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I am submitting herewith a thesis written by John M. Younkin entitled "Π-Electron Affinities for Some Conjugated Organic Molecules." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Physics.

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Π-ELECTRON AFFINITIES FOR SOME CONJUGATED ORGANIC MOLECULES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee

John M. Younkin

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ABSTRACT

The electron affinity of a molecule is defined as the difference in energy between the neutral in its ground state and the ion in its ground state, i.e., $EA = E^{\circ} - E^{-}$. When the total energy of the negative ion is greater than that of the neutral molecule, a virtual or compound state exists (negative electron affinity). When the energy of the negative ion is below that of the neutral, a bound state exists (positive electron affinity). Virtual states can be studied by electron scattering techniques, whereas bound states can be studied by photodetachment methods for simple molecules or by the collisional ionization method for complex molecules.

The lowest negative ion state of a conjugated hydrocarbon results in the addition of an electron into a π-molecular orbital, and the energy of this vacant orbital is determined by the structure of the molecule. The large variety of conjugated hydrocarbons allows for considerable range in "π-electron affinities," and both bound and virtual states are known to exist.

In the present work energy levels are calculated for some conjugated systems containing C, N, and O atoms using a semi-empirical SCFMO method based on a variable β-γ modification of the Pariser-Parr-Pople approximation to the Hartree-Fock equations. Koopmans' theorem is assumed in relating the energy of the lowest vacant molecular orbital (ϵ_{LVMO}) to electron affinities determined in recent beam experiments.

The correlation is used to predict electron affinities and excitation energies of negative ion states of other conjugated organic molecules.

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CHAPTER I

INTRODUCTION

The electron affinity of a molecule is defined as the difference in energy between the neutral in its ground state and the ion in its ground state, i.e., $EA = E^{\circ} - E^{-}$. When the total energy of the negative ion is greater than that of the neutral molecule, a virtual or compound state exists (negative electron affinity). Conversely when the energy of the negative ion is below that of the neutral, a bound state exists (positive electron affinity). Electron affinity values reported for atoms and small molecules (less than 5 atoms) range from approximately -2 eV to +4 eV. Electron affinities for atoms and some diatomic molecules have been accurately determined by use of the photodetachment technique. Studies of electron photodetachment or radiative attachment have provided values for atomic electron affinities with accuracies often less than 10 milli-electron volts (meV). The first accurate halogen atom electron affinities are credited to Berry and Reimann.[1] There exist very few accurate determinations of molecular electron affinities because of the complexity of molecular negative ions and the inherent difficulty in determining electron affinities. In a few cases (notably NO and O_2) where the photo-electron spectroscopy technique of Hall and associates[2,3] have been applied, electron affinities are known with accuracies of less than 10 meV. In cases where the electron affinity is negative, the

resonance scattering technique employed by Schulz and coworkers[4,5] can provide adiabatic molecular electron affinities with accuracies of about 50 meV. Electron affinities for complex molecules are being determined with accuracies of approximately 0.2 eV by Compton and colleagues[6-9] employing a collisional ionization method.

There is considerable interest in negative ion states in complex organic molecules. Anions of conjugated hydrocarbons in solution or crystal structures have been studied in detail. Very little information exists as to the structure of negative ions in the gas phase. The lowest negative ion state of a simple conjugated hydrocarbon results in the addition of an electron into a π-molecular orbital, and the energy of this vacant orbital is determined by the structure of the molecule. The large variety of conjugated hydrocarbons allows for considerable range in "π-electron affinities," and both bound and virtual states are known to exist. Recent beam experiments have provided reliable electron affinities for both bound[7-9] and virtual[5] states.

It can be inferred from Koopmans' theorem[10] that the Hartree-Fock energy of the lowest vacant molecular orbital (ϵ_{LVMO}) gives an approximation to the electron affinity. Many attempts have been made to correlate measured electron affinity values with the molecular orbital energy ϵ_{LVMO}. One of the more successful of these correlations was due to Kunii and Kuroda.[11,12] In the present work we have calculated energy levels for some conjugated systems containing C, N, and O atoms using a

semi-empirical self-consistent field molecular orbital (SCFMO) method based on a variable β-γ modification of the Pariser-Parr-Pople approximation to the Hartree-Fock equations. These calculated energies are correlated with recently measured electron affinities to predict electron affinities and excitation energies of negative ion states of other conjugated organic molecules. The agreement between experiment and theory is found to be exceptionally good.

CHAPTER II

THEORY

I. SCHRÖDINGER EQUATION

The electronic structure of atoms is described theoretically by the Schrödinger equation

$$H\Psi = E\Psi \quad , \tag{1}$$

in which the Hamiltonian operator H includes all interaction terms for the electrons and nuclei. The solution of this equation for even the simplest atoms is tremendously complex. The simplest type of atom consists of one electron moving in the field of a single charged nucleus, i.e., neutral hydrogen. This one-electron atom is the only type for which it is possible to obtain an explicit closed analytic solution of the Schrödinger equation. More complicated atoms defy accurate quantitative analysis from first principles. It is necessary to make simplifying approximations to obtain solutions for even the two-electron atom.

