent H and F, the categories of molecules they studied are AX_2, AXY, AX_3 AX_2Y, AX_4, AX_3Y, AX_2Y_2, XAB, X_2AB, XAAX, X_2ABX, X_2AAX_2, X_3ABX, X_3ABX_2, and X_3AAX_3. Their results also indicate that the INDO theory produces calculations which are for the most part in keeping with experimental values.[16] A summary of their results with special emphasis on quantitative variance from experimental values may be found in

Pople and Beveridge, Approximate Molecular Orbital Theory (see footnote 4), pp. 97-109).

A second application of the CNDO and INDO theories is in the calculation of electronic charge distribution. The diagonal element $P_{\mu\mu}$ of the density matrix represents the electronic population of atomic orbital ϕ_{μ}. A summation of all the electronic populations centered on one atom yields the electronic population of that atom.

$$(82)\quad P_{AA} = \sum_{\mu}^{A} P_{\mu\mu}$$

Dipole moment is a molecular property closely related to the electronic charge distribution. In the CNDO and INDO approximations, dipole moment is considered to be the sum of two contributions, one from the net charges at the nuclear positions and one which is a hybridization term involving the displacement of the charge away from the center of the nucleus.[1,2]

$$(83)\quad \mu = \mu_{chg} + \mu_{hyb}$$

$$(84)\quad \mu = 2.5416 \sum_{A} \Delta P_{AA} R_{A} \quad \text{debyes}$$

$$(85)\quad (\mu_{hyb})_{x} = -14.674 \sum_{A}^{*} \zeta_{A}^{-1} P_{2s_A} P_{2p_{xA}} \quad \text{debyes}$$

In equation (84) ΔP_{AA} is the net atomic charge $(Z_A - P_{AA})$, and R_A is the position vector of nucleus A. In equation (85) ζ_A is the Slater orbital exponent of valence orbitals on atom A, and the asterisk indicates that the summation is restricted to atoms other than H.

Pople and Segal as well as Pople and Beveridge report CNDO/2 dipole moment calculations for AB_2 and AB_3 type molecules[12,17] which correlate well with experimental values. They report also that

a comparison of CNDO and INDO calculations reveals that the inclusion of the one-centered exchange integral has little effect on dipole moment calculations. In all the above cases dipole moments were calculated for molecules with an equilibrium configuration as determined by CNDO or INDO theory.

Another completely different approach from the two discussed above utilizes standard bond angles and bond lengths, assuming that they closely approximate true equilibrium geometries and can therefore give meaningful results for other molecular properties. Pople and Gordon discuss this approach and propose a set of standard bond lengths and bond angles to be used in such calculations.[18]

Molecular properties of larger molecules may be calculated in this manner, and Pople and Gordon have computed LCAO molecular orbitals, charge distributions, and dipole moments from standard geometries for many organic molecules.[18] They have found that the agreement between experimental and calculated dipole moments is good, with few exceptions. One problem in their comparison, however, is that their assumed standard geometries sometimes differ from those determined by spectral data in a microwave determination of dipole moment. Pople and Beveridge outline the findings of Pople and Gordon[19], summarizing their significance with respect to theories of electron displacement. Among the molecules discussed are simple nonpolar hydrocarbons, fluorine compounds, oxygen compounds, nitrogen compounds, and mixed compounds of nitrogen, oxygen and fluorine.

Further general applications involving INDO theory and

open-shell molecules include calculations of electron spin-nuclear spin interactions,[20] spin densities,[2] hyperfine coupling constants,[20] and nuclear spin-nuclear spin interactions.[21] These applications specifically refer to free radicals, radical cations, and radical ions - paramagnetic molecules - and only INDO theory as discussed above will yield tenable results due to its inclusion of the one-center exchange integral.

Other applications of the CNDO/2 theory include a wide range of interesting problems. Several independent studies of substituent effects have been reported. Examples are a CNDO/2 calculation of substituent effects on localization,[22] a CNDO/2 study of the effect of the methyl group on the charge distribution and relative stabilities of conjugated carbonium ions,[23] and a calculation of the inductive effect of the methyl group.[24] Recent structural calculations using CNDO theory include calculations for a series of carbonium ions,[25] for intermediates and transition states in electrophilic substitution,[26] and calculations for p-benzoquinone[27] as well as for trans - and cis-diimides.[28] Also, comparisons of spectral analyses and CNDO calculations have been carried out by Sadlij and Kecki[29] and by Brownlee and Taft.[30] The latter study attempts to correlate the effect of substituents on charge distribution in fluorine molecular orbitals with fluorine proton shifts in NMR spectra.

The above are only selected references to interesting applications of CNDO and INDO theory. Since their development less than ten years ago the two theories have been widely used. One common feature of many of the applications to this point, however, has been a prevalent inherent skepticism as to the quantitative

accuracy of the calculated results. Thus, often an author uses other experimental findings to corroborate CNDO or INDO calculations and to justify his choice of one of the two theories for his structural framework. A great deal of experimental work has therefore been involved with proving that structure, dipole moments, and other calculated properties <u>do</u> correlate well with experimental data. Such work first showed the inadequacies of the CNDO theory in certain situations and led to the development of INDO theory.

In my opinion, one cannot emphasize enough that these are approximate molecular orbital theories and therefore cannot be expected to be perfectly in keeping with experiment for every calculation. The theories themselves have areas in which improvement is possible. A study on the possibility of improving the estimation of β parameters has been reported.[31] Further, specific areas of the theory have been investigated resulting, for example, in a proposal for substitution of semiempirical coulomb integrals for those originally proposed.[32] In the same study the authors also suggest the introductions of a new empirical parameter to differentiate resonance integrals between σ orbitals and those between π orbitals.

Because of the approximate nature of the theories, use of data for qualitative rather than quantitative predictions seems to be theoretically more meaningful. With further improvement in the CNDO and INDO methods, quantitative use of calculations is likely to become more feasible. In their present form, however, both methods represent a significant advance over other less

sophisticated theories, specifically those dealing only with π electrons rather than with an entire valence set of basis functions.

III - IMPLEMENTATION OF THE CNDO AND INDO THEORIES

A computer program designed for CNDO and INDO calculations was obtained from Dr. Paul A. Dobosh although it is also available through the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Indiana. In the following pages the features of the original program will be discussed, as well as the modifications necessary to adapt the program to a National Cash Register Century 200 computer with a memory size of 64K.

The program offers the user an option of selecting either the CNDO or INDO general theory for computation and performs calculations for open or closed-shell systems. The CNDO/2 parameterization is used in all CNDO calculations. The maximum size molecule that the program can accommodate is one with 35 atoms or 80 basis functions (or both). All elements through Cl may be included in the molecule if the CNDO method is chosen. If the INDO method is desired, only elements through F may be included in the molecule. INDO theory is implemented in appropriate sections of the program by an optional INDO set of calculations which makes corrections to matrix elements calculated by the CNDO method. In both the CNDO and INDO options, the basis functions assigned to each atom correspond to the minimum basis set or valence orbitals of the atom.

The program is structured into subroutines, each of which performs one of the calculations required by the CNDO or INDO theory. The main program, which appears first, serves only to input the data, convert the coordinates from angstroms to atomic

units and call the subroutines necessary to complete the calculation. The "COMMON" statement of the Fortran language is used throughout the program to store information in a labeled section of the computer's memory; through use of this feature the information can be accessed by all subroutines, and the computations performed by one subroutine can be passed on to other independent parts of the program. For example, the statement "COMMON/INFO/NATOMS, CHARGE, MULTIP, AN(35), C(35,3)" stores the values of the number of atoms, the charge of the molecule, the multiplicity, and the arrays of atomic numbers and coordinates. At any point in the entire operation of the program this information will be located in a particular block of memory known as "INFO" and can be accessed by any subroutine. Data calculated in subroutines but not stored in such a common memory space is lost when control is returned to the main program unless the subroutine is parameterized in some way.

In the original program the subroutine COEFFT serves to store the values of the coefficients needed in the calculations of the coulomb and overlap integrals. The subroutine INTGRL accomplishes these computations through application of the methods described in the theoretical section. INTGRL calls subroutines RELVEC, SS, HARMTR, and MATOUT while SS calls subroutines AINTGS and BINTGS. From this it can be seen that a major portion of the program is involved with the calculation of the overlap and coulomb matrices. RELVEC serves to calculate the unit vector distance along an interatomic axis between pairs of basis functions, each pair of basis functions giving rise to an overlap matrix

element PAIRS (I,J). Each basis function is paired with all the other basis functions of the molecule; thus the overlap matrix for HF, with 5 basis functions, is 5 X 5. The function SS, called in the calculation of the non-zero matrix elements, computes the reduced overlap integral discussed in the theoretical section. Following computation, a rotation matrix calculated by HARMTR transforms the integrals to a molecular basis, and the matrix $S_{\mu\nu}$ is stored in COMMON/ARRAYS/S.

One-center and two-center coulomb integrals are subsequently computed in INTGRL, using, again, the reduced overlap integrals calculated by SS. These integrals are calculated for pairs of <u>atoms</u>, rather than pairs of basis functions, and the matrix is therefore NATOMS X NATOMS in size, where NATOMS represents the number of atoms.

Subroutine HUCKCL initiates an LCAO/SCF-type calculation. The diagonal elements $F_{\mu\mu}$ of a Huckel-like approximation to the Fock matrix are initially replaced by the average of the ionization potential and electron affinity as described in section II. The non-diagonal elements $F_{\mu\nu}$ are estimated by $\frac{S_{\mu\nu}}{2}(\beta_A^{\circ}+\beta_B^{\circ})$, where $S_{\mu\nu}$ is the overlap integral matrix calculated in INTGRL. The Fock matrix is diagonalized through use of subroutine EIGN; the eigenvectors thus calculated are used to compute the initial density matrix. This matrix is stored in COMMON/ARRAYS/B. At this point appropriate CNDO or INDO corrections are made to the core Hamiltonian matrix. (Note that the Fock matrix is originally assumed in HUCKCL to be equal to the core Hamiltonian matrix; because the density matrix is considered zero in this first

approximation, $F_{\mu\nu} = H_{\mu\nu}$ and $F_{\mu\mu} = H_{\mu\mu}$.)

Subroutine SCFCLO is called by the main program immediately after subroutine HUCKCL and is the subroutine in which self-consistency is established through comparison of computed values of electronic energy. The initial density matrix as well as the core Hamiltonian computed in HUCKCL are used to calculate the Fock matrix (see equations (57), (58), and (59) in section II). From this initial Fock matrix an initial electronic energy is calculated (before diagonalization.) Diagonalization of the Fock matrix yields a new set of eigenvectors from which a new density matrix and a new Fock matrix are calculated. A new electronic energy value is computed after the formation of each new Fock matrix, before diagonalization. This value is compared with the old energy value, and the cycle continued if the new energy value is not within 10^{-6} Hartrees of the old energy value. The maximum number of iterations allowed is 25; if this number of cycles is completed the process will terminate regardless of whether the energy values have converged or not. If the energy values do converge the Fock matrix is diagonalized once more and then printed under the label HARTREE-FOCK ENERGY MATRIX.

Subroutine CPRINT computes the binding energy, the dipole moments, and the total energy of the molecule. Subroutines SCFOUT and EIGOUT are printing routines, the first to print one of the arrays in COMMON/ARRAYS/ as designated by a parameter and the second to print eigenvalues of the array in SCFOUT.

The program in appendix B is a complete listing of the modified version of the original program. The reader is referred

to the comments (statements with a C in the far left-hand column and underlined in red) which are descriptive of the organization of each subroutine as described above. Further comments relating the theory to particular portions of the program are included beside appropriate statements.

Modification of the program to adapt it to our computer facilities seemed at first an easy task. Originally written for an IBM 360/65 digital computer, the program had to be adapted to an NCR Century 200 digital computer. Both computers use very similar versions of FULL FORTRAN IV, the differences being idiosyncrasies of the respective compilers. The features of the original program which required modification included the use of an IMPLICIT REAL * 8 statement, the file numbers on both WRITE and READ statements, and the use of the DFLOAT function. The IMPLICIT REAL * 8 (A-H, O-Z) extends the normal precision of all real variables to 8 decimal places. It is not available in NCR FULL FORTRAN IV but a DOUBLE PRECISION statement, which extends the normal precision from 6 to 12 significant figures, may be used instead. Each variable, however, must individually be declared DOUBLE PRECISION because no statement exists in NCR FULL FORTRAN IV which will automatically apply to every real variable. Unless a real variable is expressly declared DOUBLE PRECISION, it will be considered real and allotted one-half as much memory as an equivalent double precision variable. The WRITE file number was changed from 6 to 3 and the READ file number from 5 to 1.

No DFLOAT function exists in NCR FULL FORTRAN IV. The purpose of this function is to convert integer variables to float-

ing point variables in the event that mixed-mode arithmetic is required in a statement. The problem does not occur in NCR FULL FORTRAN IV because mixed-mode arithmetic is automatically performed; integer variables in mixed-mode expressions automatically become floating-point variables. In every use of the DFLOAT function, simply removing "DFLOAT" results in the correct NCR statement.

Adapting the program first for closed-shell molecules only, we made the above changes and ran the computer program using data for hydrogen fluoride. After correcting some minor syntax errors, we obtained a successful compilation with the message "PROGRAM EXCEEDS SIZE" as we had expected. The program in its original form with the above modifications requires approximately 170,000 bytes of memory for the COMMON memory alone, while the NCR Century 200 has only 64K (actually 65,456) bytes of memory space available. The problem, then, was one of reducing the amount of memory needed for COMMON by more than two-thirds.

In NCR FULL FORTRAN IV each double precision variable requires 8 bytes of memory space. An obvious way of reducing the memory size was to reduce the size and number of the double precision arrays in COMMON. We therefore reduced the maximum number of atoms from thirty-five to ten and the maximum number of basis functions from eighty to twenty-five. This change reduced the size of COMMON/ARRAYS/ from 19,200 to 1875, COMMON/INFO/ from 144 to 44, COMMON/GAB/ from 2000 to 875, and COMMON/INF01/ from 188 to 58. As each of the variables reduced was a double precision array, a total of 131,840 bytes of memory was released by these changes. Further, the arrays G1(18), F2(18), BETAO(18), and ENEG(18,3) in subroutine

HUCKCL were originally declared DOUBLE PRECISION. The values assigned to elements of these arrays, however, never require more than 6 decimal places of precision. Because of the NCR's capacity to perform mixed-mode arithmetic, we were able to declare all these arrays single precision and to save 432 bytes of memory.

COMMON/ARRAYS/ serves in the original program as a storage place for the Z and Y coefficients used in calculation of the reduced overlap integrals. In COEFFT a total of 765 Z values were input, of which 678 were zero. 9135 Y values were input, of which 8811 were zero. All Y and Z values were declared double precision. From this it seemed obvious that a majority of the storage space required by COEFFT retained zero values. In order to reduce further the memory required by the program, we therefore removed the subroutine COEFFT entirely and devised a method of reading in as data the non-zero Z and Y coefficients.

In this method two parallel arrays are constructed for both Z and Y values. The first array consists of the array element numbers of non-zero Z values (or of non-zero Y values.) This array is called NZZ (or NZY), meaning non-zero Z (or non-zero Y). The second parallel array NZZV (or NZYV), non-zero Z value (or non-zero Y value) is composed of the actual values corresponding to the array element numbers in NZZ and NZY. For example, if Z(1) was originally input in COEFFT as Z(1)=64, in the modified version of the program NZZ(1)=1 and NZZV(1)=64. Cards from the original program are used for inputting the Z and Y values. The values are read and stored in the MAIN segment of the program. NZZ, NZZY, NZY, and NZYV are all allotted to COMMON/ARRAYS/ to be accessible to other parts of the program.

In function SS the value of Z or of Y to be used in computation was originally determined by an array element number which was a function of the variables of two "DO" loops. Thus, X = X + Z(I+1,L) * A(I+1) * B(NNI1)/2.DO or X = X + Y(I+1,J+1,L) * A(I+1) *B(IIII). Using the rule for array element succession in FULL FORTRAN IV, we converted these into linear array element numbers. According to this rule, if Z is an array of size 17 X 45, Z(I+1,L) is equivalent to Z(I+1+17*(L-1)). If Y is a 9 X 5 X 203 array, Y(I+1,J+1,L) is equivqlent to Y(I+1+9*J+5*(L-1)). A systematic comparison of the desired Z or Y array element numbers with those stored in NZZ or NZY reveals whether the desired element is one of the non-zero elements. If so, Z is assigned the value of the corresponding NZZV or NZZY element. If not, it remains zero.

This modification requires the addition of NZZ(87), NZZV(87), (NZY(224), and NZYV(224) to COMMON/ARRAYS/ but allows the reduction in the number of basis functions without loss of memory space required for storage of Y or Z coefficients. The process undoubtedly involves more computer time, but in our case free memory space was the alternative to efficiency that we preferred.

In spite of the above modifications the program failed to run properly. Memory was approximately at the 64K limit and did not seem to be the problem. For this reason we attempted to use a trace statement to get a printout of all variable values throughout the program but found that this feature of NCR FULL FORTRAN IV had not been implemented in our compiler. Inserting write statements in appropriate spots, we saw that the program was failing somewhere in subroutine INTGRL due to what the computer termed

an exponential overflow.

For several months we investigated this problem, approaching it from as many different angles as possible. One such approach revealed by accident an obvious error in the computer rather than in our program. We had considered the possibility that the complicated overlay of the program was causing the problem and decided to structure the program into two independent but LINKed programs (using the LINK feature of FORTRAN), the first containing subroutine INTGRL and the subroutines used in INTGRL and the second containing the other subroutines. We found, using this LINK procedure, that the output of the linked and non-linked programs were not equivalent but that neither program worked! We concluded that the memory overlay was not the problem but rather some inherent computer error. We sent copies of both programs to National Cash Register headquarters in Dayton, Ohio, and after several weeks of testing they confirmed that an error in the floating-point hardware of our computer was preventing the program from running correctly.

After correction of the problem we input data for formaldehyde, CH_2O, and concentrated on the first part of the program which calculates coulomb and overlap integrals. The matrices were calculated by the program but additional output from test write statements revealed another computer error. The l quantum numbers were appearing consistently as negative values. It was obvious since these are all positive integers that at least one calculation was incorrect. We carried through computations by hand and found no problem, concluding again that there was a software or hardware error. Subsequent test runs in Dayton showed that the

error was reproducible on other NCR Century 200 computers and that it thus was not a localized problem of the computer available to Sweet Briar. In the process of investigating this error, problems in the exponentiation procedure and in the double precision hardware were found. These, however, were not the causes for assignment of negative values to the l quantum number. This remains unsolved, though accidentally we discovered a way to overcome it.

In the calculation of PAIRS(I,J) the non-zero overlap matrix elements computed in INTGRL, a rather complex mathematical statement is employed.

```
        (1) PAIRS(I,J)=DSQRT((MU(ANK)*R)**(2*NC(ANK+1)*(MU(ANL)
*R) **(2*NC(ANL+1)/FACT(2*NC(ANL))))*(-1.D0)**LC(J)+MC(J))*SS(NC(ANK),
LC(I), MC(I), NC(ANL), LC(J), MU(ANK)*R, MU(ANL)*R)
```

Suspecting that the argument of the DSQRT function was becoming negative we broke this statement down as follows:

```
        (2)NEWV=((MU(ANK)*R)**(2*NC(ANK)+1)*(MU(ANL)*R)**(2(NC
(ANL+1)/FACT(2*NC(ANL))))
        (3) NEWS = SS(NC(ANK), LC(I), MC(I), NC(ANL), LC(J),
MU(ANK)*R, MU(ANL*R))
        (4) PAIRS(I,J) = DSQRT(NEWV)*(-1.D0)**((LC(J)+MC(J))*NEWS
```

In addition we added the following loop:

```
        IF (NEWV .LE. 0) GO TO 135
    135 DSQRT(NEWV) = 0
        WRITE (3, 145) NEWV
```

The above statements were placed before the final PAIRS(I,J) statement so that the possibility of extracting the square root of a negative number was eliminated. After the floating-point hardware

was corrected, a printout for HF was obtained which did not assign a negative value to 1. In a subsequent run on formaldehyde, the original PAIRS(I,J) statement was restored, resulting in the original assignment or calculation error. Again breaking up PAIRS(I,J) as described, we were able to obtain a successful printout for the first part of the program - one which correlated almost exactly with a good run on formaldehyde using the original computer program adapted to a CDC 5400 computer at the University of Virginia.

The second half of the program was tested independently of the first by inputting the correct overlap and coulomb matrices and making other necessary modifications. Printout for this half of the program using data for formaldehyde corresponded to the correct printout on the CDC 6400.

The two programs were then recompiled into one and run, using double precision variables and inputting data for formaldehyde. This trial run produced correct results.

Once the program was running properly a further modification was made to increase the number of allowed basis functions from 25 to 31. COMMON/ARRAYS/ originally allotted enough memory space for 3 arrays with dimensions equal to the number of basis functions squared. Inspection revealed that the third of these arrays was used only in calculations for open-shell molecules; since this option is not a feature of the modified program this array was eliminated, resulting in enough free memory space to increase the maximum number of basis functions to 31.

The modified program in its final form can perform CNDO and INDO calculations on closed-shell molecules with a maximum size

of 10 atoms and 31 basis functions. The CNDO option may be chosen for molecules containing atoms through Cl and the INDO option for molecules with atoms through F. The language in which the program is written is NCR FULL FORTRAN IV, and the total memory required is approximately 65,000 bytes. Output from the program includes the overlap matrix, the coulomb matrix, the density matrix, the Hartree-Fock energy matrix, the total, the electronic and the bonding energies of the molecule as well as the total dipole moment and contributions from components.

In conclusion, in the process of modifying the program my own personal attitude about computer calculations was reversed - from one of complete trust to one of innate skepticism; when errors appeared in the program throughout the year they seemed to be due chiefly to the inadequacies of the computer rather than logical or syntax problems on my part. One definite finding of the project is that the NCR CENTURY 200 computer with a FULL FORTRAN IV compiler is not the best machine available to handle programs of the size and complexity of the one with which we were dealing.

IV - EXPERIMENTAL

Brownlee and Taft have used the CNDO/2 method to study substituted fluoroacteylenes and trans-substituted fluoroethylenes.[30] With the recent extension of CNDO/2 theory to include atoms of the second row of the periodic table,[14] it is possible to compare results such as those obtained by Brownlee and Taft to results using substituted chloroacetylenes and substituted chloroethylenes. Such a comparison can yield at least a qualitative measure of the relative electronic effects of fluorine and chlorine.

Though fluorine and chlorine are both in the halogen series, the difference between the two is greater than between succeeding heavier halogens. Fluorine is a smaller atom, having a covalent radius of 0.72 Å, while chlorine has a covalent radius of 1.00 Å. The valence shell configurations of the two are $2s^2\ 2p^5$ and $3s^2\ 3p^5$ respectively. Fluorine is the most electronegative of all the elements, having an electronegativity of 3.95 on the Pauling scale, and chlorine's electronegativity is 3.03. Related to electronegativity is the inductive effect parameter σ_I[33] which is 0.52 for F and 0.47 for Cl. The resonance effect parameter σ_R[34], measuring the tendency of a substituent to delocalize π electrons, is -0.45 for F and -0.24 for Cl.

The above characteristics of fluorine and chlorine lead to some interesting differences in the bonding properties of the two atoms. Because of fluorine's smaller size, it has a higher charge density than does chlorine. Such a high charge density results in a large measure of repulsion among the lone-pair electrons on the atom.

π bond formation reduces some of the charge density due to delocalization, and thus fluorine has a tendency to contribute to π bonds. Chlorine, on the other hand, has a much more dispersed electron population than does fluorine. Its relative contribution to π bonding is therefore less.

A last significant difference mentioned between the two atoms is their electronic configuration. Though each has 2 electrons in the valence s orbitals and 5 in the valence p orbitals, the Cl atom has 5 empty 3d orbitals which contribute in some way to covalent bonding.

From these general differences one may make specific predictions about the relative effects of fluorine and chlorine on electron distribution. Fluorine's greater electronegativity should be evident in a comparison of the σ electron densities at specified atoms in fluoro- and chloro- compounds.

Figure 1.

X = CHO, CN, NO_2

Referring to figure 1, the excess σ electron density at F in molecule A should be greater than that at Cl in molecule B, and the corresponding σ electron deficit at C_2 in molecule A should be greater than that at C_2 in molecule B. The inductive effects of the two atoms fluorine and chlorine are likely to be observable at the carbon bonded to the substituent, X. Although quantitatively the σ electron density at the substituent carbon C_1 reflects to a large extent the inductive effect of the particular substituent, the greater electronegativity of fluorine

should result in a smaller absolute electron density at C_1 in molecule A than at C_1 in molecule B.

With respect to π electron distribution, one would expect the total π density at the two ethylene carbons (hereafter referred to as $\sum_{C} q_{\pi}$) to be less in chloro- compounds than in corresponding fluoro- compounds. The concentration of π electrons at C_2 in molecule A (the carbon bonded to fluorine) should be greater than at C_2 in molecule B (the carbon bonded to chlorine).

To test these predictions a CNDO/2 calculation was done on 6 monosubstituted ethylenes and then subsequently on 4 of the 6 corresponding fluoro- and chloro- compounds. Standard geometries were assumed using the best values from the literature.[35] Though not physically correct, the assumption was made that the substitution of a fluorine or chlorine group does not change appreciably the other bond lengths or bond angles of the molecule. Justification for such an assumption lies in the comparative approach being used. The same standard geometries were used for chloro- and fluoro- compounds - which seems more consistent than varying bond lengths or bond angles based on different experimental values. Also, experimental values were not available for all of the molecules for which calculations were made. The convention was used in which the double or triple bond is along the x axis with the z axis perpendicular to the molecular plane. In this way π electron density can be directly obtained from the charge density matrix, the diagonal $p_z p_z$ elements representing π contributions of atomic basis functions to the atoms on which they are centered. σ electron density can be calculated and is the sum of the contributions of the diagonal s, p_x and p_y elements. The calculated x, y, and z

coordinates are given in appendix C.

The substituents we originally hoped to consider were F, Cl, CHO, CN, NO_2, and CH_3. These represented a wide range within the limitations of the modified CNDO program. We were unable to complete calculations for all the molecules, however.

In the course of investigating this particular problem we discovered another inadequacy of the NCR Century 200 computer. A total of 44 molecules were input (NRUNS=44); after $1\frac{1}{2}$ hours the run was aborted because the operators thought the program was in an infinite loop. In fact, it was in the process of executing computation for one of the more complicated molecules. We therefore broke the data down into two decks and hoped in this way to reduce the length of each job. One of the data decks was run for 9 hours and 45 minutes, after which only 3/4 of the data had been processed. Calculations were completed for only 12 molecules during the two runs; subsequent runs gave results for 3 more molecules. My conclusions, therefore, must be based on findings with respect to this limited number of substituted ethylenes. Time prevented acquisition of data for the remainder of the ethylenes or the acetylenes.

Tables I, II, and III contain excess σ electron densities at specified atoms in monosubstituted ethylenes, substituted fluoroethylenes, and substituted chloroethylenes, respectively. Excess electron density was computed by subtracting the electron density of the appropriate undispersed orbitals from the calculated electron density.

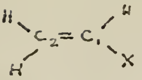


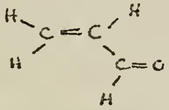
Table I. σ Electron Densities of Monosubstituted Ethylenes

X = / excess σ density	H	F	Cl	CHO*	CHO**	NO_2	CN
$C_{1\sigma}$	.0300[a]	.0466	.0147	.0307	.0274	-.0595	-.0124
$C_{2\sigma}$	.0297[a]	-.1709	-.0502	.0357	.0510	.0421	.0304

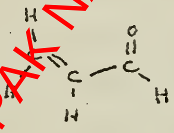
[a] q - 3.000 where q is calculated electron density

Hereafter CHO* and CHO** refer to the following configurations:

CHO*



CHO**



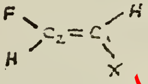


Table II. σ Electron Densities of Substituted Fluoroethylenes

X = / σ density at	CHO*	CHO**	NO_2	CN
$C_{1\sigma}$	.0331[a]	.0277	-.0598	-.0140
$C_{2\sigma}$	-.1606[a]	-.1652	-.1804	-.1846
F_σ	.2318[b]	.2330	.2369	.2321

[a] q - 3.000 [b] q - 5.000

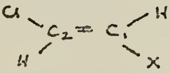


Table III. σ Electron Densities of Substituted Chloroethylenes

X = / σ density at	CHO*	CHO**	NO_2	CN
$C_{1\sigma}$	.0132[a]	.0057	-.0772	-.0318
$C_{2\sigma}$	-.0296[a]	-.0253	-.0352	-.0454
Cl_σ	.1270[b]	.1338	.0815	.1249

[a] q - 3.000 [b] q - 5.000

Tables I - III are interesting not only for the information they contain concerning the relative electronic effects of fluorine and chlorine, but also concerning the effects of substituents on the inductive abilities of the two atoms. It is useful to note, for example, that in table II the σ electron density at F is almost .02 smaller for a NO_2 substituted fluoroethylene than for any other substituent. This is an indication of the competition between NO_2 and F for electrons, and it also points out that NO_2 is the most electronegative of any of the substituents. Similarly, in table III, the electron density at Cl in the nitro- substituted molecule is at least .04 smaller than for other substituents. The fact that the difference is less in the case of the fluoro- compounds than in the case of the chlorine compounds is indicative of the fact that chlorine is less able to compete with NO_2 for σ electrons; it is less electronegative.

Table IV was tabulated from tables I - III and represents a comparison of the data of the three.

Table IV. A Comparison of σ Electron Densities in Substituted Fluoroethylenes and Chloroethylenes

σ density at / Substituents	$C_{1\sigma}$	$C_{2\sigma}$	F_σ	Cl_σ
F, CHO*	.0331	-.1606	.2330	----
Cl, CHO*	.0132	-.0296	----	.1270
F, CHO**	.0277	-.1652	.2369	----
Cl, CHO**	.0057	-.0253	----	.1338
F, NO_2	-.0598	-.1804	.2106	----
Cl, NO_2	-.0772	-.0252	----	.0815
F, CN	-.0140	-.1846	.2321	----
Cl, CN	-.0318	-.0424	----	.1249

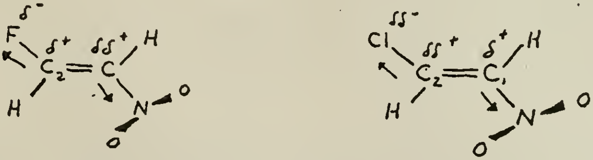
Table IV is in keeping with theoretical expectations. The greater inductive effect of fluorine is evident in every case considered. For both of the geometrical configurations of CHO- substituted molecules, there is an excess of electron density at the carbon bonded to the substituent; the excess is larger for F than for Cl. This excess represents a redistribution of σ electrons from the substituent to C_1 and reflects the successful competition of fluorine and chlorine for part of the σ electron density of the substituent. This can be illustrated through the following schematic diagram, using the CHO* configuration:

Figure 2.

(Note that in figure 1 δ refers to charge rather than electron population. The difference lies only in the sign; an excess electron density results in an excess negative charge. Also, $|\delta\delta| < |\delta|$.)

The substituents NO_2 and CN also illustrate the fact that fluorine has a greater inductive effect than chlorine; the substituents however, are both more electronegative than CHO as indicated in figure 3 using the NO_2 group as an example.

Figure 3.



The inductive effects as calculated by CNDO/2 theory are thus in keeping with those predicted. Fluorine's greater electronegativity

is evident in calculations for pairs of molecules with all 4 substituents, though it is interesting to note the variations in charge distributions that occur because of the electronegativity of the substituent. The relative electronegativities of the substituents as calculated are COH < CN < NO_2 which corresponds to the inductive substituent constant order of 0.31 < 0.56 < 0.63 for these substituents, resepctively.[36]

Tables V, VI, and VII contain excess π electron densities for the series of molecules being studied.

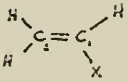


Table V. π Electron Densities of Monosubstituted Ethylenes

SUBSTITUENT X / π DENSITY AT	H	F	Cl	CHO*	CHO**	NO_2	CN
$C_{1\pi}$	$.0002^a$	-.0090	-.0151	.0093	.0168	.0456	-.0143
$C_{2\pi}$	$-.0002^a$	.0370	.0408	-.0480	-.0631	-.0324	.0304

a q - 1.000

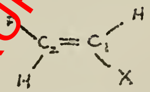


Table VI. π Electron Densities of Substituted Fluoroethylenes

SUBSTITUENT X / π DENSITY AT	H	CHO*	CHO**	NO_2	CN
$C_{1\pi}$	$.0370^a$	.0838	.0938	.1282	.0780
$C_{2\pi}$	$-.0090^a$	-.0735	-.0891	-.0595	-.0440
F_{2p_z}	$-.0281^b$	-.0624	-.0655	-.0579	-.0581

a q.- 1.000 b q - 2.000

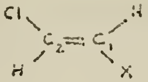


Table VII. π Electron Densitites of Substituted Chloroethylenes

π density at \ substituent X	H	CHO*	CHO**	NO_2	CN
$C_{1\pi}$	.0408[a]	.0488	.0596	.0916	.0420
$C_{2\pi}$	-.0151[a]	-.0617	-.0787	-.0500	-.0309
Cl_{3p_z}	-.0257[b]	-.0337	-.0367	-.0298	-.0305

a q - 1.000 b q - 2.000

Table VIII is a comparative representation of the total π densities at the ethylene carbons of the molecules being studied as well as the π electron densities at individual atoms in the molecule.

Table VIII. A Comparison of π Electron Densities in Substituted Fluoroethylenes and Chloroethylenes

substituents \ π densities at	$\sum_c q_\pi$	$C_{1\pi}$	$C_{2\pi}$	F_{2p_z}	Cl_{3p_z}
F, CHO*	.0103	-.0838	-.0735	-.0624	----
Cl, CHO*	-.0129	.0488	-.0617	----	-.0337
F, CHO**	.0037	.0938	-.0891	-.0655	----
Cl, CHO**	-.0191	.0596	-.0787	----	-.0367
F, NO_2	.0687	.1282	-.0595	-.0579	----
Cl, NO_2	-.0416	.0916	-.0500	----	-.0298
F, CN	.0340	.0780	-.0440	-.0581	----
Cl, CN	-.0122	.0420	-.0309	----	-.0305

Table VIII indicates that the π electron distribution at the ethylene carbons is consistently greater for fluoro- com-

pounds than for chloro- compounds. For each pair of molecules being compared, the deficit of π electrons at fluorine is greater than the deficit at chlorine, indicating that fluorine is making a larger contribution to π bonding than chlorine. The total excess π electron density at the ethylene carbons is also greater for fluoroethylenes than for chloroethylenes.

The actual distribution of the π electrons is an interesting problem. Although one would expect that the π density at C_2 (bonded to fluorine or chlorine) would be greater than at C_1, the reverse is consistently true. Apparently the π electrons contributed by both fluorine and chlorine in their respective systems appear at C_1. The explanation for this likely lies in the form of the molecular orbitals, but a detailed analysis is an area for further investigation.

Thus, the calculated σ and π distributions of substituted fluoro- and chloro- compounds reflect the greater inductive and resonance effects of fluorine than chlorine. A definite problem with the framework of this study, however, is the assumption of fixed standard geometries regardless of substitution of the fluoro- or chloro- group. As mentioned previously, the data obtained should be used only in a qualitative study rather than any sort of quantitative assessment of the trends discovered. Whether these trends would be enhanced or reduced by use of actual equilbrium geometries for the given molecules is a problem for further study.

Likewise, the use of only four different sets of molecules from which to draw general conclusions is undesirable. This factor, however, was beyond our control; similar runs for other molecules using the same computer program and the coordinates in appendix

C may reveal other important results.

The computer program would probably yield more accurate density values if it were modified to achieve self-consistency using an electron density criterion rather than the electronic energy convergence. In the case of larger molecules, in particular, there was some difficulty in obtaining proper convergence using electronic energy. By focusing on one of the elements of the density matrix or on a standard deviation of the diagonal elements, for example, this change could be instituted.

In spite of these limitations, in the three substituted ethylenes investigated the qualitative trends which the data revealed are in keeping with predictions. Because of the assumptions of standard geometries, the limited data available, and the use of electronic energy as a measure of self-consistency rather than charge density, these conclusions must remain, at best, qualitative. Nevertheless, the trends discussed above appeared in each set of data, with no exception.

V - CONCLUSIONS

The CNDO and INDO methods successfully extend other more approximate molecular orbital theories through the entire valence set of electrons. Based on the ZDO approximation, both methods rely on a self-consistent field method using the LCAO approach. The INDO theory, however, retains one-center monotomic differential overlap in order to improve correlation of theoretical and experimental data for open-shell molecules.

When applied to a series of simple molecules (AB, AB_2, AB_3, for example), the CNDO/2 parameterization has been found to be more successful than the CNDO/1 parameterization in that calculated bond lengths and dissociation constants are more in keeping with those experimentally determined. The main difference between the latter and the former is the former's neglect of the penetration integral. This modification was found to improve results considerably.

CNDO/2 theory has recently been modified to include atoms through Cl in the periodic table. This involves the estimation of orbital forms for each of the 5 3d orbitals and the inclusion of a specified empirical constant in the estimation of the resonance integral β°_{AB}. An important area for investigation is the further extension of this theory to the transition elements. Highly symmetric transition metal crystals, could, through group theory, be studied without requiring excessive numbers of basis functions.

Implementation of the CNDO and INDO theories was accomplished through adaptation of a computer program to the NCR Century 200

computer to which Sweet Briar has access. The problems involved included reducing the large amount of memory space originally required and changing minor syntax idiosyncrasies in the original version of the program. These changes did not result in successful operation but rather led to the discovery of several malfunctions of the computer. We were able to pinpoint and overcome these errors and obtain printouts for CH_2O which reproduced similar runs on another machine.

Having adapted the program, we were able to apply it to a simple problem, an investigation of the effects of F and Cl on σ and π electron densities in substituted fluoro- and chloroethylenes. Excessive computer time was required to perform calculations, nine molecules being executed in 9 hours and 45 minutes. For this reason the experiment had to be based on only a part of the molecules we had hoped to run.

Data from these calculations was in keeping with theoretical predictions in every case studied. Fluorine has greater inductive and resonance effects, and this was clearly demonstrated by the data. An area for study, however, is the actual π distribution at each carbon.

The problems encountered in structuring even a simple experiment such as the one we initiated indicate that data should be used to determine qualitative rather than quantitative trends. The CNDO and INDO theories themselves are approximations of other approximate molecular orbital theories, and one should proceed with care when attempting to make quantitative evaluations based on data obtained using these theories. They are, however, important in the development of approximate molecular orbital theories,

representing two of the most sophisticated and useful methods recently devised. Though at this stage they are still being tested, their application to specific problems is rapidly becoming more widespread; the results of such studies seem very encouraging and suggest a variety of other possible uses of these theories in the future.

APPENDIX A

Appendix A contains a CNDO and an INDO calculation for formaldehyde, CH_2O. The two indicate that the differences between the methods result in only small variations in the core Hamiltonian, Hartree-Fock and density matrices. These variations arise from the addition, at several points in the program, of INDO corrections to CNDO matrices. Because the INDO method includes the one-center monotomic differential overlap terms, the INDO calculations probably more closely approximate the true values than do the CNDO calculations.

```
  TRIAL RUN OF FORMALDEHYDE
 CNDO CLSD

      4 ATOMS    CHARGE  =    0   MULTIPLICITY   =    1

6        0.0000000         0.0000000        0.0000000
8        1.2200000         0.0000000        0.0000000
1       -0.5400000         0.9350000        0.0000000
1       -0.5400000        -0.9350000        0.0000000
```

```
P INTEGRAL MATRIX  (CONTINUED ON FOLLOWING PAGE)

     1         2         3         4         5         6         7         8
  1.0000    0.0000    0.0000    0.0000    0.3734   -0.3070    0.0000    0.0000
  0.0000    1.0000    0.0000    0.0000    0.4580   -0.3056    0.0000    0.0000
  0.0000    0.0000    1.0000    0.0000    0.0000    0.0000    0.2146    0.0000
  0.0000    0.0000    0.0000    1.0000    0.0000    0.0000    0.0000    0.2146
  0.3734    0.4580    0.0000    0.0000    1.0000    0.0000    0.0000    0.0000
 -0.3070   -0.3056    0.0000    0.0000    0.0000    1.0000    0.0000    0.0000
  0.0000    0.0000    0.2146    0.0000    0.0000    0.0000    1.0000    0.0000
  0.0000    0.0000    0.0000    0.2146    0.0000    0.0000    0.0000    1.0000
  0.5246   -0.2459    0.4257    0.0000    0.0841   -0.0754    0.0401    0.0000
  0.5246   -0.2459   -0.4257    0.0000    0.0841   -0.0754   -0.0401    0.0000


INTEGRAL MATRIX

     1         2         3         4
  0.5903    0.4101    0.4369    0.4369
  0.4101    0.8265    0.2650    0.2650
  0.4369    0.2650    0.7500    0.2810
  0.4369    0.2650    0.2810    0.7500
```

~~3)=~~ ~~0.37695~~

```
MILTONIAN  (CONTINUED ON FOLLOWING PAGE)

                1         2         3         4         5         6         7
C     S     -5.9168    0.0000    0.0000    0.0000   -0.3567    0.2934    0.0000
C     PX     0.0000   -5.6052    0.0000    0.0000   -0.4377    0.2920    0.0000
C     PY     0.0000    0.0000   -5.6052    0.0000    0.0000    0.0000   -0.2051
C     PZ     0.0000    0.0000    0.0000   -5.6052    0.0000    0.0000    0.0000

O     S     -0.3567   -0.4377    0.0000    0.0000   -7.6489    0.0000    0.0000
O     PX     0.2934    0.2920    0.0000    0.0000    0.0000   -7.0506    0.0000
O     PY     0.0000    0.0000   -0.2051    0.0000    0.0000    0.0000   -7.0506
O     PZ     0.0000    0.0000    0.0000   -0.2051    0.0000    0.0000    0.0000

H     S     -0.2892    0.1355   -0.2347    0.0000   -0.0618    0.0554   -0.0294

H     S     -0.2892    0.1355    0.2347    0.0000   -0.0618    0.0554    0.0294



 ELECTRONIC ENERGY         -44.6146910191   (INDO - CNDO) = 1.087120


 ELECTRONIC ENERGY         -44.6269983878


 ELECTRONIC ENERGY         -44.6299829841
```

OVERLAP INTEGRAL MATRIX

```
      9          10
  0.5246     0.5246
 -0.2459    -0.2459
  0.4257    -0.4257
  0.0000     0.0000
  0.0841     0.0841
 -0.0754    -0.0754
  0.0401    -0.0401
  0.0000     0.0000
  1.0000     0.1618
  0.1618     1.0000
```

CORE HAMILTONIAN

```
     8          9          10
  0.0000    -0.2892    -0.2892
  0.0000     0.1355     0.1355
  0.0000    -0.2347     0.2347
 -0.2051     0.0000     0.0000

  0.0000    -0.0618    -0.0618
  0.0000     0.0554     0.0554
  0.0000    -0.0294     0.0294
 -7.0506     0.0000     0.0000

  0.0000    -4.2571    -0.0535

  0.0000    -0.0535    -4.2571
```

```
     ELECTRONIC ENERGY         -44.6307455574


     ELECTRONIC ENERGY         -44.6309385049


     ELECTRONIC ENERGY         -44.6309921081


     ELECTRONIC ENERGY         -44.6310123716


     ELECTRONIC ENERGY         -44.6310129367
ENERGY SATISFIED

REE-FOCK ENERGY MATRIX     CONTINUED ON FOLLOWING PAGE

                 1         2         3         4         5         6         7
   C     S   -0.5769    0.0249   -0.0000    0.0000   -0.4138    0.3939    0.0000
   C     PX   0.0249   -0.2214    0.0000   -0.0000   -0.5335    0.4302    0.0000
   C     PY  -0.0000    0.0000   -0.2243   -0.0000   -0.0000    0.0000   -0.2616
   C     PZ   0.0000   -0.0000   -0.0000   -0.1948    0.0000   -0.0000   -0.0000

   O     S   -0.4138   -0.5335   -0.0000    0.0000   -1.1614   -0.1694   -0.0000
   O     PX   0.3939    0.4302    0.0000   -0.0000   -0.1694   -0.4120    0.0000
   O     PY   0.0000    0.0000   -0.2616   -0.0000   -0.0000    0.0000   -0.6442
   O     PZ   0.0000   -0.0000    0.0000   -0.4075    0.0000   -0.0000    0.0000

   H     S   -0.4155    0.2223   -0.3829   -0.0000   -0.0634    0.0500   -0.0061

   H     S   -0.4155    0.2223    0.3829    0.0000   -0.0634    0.0500    0.0061


/ALUES AND EIGENVECTORS   CONTINUED ON FOLLOWING PAGE


/ALUES---    -1.6123   -1.0383   -0.9243   -0.7441   -0.6734   -0.5397    0.1521
                 1         2         3         4         5         6         7
   C     S   -0.4900   -0.5465    0.0000    0.0250   -0.0000    0.0000    0.0000
   C     PX  -0.2912    0.3616   -0.0000    0.4993    0.0000   -0.0000   -0.0000
   C     PY   0.0000   -0.0000   -0.6192    0.0000   -0.0000   -0.2945   -0.0000
   C     PZ  -0.0000    0.0000   -0.0000   -0.0000   -0.6483    0.0000    0.7614

   O     S   -0.7741    0.4261   -0.0000   -0.2921    0.0000    0.0000    0.0000
   O     PX   0.1688    0.2619   -0.0000   -0.7660    0.0000    0.0000   -0.0000
   O     PY   0.0000   -0.0000   -0.5940    0.0000    0.0000    0.7820   -0.0000
   O     PZ  -0.0000    0.0000    0.0000   -0.0000   -0.7614    0.0000   -0.6483

   H     S   -0.1538   -0.4003   -0.3632   -0.1976   -0.0000   -0.3834   -0.0000

   H     S   -0.1538   -0.4003    0.3632   -0.1976    0.0000    0.3834    0.0000
```

HARTREE-FOCK ENERGY MATRIX

```
     8           9           10
  0.0000     -0.4155     -0.4155
 -0.0000      0.2223      0.2223
  0.0000     -0.3829      0.3829
 -0.4075     -0.0000      0.0000

  0.0000     -0.0634     -0.0634
 -0.0000      0.0500      0.0500
  0.0000     -0.0061      0.0061
 -0.3265      0.0000     -0.0000

  0.0000     -0.2983     -0.0367

 -0.0000     -0.0367     -0.2983
```

EIGENVALUES AND EIGENVECTORS

```
  0.2454      0.3339      0.4725
     8           9           10
 -0.6220     -0.0000      0.2715
  0.2343     -0.0000      0.6931
  0.0000     -0.7279     -0.0000
  0.0000      0.0000      0.0000

  0.0668      0.0000     -0.3597
 -0.1584     -0.0000      0.5396
 -0.0000      0.1889      0.0000
 -0.0000     -0.0000     -0.0000

  0.5141      0.4661      0.1128

  0.5141     -0.4661      0.1128
```

```
ITY MATRIX   CONTINUED ON FOLLOWING PAGE

                  1          2          3          4          5          6          7
 C      S      1.0739    -0.0849    -0.0000     0.0000     0.2784    -0.4900    -0.0000
 C      PX    -0.0849     0.9296     0.0000     0.0000     0.4673    -0.6737    -0.0000
 C      PY    -0.0000     0.0000     0.9403     0.0000    -0.0000     0.0000     0.2750
 C      PZ     0.0000     0.0000     0.0000     0.8405     0.0000    -0.0000     0.0000

 O      S      0.2784     0.4673    -0.0000     0.0000     1.7323     0.4093     0.0000
 O      PX    -0.4900    -0.6737     0.0000    -0.0000     0.4093     1.3676    -0.0000
 O      PY    -0.0000    -0.0000     0.2750     0.0000     0.0000    -0.0000     1.9286
 O      PZ     0.0000    -0.0000    -0.0000     0.9872    -0.0000     0.0000    -0.0000

 H      S      0.5784    -0.3972     0.6785     0.0000     0.0124     0.0411    -0.1761

 H      S      0.5784    -0.3972    -0.6785    -0.0000     0.0124     0.0411     0.1761




     TOTAL ENERGY =    -26.8312278536


    BINDING ENERGY=     -1.3068078700 A.U.
C          3.7892
O          6.1880
H          1.0114
H          1.0114


                 DIPOLE MOMENTS

COMPONENTS      X          Y          Z
DENSITIES    -1.04235   -0.00000    0.00000
S.P          -0.93704    0.00000   -0.00000
P.D           0.00000    0.00000    0.00000
TOTAL        -1.97939   -0.00000   -0.00000

POLE MOMENT=  1.97939 DEBYES
```

DENSITY MATRIX

```
     8           9           10
  0.0000      0.5784      0.5784
 -0.0000     -0.3972     -0.3972
 -0.0000      0.6785     -0.6785
  0.9872      0.0000     -0.0000

 -0.0000      0.0124      0.0124
  0.0000      0.0411      0.0411
 -0.0000     -0.1761      0.1761
  1.1595     -0.0000      0.0000

 -0.0000      1.0114     -0.1197

  0.0000     -0.1197      1.0114
```

```
 TRIAL RUN OF FORMALDEHYDE
INDO CLSD

     4 ATOMS    CHARGE  =   0   MULTIPLICITY  =   1

6       0.0000000       0.0000000       0.0000000
8       1.2200000       0.0000000       0.0000000
1      -0.5400000       0.9350000       0.0000000
1      -0.5400000      -0.9350000       0.0000000
```

OVERLAP INTEGRAL MATRIX CONTINUED ON FOLLOWING PAGE

```
              1         2         3         4         5         6         7
  1        1.0000    0.0000    0.0000    0.0000    0.3734   -0.3070    0.0000
  2        0.0000    1.0000    0.0000    0.0000    0.4580   -0.3056    0.0000
  3        0.0000    0.0000    1.0000    0.0000    0.0000    0.0000    0.2146
  4        0.0000    0.0000    0.0000    1.0000    0.0000    0.0000    0.0000
  5        0.3734    0.4580    0.0000    0.0000    1.0000    0.0000    0.0000
  6       -0.3070   -0.3056    0.0000    0.0000    0.0000    1.0000    0.0000
  7        0.0000    0.0000    0.2146    0.0000    0.0000    0.0000    1.0000
  8        0.0000    0.0000    0.0000    0.2146    0.0000    0.0000    0.0000
  9        0.5246   -0.2459    0.4257    0.0000    0.0841   -0.0754    0.0401
 10        0.5246   -0.2459   -0.4257    0.0000    0.0841   -0.0754   -0.0401
```

COULOMB INTEGRAL MATRIX

```
              1         2         3         4
  1        0.5903    0.4101    0.4369    0.4369
  2        0.4101    0.8265    0.2650    0.2650
  3        0.4369    0.2650    0.7500    0.2810
  4        0.4369    0.2650    0.2810    0.7500
```

~~ENE0(17,3)=~~ ~~0.37695~~

CORE HAMILTONIAN CONTINUED ON FOLLOWING PAGE

```
                             1         2         3         4         5         6
  1   1   C    S         -5.8052    0.0000    0.0000    0.0000   -0.3567    0.2934
  2   1   C    PX         0.0000   -5.4951    0.0000    0.0000   -0.4377    0.2920
  3   1   C    PY         0.0000    0.0000   -5.4951    0.0000    0.0000    0.0000
  4   1   C    PZ         0.0000    0.0000    0.0000   -5.4951    0.0000    0.0000

  5   2   O    S         -0.3567   -0.4377    0.0000    0.0000   -7.3232    0.0000
  6   2   O    PX         0.2934    0.2920    0.0000    0.0000    0.0000   -6.8313
  7   2   O    PY         0.0000    0.0000   -0.2051    0.0000    0.0000    0.0000
  8   2   O    PZ         0.0000    0.0000    0.0000   -0.2051    0.0000    0.0000

  9   3   H    S         -0.2852    0.1355   -0.2347    0.0000   -0.0618    0.0554

 10   4   H    S         -0.2852    0.1355    0.2347    0.0000   -0.0618    0.0554
```

INDO CORRECTIONS TO THE CNDO ELEMENTS HAVE BEEN MADE FOR THE UNDER-LINED ELEMENTS.

```
        ELECTRONIC ENERGY        -43.5275700233
```

(INDO - CNDO) = 1.087120

```
        ELECTRONIC ENERGY        -43.5348565925

        ELECTRONIC ENERGY        -43.5363804276
```

OVERLAP INTEGRAL MATRIX

```
   8            9            10
0.0000       0.5246       0.5246
0.0000      -0.2459      -0.2459
0.0000       0.4257      -0.4257
0.2146       0.0000       0.0000
0.0000       0.0841       0.0841
0.0000      -0.0754      -0.0754
0.0000       0.0401      -0.0401
1.0000       0.0000       0.0000
0.0000       1.0000       0.1618
0.0000       0.1618       1.0000
```

CORE HAMILTONIAN

```
  7            8            9            10
.0000       0.0000      -0.2892      -0.2892
.0000       0.0000       0.1355       0.1355
.2051       0.0000      -0.2347       0.2347
.0000      -0.2051       0.0000       0.0000

.0000       0.0000      -0.0618      -0.0618
.0000       0.0000       0.0554       0.0554
6.8313       0.0000      -0.0294       0.0294
.0000      -6.8313       0.0000       0.0000

.0294       0.0000      -4.2571      -0.0535

.0294       0.0000      -0.0535      -4.2571
```

```
        ELECTRONIC ENERGY        -43.5367412972


        ELECTRONIC ENERGY        -43.5368270584


        ELECTRONIC ENERGY        -43.5368475495


        ELECTRONIC ENERGY        -43.5368541937


        ELECTRONIC ENERGY        -43.5368536591
 ENERGY SATISFIED

TREE-FOCK ENERGY MATRIX

                     1         2         3         4         5         6         7
1    C     S    -0.6019    0.0137    0.0000    0.0000   -0.4085    0.3960    0.0000
1    C     PX    0.0137   -0.1918   -0.0000   -0.0000   -0.5301    0.4313   -0.0000
1    C     PY    0.0000   -0.0000   -0.2001    0.0000    0.0000   -0.0000   -0.2688
1    C     PZ    0.0000   -0.0000    0.0000   -0.1757    0.0000   -0.0000   -0.0000

2    O     S    -0.4085   -0.5301    0.0000    0.0000   -1.1622   -0.0744   -0.0000
2    O     PX    0.3960    0.4313   -0.0000   -0.0000   -0.0744   -0.3965    0.0000
2    O     PY    0.0000   -0.0000   -0.2688   -0.0000   -0.0000    0.0000   -0.5891
2    O     PZ    0.0000   -0.0000   -0.0000   -0.4064    0.0000   -0.0000    0.0000

3    H     S    -0.4158    0.2218   -0.3808    0.0000   -0.0633    0.0471   -0.0043

4    H     S    -0.4158    0.2218    0.3808   -0.0000   -0.0633    0.0471    0.0043



NVALUES AND EIGENVECTORS


NVALUES---      -1.6432   -1.0538   -0.9038   -0.6846   -0.6684   -0.5069    0.1595
                     1         2         3         4         5         6         7
1    C     S     0.5020   -0.5351    0.0000    0.0606    0.0000   -0.0000    0.0000
1    C     PX    0.2830    0.4005   -0.0000    0.4383    0.0000    0.0000   -0.0000
1    C     PY    0.0000    0.0000    0.6300   -0.0000   -0.0000   -0.2355    0.0000
1    C     PZ    0.0000    0.0000   -0.0000    0.0000   -0.6364    0.0000    0.7714

2    O     S     0.7511    0.4263   -0.0000   -0.3706   -0.0000    0.0000    0.0000
2    O     PX   -0.2254    0.1673   -0.0000   -0.7781   -0.0000   -0.0000   -0.0000
2    O     PY    0.0000    0.0000    0.5487   -0.0000    0.0000    0.8093   -0.0000
2    O     PZ    0.0000    0.0000   -0.0000    0.0000   -0.7714   -0.0000   -0.6364

3    H     S     0.1567   -0.4142    0.3886   -0.1753   -0.0000   -0.3805    0.0000

4    H     S     0.1567   -0.4142   -0.3886   -0.1753    0.0000    0.3805   -0.0000
```

HARTREE FOCK ENERGY MATRIX

```
    8          9          10
  0.0000    -0.4158    -0.4158
 -0.0000     0.2218     0.2218
 -0.0000    -0.3808     0.3808
 -0.4064     0.0000    -0.0000

  0.0000    -0.0633    -0.0633
 -0.0000     0.0471     0.0471
  0.0000    -0.0043     0.0043
 -0.3331    -0.0000     0.0000

 -0.0000    -0.3145    -0.0341

  0.0000    -0.0341    -0.3145
```

EIGENVALUES AND EIGENVECTORS

```
  0.2317     0.3411     0.4489
    8          9          10
 -0.6405    -0.0000     0.2185
  0.1820    -0.0000     0.7286
 -0.0000     0.7400     0.0000
  0.0000     0.0000     0.0000

  0.0843     0.0000    -0.3306
 -0.2136    -0.0000     0.5193
  0.0000    -0.2096    -0.0000
 -0.0000    -0.0000    -0.0000

  0.5019    -0.4519     0.1456

  0.5019     0.4519     0.1456
```

```
DENSITY MATRIX    CONTINUED  ON  FOLLOWING  PAGE

                          1          2          3          4          5          6          7
   1     C      S      1.0840    -0.0853     0.0000     0.0000     0.2524    -0.5007    -0.000
   1     C      PX    -0.0853     0.8721    -0.0000    -0.0000     0.4510    -0.6790    -0.000
   1     C      PY     0.0000    -0.0000     0.9048    -0.0000     0.0000    -0.0000     0.310
   1     C      PZ     0.0000    -0.0000    -0.0000     0.8099     0.0000    -0.0000     0.000

   2     O      S      0.2524     0.4510     0.0000     0.0000     1.7672     0.3794     0.000
   2     O      PX    -0.5007    -0.6790    -0.0000    -0.0000     0.3794     1.3693    -0.000
   2     O      PY    -0.0000    -0.0000     0.3102     0.0000     0.0000    -0.0000     1.912
   2     O      PZ     0.0000    -0.0000     0.0000     0.9818     0.0000    -0.0000    -0.000

   3     H      S      0.5793    -0.3949     0.6688    -0.0000     0.0117     0.0632    -0.189

   4     H      S      0.5793    -0.3949    -0.6688     0.0000     0.0117     0.0632     0.189




         TOTAL ENERGY =      -25.7370685760


        BINDING ENERGY=      -1.2325681925 A.U.
    C              3.6708
    O              6.2387
    H              1.0452
    H              1.0452


                    DIPOLE MOMENTS

    COMPONENTS       X          Y          Z
    DENSITIES     -1.16417    0.00000    0.00000
    S.P           -0.83845   -0.00000   -0.00000
    P.D            0.00000    0.00000    0.00000
    TOTAL         -2.00262    0.00000   -0.00000

  DIPOLE MOMENT=   2.00262 DEBYES
```

DENSITY MATRIX

```
      8          9          10
  0.0000     0.5793     0.5793
 -0.0000    -0.3949    -0.3949
  0.0000     0.6688    -0.6688
  0.9818    -0.0000     0.0000

  0.0000     0.0117     0.0117
 -0.0000     0.0632     0.0632
 -0.0000    -0.1895     0.1895
  1.1901     0.0000    -0.0000

  0.0000     1.0452    -0.1378

 -0.0000    -0.1378     1.0452
```

APPENDIX B

Appendix B contains the modified version of the CNDO-INDO computer program discussed in Section III of this paper. The data which must be input includes the Z and Y coefficients, the number of molecules which are to be executed during each run, the CNDO or INDO option desired, that the molecule has a closed-shell (only closed-shell molecules can be accommodated by the program), the number of atoms in the molecule, its charge, multiplicity, and X, Y, and Z coordinates with respect to the coordinate system chosen for the molecule. The data is input in the following way:

CARDS 1-87 - NZZ and NZZV (Format (8X,I3,2X,I6))

CARDS 88-311 - NZY and NZYV (Format (8X,I4,2X,I6))

CARD 312 NRUNS (Format (I2)

CARD 313 - An identification card with any format

CARD 314 - OPTION (wavefunction option) and OPNCLO
(The key words are CNDO or INDO and CLSD.
The format is (A4,1X,A4)

CARD 315 - NATOMS, CHARGE, MULTIP (Format (3I4)

CARDS 316 - Atomic number, X coordinate, Y coordinate,
and Z coordinate - 1 card/atom
The format is (I4,3(3X,F12.7))

```
.1..../....2..../....3..../....4..../....5..../....6..../....7... PAGLIN
```

```
 PACK  NO. 067766
NINDO     FORT/FN          CN1    N   NN       2B1 064    S2UPCHURCH
           AUTHORK UPCHURCH
        01001 P1108001                          S
        03622 P01136               060
OGRAM CNINDO
UBLE PRECISION ABC, C, XYZ, A, B
MMON/ARRAYS/ABC(1922),NZZ(87),NZZV(87),NZY(224),NZYV(224)
MMON/PERTBL/EL(18)
MMON/INFO/NATOMS,CHARGE,MULTIP,AN(10),C(10,3),N
MMON/ORB/ORB(9)
MMON/GAB/XYZ(630)
MMON/INFO1/CZ(10),U(31),ULIM(10),LLIM(10),NELECS,OCCA,OCCB
MMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
MMON/AUXINT/A(17),B(17)
TEGER  OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
TEGER ORB,EL,AN,CHARGE,CZ,U,ULIM,OCCA,OCCB
PUT IS READ IN THE FOLLOWING ORDER
 IDENTIFICATION CARD WHICH IS PRINTED AT THE BEGINNING OF THE RU
TION(WAVE FUNCTION OPTION) AND OPNCLO(OPEN OR CLOSED SHELL)
  THE FORMAT IS A4,1X,A4  AND THE KEY WORDS ARE-
     FOR THE WAVEFUNCTION(A4)     CNDO     INDO
     FOR THE OPEN-CLOSED OPTION(A6)    OPEN    CLSD
OMS,CHARGE,MULTIP    FORMAT(3I4)
MIC NUMBER, X COORDINATE, Y COORDINATE, Z COORDINATE - 1 CARD/A
 FORMAT(I4,3(3X,F12.7))
7 I=1,87
D (1,75) NZZ(I),NZZV(I)
8 I=1,224
D (1,85) NZY(I),NZYV(I)
D (1,12) NRUNS
11 K1=1,NRUNS
D (1,20) (AN(I),I=1,10)
TE (3,30) (AN(I),I=1,10)
D(1,40) OPTION,OPNCLO
TE (3,45)OPTION,OPNCLO
D(1,50) NATOMS,CHARGE,MULTIP
TE(3,60) NATOMS,CHARGE,MULTIP
10 I = 1,NATOMS
D(1,70) AN(I),C(I,1),C(I,2),C(I,3)
TE(3,70) AN(I),C(I,1),C(I,2),C(I,3)
VERSION OF COORDINATES FROM ANGSTROMS TO ATOMIC UNITS
9 J=1,3
,J) = C(I,J)/.52916700
TINUE
(OPTION.EQ.CNDO) GO TO 6
5 I=1,NATOMS
(AN(I).LE.9) GO TO 4
TE(3,3)
```

Z AND Y COEFFICIENTS FOR CALCULATION OF REDUCED OVERLAP INTEGRALS ARE INPUT

ALLOWS FOR ANY NUMBER [NRUNS] OF MOLECULES TO BE INPUT AT ONCE

```
  PROGRAM CNINDO   00                  SOURCE      XXXX567890              DATE
..1..../....2..../....3..../....4..../....5..../....6..../....7...  PAGLIN

ORMAT(5X,46HTHIS PROGRAM DOES NOT DO INDO CALCULATIONS FOR,        000480
 51H MOLECULES CONTAINING ELEMENTS HIGHER THAN FLUORINE)           000490
TOP                                                                000500
ONTINUE                                                            000510
ONTINUE                                                            000520
ONTINUE                                                            000530
ALL  INTGRL                                                        000540
ALL  HUCKCL                                                        000550
ALL  SCFCLO                                                        000560
ALL  CPRINT                                                        000570
ONTINUE                                                            000580
O TO 100                                                           000590
ONTINUE                                                            000600
ORMAT (I2)                                                         000610
ORMAT (10A4)                                                       000620
ORMAT(1H1,5X,20A4)                                                 000630
ORMAT(A4,1X,A4)                                                    000640
ORMAT(5X,A4,1X,A4)                                                 000650
ORMAT(3I4)                                                         000660
ORMAT(/5X,I4,18H ATOMS   CHARGE  =,I4,18H    MULTIPLICITY  =,I4/)  000670
ORMAT(I4,3(3X,F12.7))                                              000680
ORMAT (8X,I3,2X,I6)                                                000690
ORMAT (8X,I4,2X,I6)                                                000700
ALL EXIT                                                           000710
TOP                                                                000720
ND                                                                 000730

  / ALLOCATION

3C         03C10 NZZ          03D6C NZZV         03EC8 NZY
ZYV

  / ALLOCATION

  / ALLOCATION

ATOMS      00004 CHARGE       C0008 MULTIP       0000C AN
(          00124 N

  / ALLOCATION

RB

  / ALLOCATION

YZ

  / ALLOCATION

           00028 U            000A4 ULIM         000CC LLIM
LECS       000F8 OCCA         000FC OCCB
```

```
 PROGRAM CNINDO   00                            SOURCE       XXXX567890                DATE
.1..../....2..../....3..../....4..../....5..../....6..../....7... PAGLIN

OCK DATA                                                                              000740
MMON/ORB/ORB(9)                                                                       000750
MMON/PERTBL/EL(18)                                                                    000760
MMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN                                000770
TEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN                                      000780
TEGER ORB,EL                                                                          000790
TA CNDO/4HCNDO/                                                                       000800
TA INDO/4HINDO/                                                                       000810
TA OPEN /4HOPEN/                                                                      000820
TA CLOSED/4HCLSD/                                                                     000830
TA ORB(1)/4H   S/                                                                     000840
TA ORB(2)/4H  PX/                                                                     000850
TA ORB(3)/4H  PY/                                                                     000860
TA ORB(4)/4H  PZ/                                                                     000870
TA ORB(5)/4H DZ2/                                                                     000880
TA ORB(6)/4H DXZ/                                                                     000890
TA ORB(7)/4H DYZ/                                                                     000900
TA ORB(8)/4HDX-Y/                                                                     000910
TA ORB(9)/4H DXY/                                                                     000920
TA EL(1)/4H   H/                                                                      000930
TA EL(2)/4H  HE/                                                                      000940
TA EL(3)/4H  LI/                                                                      000950
TA EL(4)/4H  BE/                                                                      000960
TA EL(5)/4H   B/                                                                      000970
TA EL(6)/4H   C/                                                                      000980
TA EL(7)/4H   N/                                                                      000990
TA EL(8)/4H   O/                                                                      001000
TA EL(9)/4H   F/                                                                      001010
TA EL(10)/4H  NE/                                                                     001020
TA EL(11)/4H  NA/                                                                     001030
TA EL(12)/4H  MG/                                                                     001040
TA EL(13)/4H  AL/                                                                     001050
TA EL(14)/4H  SI/                                                                     001060
TA EL(15)/4H   P/                                                                     001070
TA EL(16)/4H   X/                                                                     001080
TA EL(17)/4H  CL/                                                                     001090
TA EL(18)/4H  AR/                                                                     001100
D                                                                                     001110


 / ALLOCATION

B

 / ALLOCATION


 / ALLOCATION

TION      00004 OPNCLO     00008 HUCKEL     0000C CNDO
DO        00014 CLOSED     00018 OPEN

ALLOCATION
```

```
  PROGRAM CNINDO   00                    SOURCE       XXXX567890               DATE
..1..../....2..../....3..../....4..../....5..../....6..../....7...  PAGLIN

JBROUTINE INTGRL     CALCULATION OF  OVERLAP  AND  COULOMB  INTEGRALS   001120
OUBLE PRECISION S, XX, C, XXX, GAMMA, P, T, TEMP, C1, C2, YYY,          001130
 B, MU, NUM, K1, K2, NEWS, NEWV,PAIRS,TERM1,TERM2,NUM,DEN               001140
TOMIC INTEGRALS FOR CNDO CALCULATIONS                                   001150
OMMON/ARRAYS/S(31,31),XX(961),DUMMY(622)                                001160
OMMON/INFO/NATOMS,CHARGE,MULTIP,AN(10),C(10,3),N                        001170
OMMON/INFO1/CZ(10),U(31),ULIM(10),LLIM(10),NELECS,OCCA,OCCB             001180
OMMON/GAB/XXX(155),GAMMA(10,10),T(9,9),PAIRS(9,9),TEMP(9,9)             001190
 ,C1(3),C2(3),YYY(126)                                                  001200
OMMON/AUXINT/A(17),B(17)                                                001210
OMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN                 001220
IMENSION MU(18),NC(18),LC(9),MC(9),E(3)                                 001230
IMENSION P(31,31)                                                       001240
QUIVALENCE (P(1),XX(1))                                                 001250
NTEGER AN,ULIM,ULK,ULL,CZ,U,CHARGE,ANL,ANK,OCCA,OCCB                    001260
NTEGER  OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN                      001270
ETERMINATION OF SIZE OF AO BASIS IN AND CORE CHARGE CZ                  001280
=0                                                                      001290
) 60 I=1,NATOMS                                                         001300
.IM(I) = N+1                                                            001310
=1                                                                      001320
' (AN(I).LT.11) GO TO 20                                                001330
=N+9                                                                    001340
:(I)=AN(I)-10                                                           001350
) TO 50                                                                 001360
' (AN(I).LT.3) GO TO 40                                                 001370
=N+4                                                                    001380
:(I) = AN(I)-2                                                          001390
) TO 50                                                                 001400
=N+1                                                                    001410
:(I)= AN(I)                                                             001420
NTINUE                                                                  001430
.IM(I) = N                                                              001440
NTINUE                                                                  001450
LL U ARRAY---U(J) IDENTIFIES THE ATOM TO WHICH ORBITAL J IS             001460
TACHED E.G. ORBITAL 32 ATTACHED TO  ATOM 7, ETC.                        001470
 70 K=1,NATOMS                                                          001480
K = LLIM(K)                                                             001490
K = ULIM(K)                                                             001500
M = ULK+1-LLK                                                           001510
 70 I=1,LIM                                                             001520
= LLK+I-1                                                               001530
J) = K                                                                  001540
SIGNMENT OF ORBITAL EXPONENTS TO ATOMS BY SLATERS RULES                 001550
(2)=1.7D0                                                               001560
(1)=1.2D0                                                               001570
(1)=1                                                                   001580
(2)=1                                                                   001590
 80 I=3,10                                                              001600
(I)=2                                                                   001610
(I)=.325D0*(I-1)                                                        001620
 90 I=11,18                                                             001630
(I)=3                                                                   001640
(I)=(.65D0*(I)-4.95D0)/3.D0                                             001650
SIGNMENT OF ANGULAR MOMENTUM QUANTUM NOS. TO ATOMIC ORBITALS            001660
```

```
(1)=0
(2)=1
(3)=1
(4)=1
(5)=2
(6)=2
(7)=2
(8)=2
(9)=2
(1)=0
(2)=1
(3)=-1
(4)=0
(5)=0
(6)=1
(7)=-1
(8)=2
(9)=-2
EP THRU PAIRS OF ATOMS
 320 K=1,NATOMS
 320 L=K,NATOMS
 100 I=1,3
(I) = C(K,I)
(I) = C(L,I)
LCULATE UNIT VECTOR ALONG INTERATOM AXIS
LL RELVEC(R,E,C1,C2)
K = LLIM(K)
. = LLIM(L)
K = ULIM(K)
. = ULIM(L)
RBK=ULK-LLK+1
RBL=ULL-LLL+1
K=AN(K)
.=AN(L)
OP THRU PAIRS OF BASIS FUNCTIONS, ONE ON EACH ATOM
 200 I=1,NORBK
 200 J=1,NORBL
(K.EQ.L) GO TO 160
(MC(I).NE.MC(J)) GO TO 150    SEE STATEMENT 150
(MC(I).LT.0) GO TO 140
WV= ((MU(ANK)*R)**(2*NC(ANK)+1)*(MU(ANL)*R)**(2*NC(ANL)+1)/   *
ACT(2*NC(ANK))*FACT(2*NC(ANL))))
WS = SS(NC(ANK),LC(I),MC(I),NC(ANL),LC(J),MU(ANK)*R,MU(ANL)*R)
 (NEWV .LE. 0) GO TO 135
IRS (I,J)=DSQRT (NEWV)*(-1.D0)**(LC(J)+MC(J))*NEWS
 TO 190
IRS (I,J)=0.D0
 TO 190
IRS(I,J)=PAIRS(I-1,J-1)
 TO 190
IRS(I,J)=0.D0D    ZERO DIFFERENTIAL OVERLAP APPROXIMATION
 TO 190
(I.EQ.J) GO TO 170
IRS(I,J)=0.D0D
 TO 190
```

was the problem area. We created variables NEWV and NEWS to break up PAIRS(I,J) in
ement 130. PAIRS(I,J) are the overlap integral matix elements.

```
:RS(I,J)=1.0D0
ITINUE
ITINUE
JLK=LC(NORBK)
JLL=LC(NORBL)
(L=MAX0(LCULK,LCULL)
R.GT.0.000001D0) GO TO 220
 TO 250
ATE INTEGRALS FROM DIATOMIC BASIS TO MOLECULAR BASIS
.L HARMTR(T,MAXL,E)
 230 I=1,NORBK
 230 J=1,NORBL
IP(I,J) = 0.D0
 230 KK=1,NORBL
IP(I,J) = TEMP(I,J)+T(J,KK)*PAIRS(I,KK)
ITINUE
 240 I=1,NORBK
 240 J=1,NORBL
:RS(I,J) = 0.D0
 240 KK=1,NORBK
:RS(I,J) = PAIRS(I,J)+T(I,KK)*TEMP(KK,J)
ITINUE
.L S MATRIX
ITINUE
 260 I=1,NORBK
:P=LLK+I-1
 260 J=1,NORBL
.P=LLL+J-1
.LKP,LLLP)=PAIRS(I,J)
IPUTATION OF 1-CENTER COULOMB INTEGRALS OVER SLATER S FUNCTIONS
:NC(ANK)
:NC(ANL)
:MU(ANK)
:MU(ANL)
 K.NE.L) GO TO 290
:M1 = FACT(2*N1-1)/((2.D0*K2)**(2*N1))
:M2 = 0.D0
I = 2*N1
 280 J=1,LIM
I =J*(2.D0*K1)**(2*N1-J)*FACT(4*N1-J-1)
I = FACT(2*N1-J)*2.D0*N1*(2.D0*(K1+K2))**(4*N1-J)
:M2 = TERM2 + NUM/DEN
TINUE
TO 310
PUTATION OF 2-CENTER COULOMB INTEGRALS OVER SLATER S FUNCTIONS
M1=(R/2.D0)**(2*N2)*SS(0,0,0,2*N2-1,0,0.D0,2.D0*K2*R)
M2 = 0.D0
 = 2*N1
300 J=1,LIM
M2 = TERM2+(J*(2.D0*K1)**(2*N1-J)*(R/2.D0)**(2*N1-J+2*N2))/
 (FACT(2*N1-J)*2.D0*N1)*SS(2*N1-J,0,0,2*N2-1,0,2.D0*K1*R,2.D0*
  K2*R)
MA(K,L) = ((2.D0*K2)**(2*N2+1)/FACT(2*N2))*(TERM1-TERM2)
TINUE
METRIZATION OF OVERLAP AND COULOMB INTEGRAL MATRICES
```

```
 PROGRAM CNINDO  00                  SOURCE      XXXX567890            DATE 2
•1••••/••••2••••/••••3••••/••••4••••/••••5••••/••••6••••/••••7••• PAGLIN

 330 I=1,N                                                         002770
 330 J=I,N                                                         002780
J,I) = S(I,J)                                                      002790
 340 I=1,NATOMS                                                    002800
 340 J=I,NATOMS                                                    002810
MMA(J,I) = GAMMA(I,J)                                              002820
ITE(3,350)                                                         002830
RMAT(1H1,1X,23HOVERLAP INTEGRAL MATRIX)                            002840
.L MATOUT(N,1)                                                     002850
ANSFER GAMMA TO 80X80 MATRIX P FOR PRINTING                        002860
 360 I=1,NATOMS                                                    002870
 360 J=1,NATOMS                                                    002880
I,J)=GAMMA(I,J)                                                    002890
ITE(3,370)                                                         002900
RMAT(1X,23HCOULOMB INTEGRAL MATRIX)                                002910
.L MATOUT(NATOMS,2)                                                002920
TURN                                                               002930
)                                                                  002940


 / ALLOCATION

        01E08 XX          03C10 DUMMY       01E08 P


 / ALLOCATION

'OMS    00004 CHARGE      00008 MULTIP      0000C AN
        00124 N

 / ALLOCATION

        00028 U           000A4 ULIM        000CC LLIM
.ECS    000F8 OCCA        000FC OCCB

 / ALLOCATION

        004D8 GAMMA       007F8 T           00A80 PAIRS
IP      00F90 C1          00FA8 C2          00FC0 YYY


 / ALLOCATION

        00088 B

 / ALLOCATION

ION     00004 OPNCLO      00008 HUCKEL      0000C CNDO
O       00014 CLOSED      00018 OPEN

CE ALLOCATION


UBROUTINE
```

```
UBLE PRECISION FUNCTION SS(NN1,LL1,MM,NN2,LL2,ALPHA,BETA)
UBLE PRECISION S, XX, A, B, P, PT, X, PPP1, PPP2, PPP3, PPP
OCEDURE FOR CALCULATING REDUCED OVERLAP INTEGRALS
MMON/ARRAYS/S(31,31),XX(961),NZZ(87),NZZV(87),NZY(224),NZYV(224)
MMON/AUXINT/A(17),B(17)
TEGER ULIM
=NN1
=LL1
MM
=NN2
=LL2
=(ALPHA + BETA)/2.D0
=(ALPHA - BETA)/2.D0
= 0.D0
IABS(M)
VERSE QUANTUM NUMBERS IF NECESSARY
((L2.LT.L1).OR.((L2.EQ.L1).AND.(N2.LT.N1))) GO TO 20
 TO 30
= N1
= N2
= K
 L1
= L2
= K
=-PT
NTINUE
= MOD((N1+N2-L1-L2),2)
ND A AND B INTEGRALS
L AINTGS(P,N1+N2)
L BINTGS(PT,N1+N2)
((L1.GT.0).OR.(L2.GT.0)) GO TO 60
GIN SECTION USED FOR OVERLAP INTEGRALS INVOLVING S FUNCTIONS
ND Z TABLE NUMBER L
= (90-17*N1+N1**2-2*N2)/2
IM = N1+N2
IM = 0
 50 I=LLIM,ULIM
)
I1=N1+N2-I+1
 48 J=1,87
 (I+1+17*(L-1)-NZZ(J)) 48,42,48  }
NZZV(J)                            } ASSIGNMENT OF NON-ZERO Z VALUES.
 TO 49
NTINUE
NTINUE
X+Z*A(I+1)*B(NNI1)/2.D0
NTINUE
X
 TO 80
GIN SECTION USED FOR OVERLAPS INVOLVING NON-S FUNCTIONS
ND Y TABLE NUMBER L
5-M)*(24-10*M+M**2)*(83-30*M+3*M**2)/120+
30-9*L1+L1**2-2*N1)*(28-9*L1+L1**2-2*N1)/8+
30-9*L2+L2**2-2*N2)/2
M = 0
```

```
 PROGRAM CNINDO  00                     SOURCE       XXXX567890           DATE 2
•1••••/••••2••••/••••3••••/••••4••••/••••5••••/••••6••••/••••7•••  PAGLIN

 70 I=LLIM,8                                                        003500
IM=4 - MOD(K+I,2)                                                   003510
 70 J=LLIM,ULIM                                                     003520
0                                                                   003530
II=2*J+MOD(K+I,2)+1                                                 003540
 68 I1=1,224                                                        003550
 ((I+1+9*J+9*5*(L-1))-NZY(I1)) 68,62,68                             003560
NZYV(I1)                                                            003570
 TO 69                                                              003580
NTINUE                                                              003590
NTINUE                                                              003600
X+Y*A(I+1)*B(IIII)                                                  003610
NTINUE                                                              003620
P1=(2*L1+1)*FACT(L1-M)                                              003630
P2=(2*L2+1)*FACT(L2-M)                                              003640
P3=(4.D0*FACT(L1+M)*FACT(L2+M))                                     003650
P=PPP1*PPP2/PPP3                                                    003660
 (PPP .GT. 0) GO TO 72                                              003670
ITE (3, 101) PPP                                                    003680
P=0                                                                 003690
=X*(FACT(M+1)/8.D0)**2*DSQRT(PPP)                                   003700
NTINUE                                                              003710
RMAT (1X,4HPPP=, D15.6)                                             003720
TURN                                                                003730
D                                                                   003740
```

Assignment of non-zero Y coefficients

```
 / ALLOCATION

         01E08 XX            03C10 NZZ           03D6C NZZV
Y        04248 NZYV

 / ALLOCATION

         00088 B

SUBROUTINE

   QDBLE        IABS         MOD          AINTGS       BINTGS       :CHS
   FACT         QFWRIT       QIOED        QFINIO       DSQRT        QSTOP

LLOCATION

         00108 N1            0010C L1            00110 M
         00118 L2            0011C P             00124 PT
         00134 K             00138 L             0013C ULIM
:M       00144 I             00148 Z             0014C NNI1
         00154 Y             00158 IIII          0015C I1
P1       00168 PPP2          00170 PPP3          00178 PPP

LOCATION
```

```
BROUTINE HARMTR(T,MAXL,E) ROTATES INTEGRALS FROM DIATOMIC TO MOLECULAR BASIS  003750
JBLE PRECISION T, E, COST,SINT,COSP,SINP, COS2T,SIN2T,COS2P,SIN2   003760
SQRT3                                                              003770
MENSION T(9,9),E(3)                                                003780
ST = E(3)                                                          003790
((1.D0-COST**2).GT.0.0000000001) GO TO 20                          003800
NT = 0.D0                                                          003810
 TO 30                                                             003820
NT=DSQRT(1.D0-COST**2)                                             003830
NTINUE                                                             003840
(SINT.GT.0.000001D0)  GO TO 50                                     003850
SP = 1.D0                                                          003860
NP = 0.D0                                                          003870
 TO 70                                                             003880
SP = E(1)/SINT                                                     003890
NP = E(2)/SINT                                                     003900
NTINUE                                                             003910
 80 I=1,9                                                          003920
 80 J=1,9                                                          003930
I,J) = 0.D0                                                        003940
1,1) =1.D0                                                         003950
 (MAXL.GT.1) GO TO 100                                             003960
 (MAXL.GT.0) GO TO 110                                             003970
 TO 120                                                            003980
S2T = COST**2-SINT**2                                              003990
N2T = 2.D0*SINT*COST                                               004000
S2P = COSP**2-SINP**2                                              004010
N2P = 2.D0*SINP*COSP                                               004020
ANSFORMATION MATRIX ELEMENTS FOR D FUNCTIONS                       004030
RT3=DSQRT(3.D0)                                                    004040
5,5) = (3.D0*COST**2-1.D0)/2.D0                                    004050
5,6) = -SQRT3   *SIN2T/2.D0                                        004060
5,8) = SQRT3   *SINT**2/2.D0                                       004070
6,5) = SQRT3   *SIN2T*COSP/2.D0                                    004080
6,6) = COS2T*COSP                                                  004090
6,7) = -COST*SINP                                                  004100
6,8) =-T(6,5)/SQRT3                                                004110
6,9) = SINT*SINP                                                   004120
7,5) = SQRT3   *SIN2T*SINP/2.D0                                    004130
7,6) = COS2T*SINP                                                  004140
7,7) = COST*COSP                                                   004150
7,8) = -T(7,5)/SQRT3                                               004160
7,9) = -SINT*COSP                                                  004170
3,5) = SQRT3   *SINT**2*COS2P/2.D0                                 004180
3,6) = SIN2T*COS2P/2.D0                                            004190
3,7) = -SINT*SIN2P                                                 004200
(8,8) = (1.D0+COST**2)*COS2P/2.D0                                  004210
3.9) = -COST*SIN2P                                                 004220
9,5) = SQRT3   *SINT**2*SIN2P/2.D0                                 004230
9,6) = SIN2T*SIN2P/2.D0                                            004240
9,7) = SINT*COS2P                                                  004250
9,8) = (1.D0+COST**2)*SIN2P/2.D0                                   004260
9,9) = COST*COS2P                                                  004270
ITINUE                                                             004280
NSFORMATION MATRIX ELEMENTS FOR P FUNCTIONS                        004290
```

```
  PROGRAM CNINDO   00                         SOURCE      XXXX567890               DATE
.1..../....2..../....3..../....4..../....5..../....6..../....7... PAGLIN

(2,2) = COST*COSP                                                              004300
(2,3) = -SINP                                                                  004310
(2,4) = SINT*COSP                                                              004320
(3,2) = COST*SINP                                                              004330
(3,3) = COSP                                                                   004340
(3,4) = SINT*SINP                                                              004350
(4,2) = -SINT                                                                  004360
(4,4) = COST                                                                   004370
NTINUE                                                                         004380
TURN                                                                           004390
D                                                                              004400


SUBROUTINE

   QDBLE        DSQRT        QSTOP

ALLOCATION

RMTR      00084 COST        0008C SINT        00094 COSP
NP        000A4 I           000A8 J           000AC COS2T
N2T       000BC COS2P       000C4 SIN2P       000CC SQRT3


LLOCATION
```

```
 PROGRAM CNINDO   00                    SOURCE       XXXX567890                DATE 2
•1••••/••••2••••/••••3••••/••••4••••/••••5••••/••••6••••/••••7••• PAGLIN

BROUTINE RELVEC(R,E,C1,C2) CALCULATES UNIT VECTOR ALONG INTERATOMIC AXIS  004410
UBLE PRECISION E, C1, C2,X,R                                            004420
MENSION E(3),C1(3),C2(3)                                                004430
= 0.D0                                                                  004440
 10 I=1,3                                                               004450
I) = C2(I)-C1(I)                                                        004460
X+E(I)*E(I)                                                             004470
NTINUE                                                                  004480
DSQRT(X)                                                                004490
 40 I=1,3                                                               004500
 (R.GT..000001D0) GO TO 30                                              004510
 TO 40                                                                  004520
I) =E(I)/R                                                              004530
NTINUE                                                                  004540
TURN                                                                    004550
D                                                                       004560

SUBROUTINE

  DSQRT        QSTOP

ALLOCATION

.VEC       0004C X             00054 I

LLOCATION
```

```
  PROGRAM CNINDO  00                        SOURCE       XXXX567890              DATE
.1..../....2..../....3..../....4..../....5..../....6..../....7...  PAGLIN

UBLE PRECISION FUNCTION FACT (N)     computes  N  factorial.               004570
UBLE PRECISION PRODT                                                        004580
ODT = 1.D0                                                                  004590
 30 I=1,N                                                                   004600
ODT=PRODT*I                                                                 004610
CT=PRODT                                                                    004620
TURN                                                                        004630
D                                                                           004640

SUBROUTINE

   :CNVIR      QSTOP

ALLOCATION

CT         00028 PRODT        00030 I
```

```
BROUTINE BINTGS(X,K)  called in SS.                                    004650
LLS ARRAY OF B-INTEGRALS. NOTE THAT B(I) IS B(I-1) IN THE              004660
UAL NOTATION                                                           004670
R X.GT.3                       EXPONENTIAL FORMULA IS USED             004680
R 2.LT.X.LE.3 AND K.LE.10      EXPONENTIAL FORMULA IS USED             004690
R 2.LT.X.LE.3 AND K.GT.10      15 TERM SERIES IS USED                  004700
R 1.LT.X .E.2 AND K.LE.7       EXPONENTIAL FORMULA IS USED             004710
R 1.LT.X.LE.2 AND K.GT.7       12 TERM SERIES IS USED                  004720
R .5.LT.X.LE.1 AND K.LE.5      EXPONENTIAL FORMULA IS USED             004730
R .5.LT.X.LE.1 AND K.GT.5       7 TERM SERIES IS USED                  004740
R X.LE..5                       6 TERM SERIES IS USED                  004750
****************************************************************       004760
UBLE PRECISION A, B, ABSX, EXPX, EXPMX, Y                              004770
MMON/AUXINT/A(17),B(17)                                                004780
 5 I=1,17                                                              004790
I)=0.D0                                                                004800
NTINUE                                                                 004810
=0                                                                     004820
SX=DABS(X)                                                             004830
(ABSX.GT.3.D0) GO TO 120                                               004840
(ABSX.GT.2.D0) GO TO 20                                                004850
(ABSX.GT.1.D0) GO TO 50                                                004860
(ABSX.GT..5D0) GO TO 80                                                004870
(ABSX.GT..000001D0) GO TO 110                                          004880
 TO 170                                                                004890
ST=6                                                                   004900
 TO 140                                                                004910
(K.LE.5) GO TO 120                                                     004920
ST=7                                                                   004930
 TO 140                                                                004940
(K.LE.7) GO TO 120                                                     004950
ST=12                                                                  004960
 TO 140                                                                004970
(K.LE.10) GO TO 120                                                    004980
ST=15                                                                  004990
 TO 140                                                                005000
PX=DEXP(X)                                                             005010
PMX=1.D0/EXPX                                                          005020
1)=(EXPX-EXPMX)/X                                                      005030
 130 I=1,K                                                             005040
I+1)=(I*B(I)+(-1.D0)**I*EXPX-EXPMX)/X                                  005050
 TO 190                                                                005060
 160 I=I0,K                                                            005070
0.D0                                                                   005080
 150 M=I0,LAST                                                         005090
Y+(-X)**M*(1.D0-(-1.D0)**(M+I+1))/(FACT(M)*(M+I+1))                    005100
I+1)=Y                                                                 005110
 TO 190                                                                005120
 180 I=I0,K                                                            005130
I+1)=(1.D0-(-1.D0)**(I+1))/(I+1)                                       005140
NTINUE                                                                 005150
TURN                                                                   005160
D                                                                      005170
```

```
 PROGRAM CNINDO   00                    SOURCE      XXXX567890              DATE 2
.1..../....2..../....3..../....4...../..../....5..../....6..../....7...  PAGLIN

BROUTINE AINTGS(X,K)      CALLED IN SS. FILLS ARRAY OF A INTEGRALS.    005180
UBLE PRECISION A, B                                                    005190
MMON/AUXINT/A(17),B(17)                                                005200
 5 I=1,17                                                              005210
I)=0.D0                                                                005220
NTINUE                                                                 005230
1) =DEXP(-X)/X                                                         005240
 10  I=1,K                                                             005250
I+1) =(A(I)*I+DEXP(-X))/X                                              005260
TURN                                                                   005270
D                                                                      005280

 / ALLOCATION

         00088 B

SUBROUTINE

  DEXP         QDBLE        :CNVIR       QSTOP

ALLOCATION

NTGS       0004C I

LOCATION
```

```
 PROGRAM CNINDO  00                SOURCE      XXXX567890          DATE :
•1••••/••••2••••/••••3••••/••••4••••/••••5••••/••••6••••/••••7••• PAGLIN

BROUTINE MATOUT(N,MATOP)    PRINTING ROUTINE FOR OVERLAP AND COULOMB  005290
UBLE PRECISION A            INTEGRAL MATRICES.                        005300
MMON/ARRAYS/A(31,31,2),DUMMY(622)                                     005310
 80 M=1,N,11                                                          005320
M+10                                                                  005330
 (K.LE.N) GO TO 30                                                    005340
N                                                                     005350
NTINUE                                                                005360
ITE(3,40) (J,J=M,K)                                                   005370
RMAT(//,7X,11(4X,I2,3X),//)                                           005380
 60 I=1,N                                                             005390
ITE(3,50) I,(A(I,J,MATOP),J=M,K)                                      005400
RMAT(1X,I2,4X,50(F9.4))                                               005410
NTINUE                                                                005420
ITE(3,70)                                                             005430
RMAT(//)                                                              005440
NTINUE                                                                005450
TURN                                                                  005460
D                                                                     005470

 / ALLOCATION

        03C10 DUMMY

SUBROUTINE

  QFWRIT      QIOEI      QFINIO      QIOED      QSTOP

ALLOCATION

TOUT     00040 M          00044 K          00048 J

LOCATION
```

```
BROUTINE HUCKCL   MAKES EXTENDED-HUCKEL APPROXIMATION OF FOCK MATRIX ELEMENTS.
UBLE PRECISION A, B, C, XXX, G, Q, YYY, ENERGY, XXY, RHO,TEMP
TENDED HUCKEL THEORY FOR CLOSED SHELLS
ERLAPS ARE IN MATRIX A, COULOMB INTEGRALS (GAMMA) ARE IN MATRIX
MMON/ARRAYS/A(31,31),B(31,31),DUMMY(622)
MMON/INFO/NATOMS,CHARGE,MULTIP,AN(10),C(10,3),N
MMON/INFO1/CZ(10),U(31),ULIM(10),LLIM(10),NELECS,OCCA,OCCB
MMON/GAB/XXX(155),G(10,10),Q(31),YYY(31),ENERGY,XXY(312)
MMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
MENSION ENEG(18,3),BETA0(18)
MENSION G1(18),F2(18)
TEGER CHARGE,OCCA,OCCB,UL,AN,CZ,U,ULIM,ANI
TEGER  OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
(3)=.092012
(4)=.1407
(5)=.199265          G1 (18), F2(18), ENEG(18,3) AND BETA0(18)
(6)=.267708          WERE ORIGINALLY DOUBLE PRECISION VARIABLES.
(7)=.346029
(8)=.43423
(9)=.532305
(3)=.049865
(4)=.089125
(5)=.13041
(6)=.17372
(7)=.219055
(8)=.266415
(9)=.31580
EG(1,1)=7.1761
EG(3,1)=3.1055
EG(3,2)=1.258
EG(4,1)=5.94557
EG(4,2)=2.563
EG(5,1)=9.59407
EG(5,2)=4.001
EG(6,1)=14.051
EG(6,2)=5.572
EG(7,1)=19.31637
EG(7,2)=7.275
EG(8,1)=25.39017
EG(8,2)=9.111
EG(9,1)=32.2724
EG(9,2)=11.08
EG(11,1)=2.804
EG(11,2)=1.302
EG(11,3)=0.150
EG(12,1)=5.1254
EG(12,2)=2.0516
EG(12,3)=0.16195
EG(13,1)=7.7706
EG(13,2)=2.9951
EG(13,3)=0.22425
EG(14,1)=10.0327
EG(14,2)=4.1325
EG(14,3)=0.337
EG(15,1)=14.0327
```

```
 PROGRAM CNINDO  00                         SOURCE       XXXX567890              DATE
1...../....2..../....3..../....4..../....5..../....6..../....7...  PAGLIN

G(15,2)=5.4638                                                     006030
G(15,3)=0.500                                                      006040
G(16,1)=17.6496                                                    006050
G(16,2)=6.989                                                      006060
G(16,3)=0.71325                                                    006070
G(17,1)=21.5906                                                    006080
G(17,2)=8.7081                                                     006090
G(17,3)=0.97695                                                    006100
AO(1)= -9.                                                         006110
AO(3)= -9.                                                         006120
AO(4)= -13.                                                        006130
AO(5)= -17.                                                        006140
AO(6)= -21.                                                        006150
AO(7)=-25.                                                         006160
AO(8)= -31.                                                        006170
AO(9)= -39.                                                        006180
AO(11)=-7.7203                                                     006190
AO(12)=-9.4471                                                     006200
AO(13)=-11.301                                                     006210
AO(14)=-13.065                                                     006220
AO(15)=-15.070                                                     006230
AO(16)=-18.150                                                     006240
AO(17)=-22.330                                                     006250
D NELECS AND FILL H CORE(DIAGONAL) WITH (I+A)/2  (AVERAGE OF IONIZATION 006260
ECS=0                                            POTENTIAL AND ELECTRON 006270
60 I=1,NATOMS                                    AFFINITY.)        006280
ECS=NELECS+CZ(I)                                                   006290
=LLIM(I)                                                           006300
=ULIM(I)                                                           006310
=AN(I)                                                             006320
)                                                                  006330
50 J=LL,UL                                                         006340
+1                                                                 006350
(L.EQ.1) GO TO 10                                                  006360
(L.LT.5) GO TO 40                                                  006370
,J)=-ENEG(ANI,3)/27.21D0                                           006380
TO 50                                                              006390
,J)=-ENEG(ANI,2)/27.21D0                                           006400
TO 50                                                              006410
,J)   =-ENEG(ANI,1)/27.21D0                                        006420
TINUE                                                              006430
TINUE                                                              006440
ECS=NELECS-CHARGE                                                  006450
A=NELECS/2                                                         006460
M HUCKEL HAMILTONIAN IN A (OFF DIAGONAL TWO CENTER TERMS)          006470
90 I=2,N                                                           006480
(I)                                                                006490
N(K)                                                               006500
I-1                                                                006510
90 J=1,UL                                                          006520
U(J)                                                               006530
AN(KK)                                                             006540
((L.GT.9).OR.(LL.GT.9)) GO TO 70                                   006550
,J)=A(I,J)*(BETAO(L)+BETAO(LL))/54.42D0                            006560
,I)=A(I,J)                                                         006570
```

```
O TO 90
(I,J)=0.75D0*A(I,J)*(BETAO(L)+BETAO(LL))/54.42D0
(J,I)=A(I,J)
ONTINUE
O 100 I=1,N
(I)=A(I,I)
HO=1.D-6
ALL EIGN(N,RHO)
IGENVECTORS (IN B) ARE CONVERTED INTO DENSITY MATRIX (IN B)
O 140 I=1,N
O 120 J=I,N
X(J)=0.0D0
O 110 K=1,OCCA
X(J)= XXX(J)+2.D0*B(I,K)*B(J,K)
ONTINUE
O 130 J=I,N
 I,J)= XXX(J)
ONTINUE
O 150 I=1,N
O 150 J=I,N
 J,I)=B(I,J)
D V(AB) TO HCORE--CNDO
   170  I=1,N
U(I)
 I)=Q(I)   +0.5D0*G(J,J)
 160 K=1,NATOMS
 I)=Q(I)-(CZ(K))*G(J,K)
NTINUE
IT SEGMENT IF ONLY CNDO APPROXIMATIONS ARE DESIRED
 (OPTION.EQ.CNDO) GO TO 290
DO MODIFICATION (CORRECTION TO U(I,I) )
 280 I=1,NATOMS
AN(I)
LLIM(I)
 ((K.GT.1).AND.(K.LT.10)) GO TO 190
 TO 280
 (K.LE.3) GO TO 210
J) =Q(J)+(CZ(I)-1.5D0)*G1(K)/6.D0
(K.EQ.3) GO TO 220
(K.EQ.4) GO TO 240
MP = G1(K)/3.D0+(CZ(I)-2.5D0)*2.D0*F2(K)/25.D0
 TO 260
MP=G1(K)/4.D0
 TO 260
MP=G1(K)/12.D0
NTINUE
 270 L=1,3
KK= J+L
KKKK)=Q(KKKK)+TEMP
NTINUE
NTINUE
 310 I=1,N
 300 J=I,N
J,I)=A(I,J)
I,I)=Q(I)
```

```
  PROGRAM CNINDO   00                        SOURCE       XXXX567890                 DATE
••1••••/••••2••••/••••3••••/••••4••••/••••5••••/••••6••••/••••7•••   PAGLIN

RITE(3,320)                                                          007130
ORMAT(1X,18H CORE HAMILTONIAN /)                                     007140
ALL SCFOUT(0,1)                                                      007150
ETURN                                                                007160
ND                                                                   007170


  / ALLOCATION

         01E08 B             03C10 DUMMY

  / ALLOCATION

ATOMS    00004 CHARGE        00008 MULTIP        0000C AN
         00124 N

  / ALLOCATION

         00028 U             000A4 ULIM          000BC LLIM
LECS     000F8 OCCA          000FC OCCB

  / ALLOCATION

X        004D8 G             007F8 Q             008F0 YYY
NERGY    009F0 XXY

  / ALLOCATION

TION     00004 OPNCLO        00008 HUCKEL        0000C CNDO
DO       00014 CLOSED        00018 OPEN

 SUBROUTINE

   EIGN         ICNVIR        QFWRIT        QFINIO        SCFOUT        QSTOP

 ALLOCATION

ICKCL    001B8 I             001BC LL            001C0 UL
I        001C8 L             001CC J             001D0 K
         001D8 RHO           001E0 TEMP          001E8 KKKK

LLOCATION

EG       002C4 BETAO         0030C G1            00354 F2
```

```
UBROUTINE SCFCLO    subroutine for establishing self-consistency.
OUBLE PRECISION A, B, XXX, G, Q, YYY, ENERGY, XXY, C, RHO, PAA
 OLDENG
NDO/INDO CLOSED SHELL SCF SEGMENT
AMMA MATRIX CONTAINED IN G, CORE HAMILTONIAN CONTAINED IN Q AND
PPER TRIANGLE OF A, AND INITIAL DENSITY MATRIX CONTAINED IN B
PTIONS   CNDO OR INDO
OMMON/ARRAYS/A(31,31),B(31,31),DUMMY(622)
OMMON/GAB/XXX(153),G(10,10),Q(31),YYY(31),ENERGY,XXY(312)
OMMON/INFO/NATOMS,CHARGE,MULTIP,AN(10),C(10,3),N
OMMON/INFO1/CZ(10),U(31),ULIM(10),LLIM(10),NELECS,OCCA,OCCB
OMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
NTEGER  OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
NTEGER CHARGE,OCCA,OCCB,UL,ULIM,U,AN,CZ,Z
IMENSION G1(18),F2(18)
(3)=.092012
(4)=.1407
(5)=.199265
(6)=.267708
(7)=.346029
(8)=.43423
(9)=.532305
(3)=.049865
(4)=.089125
(5)=.13041
(6)=.17372
(7)=.219055
(8)=.266415
(9)=.31580
0
=25
0=1.D-6
NTINUE
= Z+1
ERGY = 0.D0
ANSFER CORE HAMILTONIAN TO LOWER TRIANGLE OF A
 20 I=1,N
I,I)=Q(I)
 20 J=I,N
J,I)=A(I,J)
 30 I=1,N
=U(I)
I,I)=A(I,I)-B(I,I)*G(II,II)*0.5D0
 30 K=1,N
=U(K)
I,I)=A(I,I)+B(K,K)*G(II,JJ)
=N-1
 40 I=1,NM
=U(I)
=I+1
 40 J=LL,N
=U(J)
J,I)=A(J,I)-B(J,I)*G(II,JJ)*0.5D0
DO MODIFICATION
 (OPTION.EQ.CNDO) GO TO 90
```

```
 80 II=1,NATOMS
AN(II)
LLIM(II)
 (K.EQ.1) GO TO 80
A=B(I,I)+B(I+1,I+1)+B(I+2,I+2)+B(I+3,I+3)
I,I)=A(I,I)-(PAA-B(I,I)) *G1(K)/6.D0
 70 J=1,3
L=I+J
LLL,LLL)=A(LLL,LLL)-B(I,I)*G1(K)/6.D0-(PAA-B(I,I))*7.D0*
(K)/50.D0+B(LLL,LLL)*11.D0*F2(K)/50.D0
LLL,I)=A(LLL,I)+B(I,LLL)*G1(K)/2.D0
=I+1
=I+2
=I+3
I2,I1)=A(I2,I1)+B(I2,I1)*11.D0*F2(K)/50.D0
I3,I1)=A(I3,I1)+B(I3,I1)*11.D0*F2(K)/50.D0
I3,I2)=A(I3,I2)+B(I3,I2)*11.D0*F2(K)/50.D0
NTINUE
NTINUE
 100 I=1,N
ERGY=ENERGY+0.5D0*B(I,I)*(A(I,I)+Q(I))
 105 I=1,NM
=I+1
 105 J=LL,N
ERGY=ENERGY+B(I,J)*(A(I,J)+A(J,I))
ITE(3,110) ENERGY
RMAT(//,10X,22H ELECTRONIC ENERGY    ,F16.10)
(DABS(ENERGY-OLDENG).GE..00001D0) GO TO 150
26
ITE(3,140)
RMAT(5X,18H ENERGY SATISFIED /)
 TO 170
NTINUE
DENG=ENERGY
NTINUE
 (Z.LE.IT) GO TO 210
MMETRIZE F FOR PRINTING (MATRIX A)
 190 I=1,N
 190 J=I,N
I,J)=A(J,I)
ITE(3,200)
RMAT(1X,27H HARTREE-FOCK ENERGY MATRIX)
L SCFOUT(0,1)
NTINUE
L EIGN(N,RHO)
 (Z.LE.IT) GO TO 240
ITE(3,230)
RMAT(1X,28HEIGENVALUES AND EIGENVECTORS)
L SCFOUT(1,2)
NTINUE
GENVECTORS (IN B) ARE CONVERTED INTO DENSITY MATRIX (IN B)
 280 I=1,N
 260 J=I,N
(J)=0.0D0
 250 K=1,OCCA
```

COMPARISON STATEMENT TO DETERMINE WHETHER OR NOT SELF-CONSISTENCY HAS BEEN ACHIEVED.

```
   PROGRAM CNINDO  00                   SOURCE      XXXX567890                DATE
••1••••/••••2••••/••••3••••/••••4••••/••••5••••/••••6••••/••••7•••  PAGLIN

<X(J)= XXX(J)+B(I,K)*B(J,K)*2.0D0                                   008280
)NTINUE                                                             008290
) 270 J=I,N                                                         008300
I,J)= XXX(J)                                                        008310
)NTINUE                                                             008320
) 290 I=1,N                                                         008330
) 290 J=I,N                                                         008340
J,I)=B(I,J)                                                         008350
' (Z.LE.IT) GO TO 10                                                008360
)NTINUE                                                             008370
:TURN                                                               008380
ID                                                                  008390


  / ALLOCATION

         01E08 B           03C10 DUMMY

  / ALLOCATION

.X       004D8 G           007F8 Q            008F0 YYY
IERGY    009F0 XXY

  / ALLOCATION

TOMS     00004 CHARGE      00008 MULTIP       0000C AN
         00124 N

  / ALLOCATION

         00028 U           000A4 ULIM         000CC LLIM
LECS     000F8 OCCA        000FC OCCB

  / ALLOCATION

TION     00004 OPNCLO      00008 HUCKEL       0000C CNDO
DO       00014 CLOSED      00018 OPEN

SUBROUTINE

   QFWRIT    QIOECS     QFINIO     DABS       SCFOUT     EIGN

ALLOCATION

FCLO     000CC Z           000D0 IT           000D4 RHO
         000E0 J           000E4 II           000E8 K
         000F0 NM          000F4 LL           000F8 PAA
.L       00104 I1          00108 I2           0010C I3
DENG

LLOCATION

         00160 F2
```

```
JBROUTINE CPRINT                                                    008400
OUBLE PRECISION A, B, XXX, G, Q, YYY, ENERGY, XXY, C, DPM, DM,      008410
MSP, DMPD, ATENG, RAD, TCHG, SLTR1, FACTOR, DP                      008420
NDO-INDO SCF CLOSED SHELL- PRINTOUT SEGMENT                         008430
OMMON/ARRAYS/A(31,31),B(31,31),DUMMY(622)                           008440
OMMON/GAB/XXX(155),G(10,10),Q(31),YYY(31),ENERGY,XXY(312)           008450
OMMON/INFO/NATOMS,CHARGE,MULTIP,AN(10),C(10,3),N                    008460
OMMON/INFO1/CZ(10),U(31),ULIM(10),LLIM(10),NELECS,OCCA,OCCB         008470
OMMON/PERTBL/EL(18)                                                 008480
OMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN             008490
NTEGER  OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN                  008500
NTEGER CHARGE,AN,U,ULIM,EL,OCCA,OCCB,UL,CZ,ANI                      008510
IMENSION DPM(3),DM(3),DMSP(3),DMPD(3)                               008520
IMENSION ATENG(18)                                                  008530
F (OPTION.EQ.CNDO) GO TO 20                                         008540
TENG(1)=-0.6387302462  DO                                           008550
TENG(3)=-.2321972405   DO                                           008560
TENG(4)=-1.1219620354  DO                                           008570
TENG(5)=-2.8725750048  DO                                           008580
TENG(6)=-5.9349548261  DO                                           008590
TENG(7)=-10.6731741251 DO                                           008600
TENG(8)=-17.2920850650 DO                                           008610
TENG(9)=-26.2574377875 DO                                           008620
) TO 30                                                             008630
ONTINUE                                                             008640
TENG(1)=-0.6387302462  DO                                           008650
TENG(3)=-.2321972405   DO                                           008660
TENG(4)=-1.1454120355  DO                                           008670
TENG(5)=-2.9774239048  DO                                           008680
TENG(6)=-6.1649936261  DO                                           008690
TENG(7)=-11.0768746252 DO                                           008700
ENG(8)=-18.0819658651  DO                                           008710
ENG(9)=-27.5491302880  DO                                           008720
ENG(11)=-.1977009568   DO                                           008730
ENG(12)=-.8671913833   DO                                           008740
ENG(13)=-2.0364557744  DO                                           008750
ENG(14)=-3.8979034686  DO                                           008760
ENG(15)=-6.7966009163  DO                                           008770
ENG(16)=-10.7658174344DO                                            008780
ENG(17)=-16.0467017940DO                                            008790
ONTINUE                                                             008800
=NATOMS-1                                                           008810
RITE(3,40)                                                          008820
ORMAT(1X,15H DENSITY MATRIX)                                        008830
ALL SCFOUT(0,2)                                                     008840
) 50 I=1,K                                                          008850
=I+1                                                                008860
) 50 J=L,NATOMS                                                     008870
AD=DSQRT((C(I,1)-C(J,1))**2+(C(I,2)-C(J,2))**2                      008880
      +(C(I,3)-C(J,3))**2)                                          008890
NERGY =ENERGY +(CZ(I)*CZ(J))/RAD                                    008900
RITE(3,60) ENERGY                                                   008910
ORMAT(//,10X,16H TOTAL ENERGY = F16.10)                             008920
) 70 I=1,NATOMS                                                     008930
NI=AN(I)                                                            008940
```

```
ERGY=ENERGY-ATENG(ANI)
ITE(3,80) ENERGY
RMAT(//,10X,16HBINDING ENERGY= ,F16.10,5H A.U.)
 110 I=1,NATOMS
HG = 0.D0
=LLIM(I)
=ULIM(I)
 90 J=LL,UL
HG = TCHG+B(J,J)
I=AN(I)
ITE(3,100) I,EL(ANI),TCHG
RMAT(I3,A4,8X,F7.4)
X(I)=TCHG
NTINUE
 120 I=1,3
(I)=0.0D0
SP(I)=0.0D0
PD(I)=0.0D0
 200 J=1,NATOMS
 (AN(J).LT.3) GO TO 180
 (AN(J).LT.11) GO TO 140
TR1=(.65D0*AN(J)-4.95D0)/3.D0
CTOR=2.5416D0*7.D0/(DSQRT(5.D0)*SLTR1)
DEX=LLIM(J)
 170 K=1,3
MM=INDEX+K
SP(K)=DMSP(K)-B(INDEX,MMMM)*10.27175D0/SLTR1
PD(1)=DMPD(1)-FACTOR*(B(INDEX+2,INDEX+8)+B(INDEX+3,INDEX+5)
+B(INDEX+1,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+1,INDEX+4))
PD(2)=DMPD(2)-FACTOR*(B(INDEX+1,INDEX+8)+B(INDEX+3,INDEX+6)
+B(INDEX+2,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+2,INDEX+4))
PD(3)=DMPD(3)-FACTOR*(B(INDEX+1,INDEX+5)+B(INDEX+2,INDEX+6)
+2.D0/DSQRT(3.D0)*B(INDEX+3,INDEX+4))
 TO 180
DEX=LLIM(J)
 150 K=1,3
MM=INDEX + K
SP(K)=DMSP(K)-B(INDEX,MMMM)*7.33697D0/
.325D0*(AN(J)-1))
 190 I=1,3
(I)=DM(I)+(CZ(J)-XXX(J))*C(J,I)*2.5416D0
NTINUE
 210 I=1,3
M(I)=DM(I)+DMSP(I)+DMPD(I)
ITE (3,220)
RMAT(//,20X,16H DIPOLE MOMENTS,/)
ITE(3,230)
RMAT(5X,11H COMPONENTS,3X,2H X,8X,2H Y,8X,2H Z)
ITE(3,240)DM(1),DM(2),DM(3)
RMAT(5X,10H DENSITIES,3(1X,F9.5))
ITE(3,250)DMSP(1),DMSP(2),DMSP(3)
RMAT(5X,4H S.P,6X,3(1X,F9.5))
ITE(3,260)DMPD(1),DMPD(2),DMPD(3)
RMAT(5X,4H P.D,6X,3(1X,F9.5))
ITE(3,270)DPM(1),DPM(2),DPM(3)
```

```
 PROGRAM CNINDO   00                     SOURCE       XXXX567890                DATE :
1..../....2..../....3..../....4..../....5..../....6..../....7...  PAGLIN

MAT(5X,6H TOTAL,4X,3(1X,F9.5),/)                                  009500
DSQRT(DPM(1)**2+DPM(2)**2+DPM(3)**2)                              009510
TE(3,280) DP                                                      009520
MAT(3X,15H DIPOLE MOMENT=,F9.5,7H DEBYES,//)                      009530
JRN                                                               009540
                                                                  009550


 / ALLOCATION

        01E08 B                03C10 DUMMY

 / ALLOCATION

        004D8 G                007F8 Q                008F0 YYY
RGY     009F0 XXY

 / ALLOCATION

DMS     00004 CHARGE           00008 MULTIP           0000C AN
        00124 N

 / ALLOCATION

        00028 U                000A4 ULIM             000CC LLIM
ECS     000F8 OCCA             000FC OCCB

 / ALLOCATION


 / ALLOCATION

ION     00004 OPNCLO           00008 HUCKEL           0000C CNDO
D       00014 CLOSED           00018 OPEN

JBROUTINE

  QFINIO      SCFOUT      DSQRT       ICNVIR      QIOED       QIOEI


.LOCATION

INT     00168 K                0016C I                00170 L
        00178 RAD              00180 ANI              00184 TCHG
        00190 UL               00194 SLTR1            0019C FACTOR
EX      001A8 MMMM             001AC DP

.OCATION

        001CC DM               001E4 DMSP             001FC DMPD
NG
```

```
UBROUTINE EIGN(NN,RHO)   DIAGONALIZATION ROUTINE
OUBLE PRECISION RHO, A, VEC, GAMMA, BETA, BETASQ, EIG, W, XYZ,
, Q, RHOSQ, S, SGN, SQRTS, D, TEMP, WTAW, SUM, QJ, WJ, SHIFT,
OSA, G, PPBS, PPBR, COSAP, SINA, SINA2, DIA, J, A2, R2, R1, R12,
IF, PP
HO= UPPER LIMIT FOR OFF-DIAGONAL ELEMENT
N= SIZE OF MATRIX
 = F MATRIX (ONLY LOWER TRIANGLE IS USED + THIS IS DESTROYED)
IG = RETURNED EIGENVALUES IN ALGEBRAIC ASCENDING ORDER
EC = RETURNED EIGENVECTORS IN COLUMNS
OMMON/ARRAYS/A(31,31),VEC(31,31),DUMMY(622)
OMMON/GAB/GAMMA(31),BETA(31),BETASQ(31),EIG(31),W(31),XYZ(475)
HE FOLLOWING DIMENSIONED VARIABLES ARE EQUIVALENCED
IMENSION P(31),Q(31)
QUIVALENCE (P(1),BETA(1)),(Q(1),BETA(1))
IMENSION IPOSV(31),IVPOS(31),IORD(31)
QUIVALENCE (IPOSV(1),GAMMA(1)),(IVPOS(1),BETA(1)),
IORD(1),BETASQ(1))
HOSQ=RHO*RHO
=NN
F (N .EQ. 0) GO TO 640
1=N-1
2=N-2
AMMA(1)=A(1,1)
F(N2) 200,190,40
O 180 NR=1,N2
=A(NR+1,NR)
=0.D0
O 50 I=NR,N2
=A(I+2,NR)*A(I+2,NR) +S
REPARE FOR POSSIBLE BYPASS OF TRANSFORMATION
RRR=NR+1
(NRRR,NR)=0.D0
F (S) 170,170,60
=S+B*B
GN=+1.D0
F (B) 70,80,80
GN=-1.D0
QRTS=DSQRT(S)
=SGN/(SQRTS+SQRTS)
EMP=DSQRT(.5D0+B*D)
(NR)=TEMP
(NRRR,NR)=TEMP
=D/TEMP
=-SGN*SQRTS
 IS FACTOR OF PROPORTIONALITY. NOW COMPUTE AND SAVE W VECTOR.
XTRA SINGLY SUBSCRIPTED W VECTOR USED FOR SPEED.
O 90 I=NR,N2
EMP=D*A(I+2,NR)
I1=I+1
 II1)=TEMP
I2=I+2
 II2,NR)=TEMP
REMULTIPLY VECTOR W BY MATRIX A TO OBTAIN P VECTOR.
IMULTANEOUSLY ACCUMULATE DOT PRODUCT WP,(THE SCALAR K)
```

```
TAW=0.D0
) 140 I=NR,N1
JM=0.D0
) 100 J=NR,I
JM=SUM+A(I+1,J+1)*W(J)
.=I+1
F(N1-I1) 130,110,110
) 120 J=I1,N1
JM=SUM+A(J+1,I+1)*W(J)
 I)=SUM
AW=WTAW+SUM*W(I)
 VECTOR AND SCALAR K  NOW STORED. NEXT COMPUTE Q VECTOR
) 150 I=NR,N1
 I)=P(I)-WTAW*W(I)
W FORM PAP MATRIX, REQUIRED PART
 160 J=NR,N1
1=J+1
=Q(J)
=W(J)
 160 I=J,N1
1=I+1
II1,JJ1)=A(I+1,J+1)-2.D0*(W(I)*QJ+WJ*Q(I))
TA(NR)=B
TASQ(NR)=B*B
MMA(NRRR)=A(NR+1,NR+1)
A(N,N-1)
1= N-1
TA(NN1)=B
TASQ(NN1)=B*B
MMA(N)=A(N,N)
TASQ(N)=0.D0
JOIN AN IDENTITY MATRIX TO BE POSTMULTIPLIED BY ROTATIONS.
 220 I=1,N
 210 J=1,N
C(I,J)=0.D0
C(I,I)=1.D0
N
M=0.D0
AS=1
 TO 350
M=SUM+SHIFT
SA=1.D0
GAMMA(1)-SHIFT
=G
BS=PP*PP+BETASQ(1)
BR=DSQRT(PPBS)
 320 J=1,M
SAP=COSA
 (PPBS.GT.1.D-12) GO TO 250
NA=0.D0
NA2=0.D0
SA=1.D0
 TO 290
NA=BETA(J)/PPBR
NA2=BETASQ(J)/PPBS
```

```
••1••••/••••2••••/••••3••••/••••4••••/••••5••••/••••6••••/••••7••• PAGLIN

OSA=PP/PPBR                                                         010660
OSTMULTIPLY IDENTITY BY P-TRANSPOSE MATRIX                          010670
T=J+NPAS                                                            010680
F(NT .LT. N) GO TO 270                                              010690
T=N                                                                 010700
) 280 I=1,NT                                                        010710
EMP=COSA*VEC(I,J)+SINA*VEC(I,J+1)                                   010720
J1=J+1                                                              010730
EC(I,JJ1)=-SINA*VEC(I,J)+COSA*VEC(I,J+1)                            010740
EC(I,J)=TEMP                                                        010750
IA=GAMMA(J+1)-SHIFT                                                 010760
=SINA2*(G+DIA)                                                      010770
MMA(J)=G+U                                                          010780
=DIA-U                                                              010790
=DIA*COSA-SINA*COSAP*BETA(J)                                        010800
(J .NE. M) GO TO 310                                                010810
TA(J)=SINA*PP                                                       010820
TASQ(J)=SINA2*PP*PP                                                 010830
) TO 330                                                            010840
BS=PP*PP+BETASQ(J+1)                                                010850
BR=DSQRT(PPBS)                                                      010860
TA(J)=SINA*PPBR                                                     010870
TASQ(J)=SINA2*PPBS                                                  010880
1=M+1                                                               010890
MMA(MM1)=G                                                          010900
ST FOR CONVERGENCE OF LAST DIAGONAL ELEMENT                         010910
AS=NPAS+1                                                           010920
(BETASQ(M) .GT. RHOSQ) GO TO 370                                    010930
1=M+1                                                               010940
G(MM1)=GAMMA(M+1)+SUM                                               010950
TA(M)=0.D0                                                          010960
TASQ(M)=0.D0                                                        010970
M-1                                                                 010980
(M .EQ. 0) GO TO 400                                                010990
(BETASQ(M) .LE. RHOSQ) GO TO 340                                    011000
KE ROOT OF CORNER 2 BY 2 NEAREST TO LOWER DIAGONAL IN VALUE         011010
 ESTIMATE OF EIGENVALUE TO USE FOR SHIFT                            011020
=GAMMA(M+1)                                                         011030
=0.5D0*A2                                                           011040
=0.5D0*GAMMA(M)                                                     011050
2=R1+R2                                                             011060
F=R1-R2                                                             011070
MP=DSQRT(DIF*DIF+BETASQ(M))                                         011080
=R12+TEMP                                                           011090
=R12-TEMP                                                           011100
F=DABS(A2-R1)-DABS(A2-R2)                                           011110
(DIF .LT. 0.D0) GO TO 390                                           011120
IFT=R2                                                              011130
 TO 230                                                             011140
IFT=R1                                                              011150
 TO 230                                                             011160
3(1)=GAMMA(1)+SUM                                                   011170
ITIALIZE AUXILIARY TABLES REQUIRED FOR REARRANGING THE VECTORS      011180
 410 J=1,N                                                          011190
OSV(J)=J                                                            011200
```

```
 PROGRAM CNINDO   00                    SOURCE       XXXX567890               DATE :
.1..../....2..../....3..../....4..../....5..../....6..../....7...  PAGLIN

'POS(J)=J                                                           011210
IRD(J)=J                                                            011220
E A TRANSPOSITION SORT TO ORDER THE EIGENVALUES                     011230
N                                                                   011240
 TO 450                                                             011250
 440 J=1,M                                                          011260
 (EIG(J) .LE. EIG(J+1)) GO TO 440                                   011270
MP=EIG(J)                                                           011280
G(J)=EIG(J+1)                                                       011290
1=J+1                                                               011300
G(JJ1)=TEMP                                                         011310
EMP=IORD(J)                                                         011320
RD(J)=IORD(J+1)                                                     011330
RD(JJ1)=ITEMP                                                       011340
NTINUE                                                              011350
M=1                                                                 011360
(M .NE. 0) GO TO 420                                                011370
(N1 .EQ. 0) GO TO 510                                               011380
 500 L=1,N1                                                         011390
=IORD(L)                                                            011400
=IPOSV(NV)                                                          011410
(NP .EQ. L) GO TO 500                                               011420
=IVPOS(L)                                                           011430
POS(NP)=LV                                                          011440
OSV(LV)=NP                                                          011450
 490 I=1,N                                                          011460
MP=VEC(I,L)                                                         011470
C(I,L)=VEC(I,NP)                                                    011480
C(I,NP)=TEMP                                                        011490
NTINUE                                                              011500
NTINUE                                                              011510
CK TRANSFORM THE VECTORS OF THE TRIPLE DIAGONAL MATRIX              011520
 570 NRR=1,N                                                        011530
N1                                                                  011540
K=1                                                                 011550
(K .LE. 0) GO TO 560                                                011560
M=0.D0                                                              011570
 540 I=K,N1                                                         011580
M=SUM+VEC(I+1,NRR)*A(I+1,K)                                         011590
M=SUM+SUM                                                           011600
 550 I=K,N1                                                         011610
1=I+1                                                               011620
C(II1,NRR)=VEC(I+1,NRR)-SUM*A(I+1,K)                                011630
 TO 520                                                             011640
NTINUE                                                              011650
NTINUE                                                              011660
TURN                                                                011670
D                                                                   011680


  / ALLOCATION

          01E08 VEC           03C10 DUMMY

  / ALLOCATION
```

```
    PROGRAM CNINDO  00                   SOURCE       XXXX567890               DAT
•••1••••/••••2••••/••••3••••/••••4••••/••••5••••/••••6••••/••••7••• PAGLIN

SUBROUTINE SCFOUT(OP,MOP)
DOUBLE PRECISION A, XXX, C
THIS ROUTINE PRINTS THE ARRAY IN COMMON/ARRAYS/ WHICH IS DESIGNATE
MOP. IF OP = 1 THE EIGENVALUES CONTAINED IN COMMON/1/ ARE ALSO
PRINTED. IF OP= 0 THE EIGENVALUES ARE NOT PRINTED
COMMON/ARRAYS/A(31,31,2),DUMMY(622)
COMMON/GAB/XXX(630)
COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(10),C(10,3),N
COMMON/INFO1/CZ(10),U(31),ULIM(10),LLIM(10),NELECS,OCCA,OCCB
COMMON/ORB/ORB(9)
COMMON/PERTBL/EL(18)
INTEGER OP,AN,ANII,CZ,U,ORB,ULIM,EL,CHARGE,OCCA,OCCB
DO 120 M=1,N,11
K=M+10
IF (K.LE.N) GO TO 30
K=N
CONTINUE
WRITE(3,100)
IF (OP.EQ.1) GO TO 40
GO TO 50
CALL EIGOUT(M,K)
CONTINUE
WRITE(3,60) (I,I=M,K)
FORMAT(13X,50I9)
DO 110 I=1,N
I=U(I)
NII=AN(II)
=I-LLIM(II)+1
RITE(3,80) I,II,EL(ANII),ORB(L),(A(I,J,MOP),J=M,K)
ORMAT(1X,I2,I3,A4,1X,A4,50(F9.4))
F (I.EQ.ULIM(II)) GO TO 90
O TO 110
RITE(3,100)
ORMAT(1X)
ONTINUE
ONTINUE
RITE(3,100)
RITE(3,100)
ETURN
ND

   / ALLOCATION

            03C10 DUMMY

   / ALLOCATION

XX

   / ALLOCATION

ATOMS       00004 CHARGE        00008 MULTIP        0000C AN
            00124 N
```

```
   PROGRAM CNINDO   00                          SOURCE      XXXX567890                DATE
..1..../....2..../....3..../....4..../....5..../....6..../....7...  PAGLIN

UBROUTINE EIGOUT(M,K)                                                 012090
OUBLE PRECISION XXX, EPSILN, YYY                                      012100
HIS ROUTINE IS CALLED IN SCFOUT TO PRINT THE EIGENVALUES M TO K       012110
OMMON/GAB/XXX(93),EPSILN(31),YYY(506)                                 012120
RITE(3,10) (EPSILN(I),I=M,K)                                          012130
ORMAT(//,15H EIGENVALUES---,20(F9.4),//)                              012140
ETURN                                                                 012150
ND                                                                    012160


  / ALLOCATION

X          002E8 EPSILN      003E0 YYY

SUBROUTINE

   QFWRIT      QIOED        QFINIO      QSTOP

ALLOCATION

GOUT       00028 I

LLOCATION
```

```
FORTRAN IV   RF03              PROGRAM CNINDO  00                    MEMORY MAP

OCATION              START ADDR   END ADDR   DEC LENGTH      START ADDR   END ADDR   DE

BJECT PROGRAM ON PACK  067766

L MEMORY                                        65064
DENT EXEC                                        3584
RAM                    00 0E00     00 98F0      35568
L COMMON               00 9AC8     00 F800      23864     REDUCED  FROM  170,000
 OVERLAY AREA                                     512
R EXEC                                           1536

 PROGRAM (RES)         00 0E00     00 72E8      25832
ERS                    00 0E00     00 0FB0        432
-BUFFER TABLES         00 0FB0     00 1114        356
S 1 SUBRTNES           00 1114     00 5A10      18684
LAY DIRECTORY          00 5A10     00 5A1C         12
NG AND DATA            00 5A1C     00 72E8       6348
S 2 SUBRTNES           00 98F0     00 98F0          0

ON ALLOCATION
     /ORB        /     00 9AC8     00 9AEC         36
     /PERTBL     /     00 9AEC     00 9B34         72
     /OPTION     /     00 9B34     00 9B50         28
     /ARRAYS     /     00 9B50     00 E118      17864
     /INFO       /     00 E118     00 E240        296
     /GAB        /     00 E240     00 F5F0       5040
     /INFO1      /     00 F5F0     00 F6F0        256
     /AUXINT     /     00 F6F0     00 F800        272
     /:COMMON    /     00 F800     00 F800          0

      UNITABLA         00 1114                      :CHS     00     00 113C
      CDDECTBH00       00 11E4                      CDVFY1   16     00 12EC
      MAXMIN   18      00 13A0                      OVLYCLLR27      00 1464
      PRINTPUT11       00 1718                      PRVFY1   05     00 1850
      QCNVRT   12      00 18B0                      QFINIO   20     00 18C4
      QIANDO   83      00 19BC                      QINOUT   39     00 20E4
      QSTP     12      00 3974                      REMAIN   13     00 39EC
      TRUNK    14      00 3BB4                      VEXPOD   11     00 3C28
      ZCONSER305       00 3F40                      ZCONSERR36      00 4318
      ZFLARITH19       00 4764                      ZFLASCBN22      00 4CEC
      ZFLOAT   14      00 5478                      ZFXASCBN18      00 5528
      ZIFIX    18      00 5720                      ZZCLOSEF02      00 58F0

INDO                   00 5A1C     00 6030       1556

            TEXT       00 5A58     00 6030

                       00 6030     00 6A88       2648

            TEXT       00 61B0     00 6A88

LVEC                   00 6A88     00 6C58        464
```

APPENDIX C

Below are the x, y, and z coordinates for a series of monosubstituted acetylenes and ethylenes as well as substituted fluoro- and chloro- acetylenes and ethylenes.

1. Monosubstituted Acetylenes

Assumptions: a) C≡C bond length is fixed at 1.204 Å
b) Substitution does not change the C≡C length

$H-C_2\equiv C_1-X$

	x	y	z
C_1	0.000	0.000	0.000
C_2	-1.204	0.000	0.000
H	-2.26	0.000	0.000
X= H	1.06	0.000	0.000
X= F	1.29	0.000	0.000
X= Cl	1.632	0.000	0.000
X= CHO			
C	1.46	0.000	0.000
O	0.659	1.015	0.000
H	.540	-0.935	0.000
X= CN			
C	1.382	0.000	0.000
N	2.539	0.000	0.000
X= NO_2			
N	1.45	0.000	0.000
O	.605	1.048	0.000
O	.605	-1.048	0.000

2. Substituted Fluoro- Acetylenes

Assumptions: see(1)

$F-C_2\equiv C_1-X$

C_1	0.000	0.000	0.000
C_2	-1.204	0.000	0.000
F	-2.494	0.000	0.000
X= H	1.06	0.000	0.000
X= F	1.29	0.000	0.000

X= Cl		1.632	0.000	0.000
X= CHO				
	C	1.46	0.000	0.000
	O	0.659	1.015	0.000
	H	0.540	-0.935	0.000
X= CN				
	C	1.38	0.000	0.000
	N	2.539	0.000	0.000
X= NO_2				
	N	1.45	0.000	0.000
	O	0.605	1.048	0.000
	O	0.605	-1.048	0.000

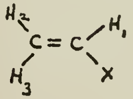
3. Substituted Chloro- Acetylenes

$Cl-C\equiv C-X$

C		0.000	0.000	0.000
C		-1.204	0.000	0.000
Cl		-2.836	0.000	0.000
X= H		1.06	0.000	0.000
X= F		1.29	0.000	0.000
X= Cl		1.632	0.000	0.000
X= CHO				
	C	1.46	0.000	0.000
	O	0.659	1.015	0.000
	H	0.540	-0.935	0.000
X= CN				
	C	1.38	0.000	0.000
	N	2.539	0.000	0.000
X= NO_2				
	N	1.45	0.000	0.000
	O	0.605	1.048	0.000
	O	0.605	-1.048	0.000

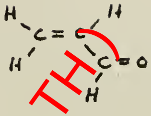
4. Monosubstituted Ethylenes

Assumptions: a) C=C bond length of 1.337 A
b) Substitution does not change molecular geometry
c) Trigonal bonds



C		0.000	0.000	0.000
C		-1.337	0.000	0.000

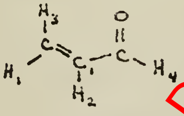
H_1	0.540	0.935	0.000
H_2	-1.88	0.935	0.000
H_3	-1.88	-0.935	0.000
X=H	0.540	-0.935	0.000
X= F	0.674	-1.28	0.000
X= Cl	0.865	-1.50	0.000
X= CHO (trans)*			
C	0.779	-1.229	0.000
O	1.991	-1.229	0.000
H	0.199	-2.140	0.000
X=CN			
C	0.730	-1.26	0.000
N	1.310	-2.27	0.000
$X=NO_2$ (planar)			
N	0.735	-1.27	0.000
O	1.34	-2.32	0.000
O	1.945	-1.27	0.000



$X=NO_2$ (not planar) (This was the most stable configuration and was used in the tables in Section IV)

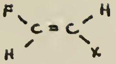
N	0.735	-1.27	0.000
O	1.0375	-1.797	1.048
O	1.0375	-1.797	-1.048
$X=CH_3$			
C	0.7455	-1.29	0.000
H	0.0302	-2.126	0.000
H	0.9566	-1.888	0.367
H	0.9566	-1.888	-0.367

For X=CHO (cis)** the following geometry was assumed:



C_1	0.000	0.000	0.000
C_2	-1.16	0.669	0.000
H_1	-2.093	0.129	0.000
H_2	0.000	-1.08	0.000
H_3	-1.16	1.75	0.000
H_4	-2.16	0.239	0.000
C	1.223	0.779	0.000
O	1.223	1.991	0.000
H	2.164	0.239	0.000

5. Substituted Fluoro- Ethylenes



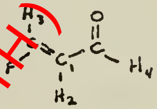
Assumptions: see (4)
(c) All substitutions are trans- unless otherwise stated

To obtain these molecules the following is substituted for

H_2	-1.88	0.935	0.000	:
F	-1.992	1.135	0.000	

For cis CHO

H_1	-2.093	0.1285	0.000



was replaced by

F	-2.28	0.135	0.000

6. Substituted Chloro- Ethylenes

Assumptions: see (4) and (5)

To obtain these molecules the following is substituted for

H_2	-1.88	0.935	0.000	:
Cl	-2.197	1.500	0.000	

For cis- CHO

H_1	-2.093	0.1285	0.000

was replaced by

Cl	-2.747	0.215	0.000

FOOTNOTES

[1] Pople, J. A., D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, *43*, S129 (1965).

[2] Pople, J. A., D. L. Beveridge, and P. A. Dobosh, *ibid.*, *47*, 2026 (1967).

[3] See, for example, Hanna, Melvin W., *Quantum Mechanics in Chemistry*, W. A. Benjamin, Inc., New York (1969), pp. 115-120.

[4] Pople, J. A. and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill Book Company, New York (1970), p. 13.

[5] Dewar, Michael J. S., *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill Book Company, New York (1969), p. 37.

[6] Atkins, P. W., *Molecular Quantum Mechanics*, Clarendon Press, Vol. 1, Oxford (1970), pp. 214-215.

[7] For a more complete discussion of the Hartree-Fock equations, the reader may consult Dewar, Michael, *The Molecular Orbital Theory of Organic Chemistry*, pp. 57-64 (see footnote 5) and Pople, J. A. and D. L. Beveridge, *Approximate Molecular Orbital Theory*, pp. 37-41 (see footnote 4).

[8] Parr, R. G., *J. Chem. Phys.*, *20*, 239 (1952).

[9] Pople, J. A., *J. Phys. Chem.*, *61*, 6 (1957).

[10] Pople and Beveridge, p. 60 (see footnote 4).

[11] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, *43*, S136 (1965).

[12] J. A. Pople and G. A. Segal, *ibid.*, *44*, 3289 (1966)

[13] Slater, J. C., *Phys. Rev.*, *36*, 57 (1930)

[14] Santry, D. P. and G. A. Segal, *J. Chem. Phys.*, *47*, 158 (1967)

[15] A table of comparisons of calculations by the two methods may be found in Pople and Beveridge, p. 95 (see footnote 4).

[16] Pople, J. A., and M. S. Gordon, *J. Chem. Phys.*, *49*, 4643 (1968)

[17] Pople and Beveridge, pp. 92,94 (see footnote 4).

[18] Pople, J. A., and M. S. Gordon, *J. Am. Chem. Soc.*, *89*, 4253 (1967).

[19] Pople and Beveridge, pp. 98-109 (see footnote 4).

[20] Pople, J. A., D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, *90*, 4201 (1968).