In order to solve the molecular Schrödinger equation for a complex molecule, an appropriate set of approximations are required to determine the molecular wave function. The first of these is the Born-Oppenheimer approximation,[13] which makes the assumption of stationary nuclei. That is, if the nuclei are assumed to be in a fixed nuclear configuration, the Schrödinger equation yields an electronic wave function Ψ and an electronic

energy E. The resulting Hamiltonian operator is then

$$H = -\frac{h^2}{8\pi^2 m}\sum_i \nabla_i^2 - e^2 \sum\sum_{\upsilon i}\frac{Z_\upsilon}{r_{\upsilon i}} + e^2 \sum\sum_{i<j}\frac{1}{r_{ij}} \quad , \tag{2}$$

where the terms represent operators for the kinetic energy of the electrons (i), the nuclear-electronic attraction (Z_υ is the atomic number of nucleus υ, $r_{\upsilon i}$ is the distance of this nucleus to the i^{th} electron), and the repulsion between electrons (r_{ij} is the distance between electrons i and j).[14] The solution of equation (1) for this Hamiltonian is mathematically impossible for systems with more than two electrons. Other approximations are also necessary. These form the basis of the approximate quantum-mechanical theory of conjugated molecules.

It is convenient to factor the wave function Ψ into sets of independent wave functions representing σ and π electrons such that

$$\Psi = \Phi_\sigma \Phi_\pi \quad . \tag{3}$$

The first assumption is that the σ electrons be ignored. Thus, the wave function is chosen to represent only the π electrons. Secondly, it is assumed that this wave function involves one-electron orbitals which are considered molecular orbitals (MO) extending over the entire molecular framework. The approximate wave function Ψ then becomes the product of the one-electron molecular orbitals ψ_i

$$\Psi = \psi_1\psi_2\psi_3 \cdots \psi_n \quad . \tag{4}$$

Each ψ_i is taken to be a linear combination of atomic orbitals (LCAO) of the molecule such that

$$\psi_i = \sum_{\upsilon} c_{i\upsilon}\phi_{\upsilon} \quad , \tag{5}$$

where ϕ_{υ} is the valence atomic orbital of the υ^{th} atom and $c_{i\upsilon}$ is the coreficient of the υ^{th} atomic orbital in the i^{th} molecular orbital. The molecular orbitals are constructed over the entire set of available valence π atomic orbitals. In conjugated hydrocarbons the available valence atomic orbitals are the set of $2p_z$ orbitals, where $z = 0$ defines the plane of the molecule.

The variational method is used to determine the set of coefficients $c_{i\upsilon}$ that gives the lowest value for the energy of the MO. That is, Equation (1) is solved by minimizing the total energy of the system

$$E = \frac{\int \Psi^* H \Psi \, d\tau}{\int \Psi^* \Psi d\tau} \quad . \tag{6}$$

If there are n unknown coefficients, the resulting n conditions determine simultaneously the eigenvalues E_1, E_2, $E_3 \cdots E_n$ and the eigenfunctions $\psi_1, \psi_2, \psi_3, \ldots \psi_n$. These energies and wave functions define the molecular orbitals of the conjugated system.

II. HÜCKEL THEORY

In principle the Hamiltonian is quite complex and produces a set of equations which are complicated to solve. It is more realistic to modify the Hamiltonian by making some simplifying approximations in the electronic interactions. The simplest of these modifications is known as the Hückel molecular orbital (HMO) theory.[15-17] It has been expanded by Coulson and Longuet-Higgins[18,19] into a useful and diversified theory. In this theory the Hamiltonian includes only one-electron and bonded nuclei terms. That is, the potential of one electron is independent of the position of the other electrons, and the interaction energy of two atomic orbitals is significant only when the two corresponding atoms are bonded.

Combining Equations (4), (5), and (6) with these approximations, the Hamiltonian matrix consists of a set of integrals of the form

$$H_{\mu\mu} \equiv \int \phi_\mu^* H \phi_\mu \, d\tau \tag{7}$$

$$H_{\mu\upsilon} \equiv \int \phi_\mu^* H \phi_\upsilon \, d\tau \tag{8}$$

$$S_{\mu\mu} \equiv \int \phi_\mu^* \phi_\mu \, d\tau \tag{9}$$

and

$$S_{\mu\upsilon} \equiv \int \phi_\mu^* \phi_\upsilon \, d\tau \quad . \tag{10}$$

The $H_{\mu\mu}$ terms are called Coulomb integrals and represent the kinetic and potential energy of a bound valence electron in the atomic orbital ϕ_μ. For all identical ϕ_μ these $H_{\mu\mu}$ are assumed constant and are denoted by the

empirical parameter α_o. The $H_{\mu\upsilon}$ terms are called resonance or bond integrals. They represent the interaction energy of atomic orbitals ϕ_μ and ϕ_υ. Since this energy is a function of the separation of the two orbitals, it is very small for non-bonded atoms and is considered to be zero in practice. For all similarly bonded atoms μ and υ, the $H_{\mu\upsilon}$ are assumed constant and are denoted by the empirical parameter β_o. The terms $S_{\mu\upsilon}$ and $S_{\mu\mu}$ are called overlap integrals and are a function of the separation of atoms μ and υ. For non-bonded atoms the overlap integral is vanishingly small. Although $S_{\mu\upsilon}$ may not approach zero for bonded atoms, it is assumed that $S_{\mu\upsilon}$ is zero for all $\mu \neq \upsilon$. In order to assure normalization of atomic orbitals, $S_{\mu\mu}$ is set equal to unity. With these simplifications it is straight forward to set up the secular equations for the system and determine completely the molecular orbitals.

III. SELF-CONSISTENT FIELD THEORY

Although the HMO theory gives qualitative results for simple ground state molecules, the approximations made in the theory leave it inadequate to handle more complex molecules and excited ion states. Its main weakness is the omission of electron-electron repulsion. The self-consistent field molecular orbital (SCFMO) theory takes into account electron repulsion by considering the interaction of one electron with all the other electrons in the molecule. The theory has been developed and discussed in detail by Roothaan.[20] In this theory the Hamiltonian includes, in

addition to the one-electron energy terms, the interaction terms for the electrons which occupy the same atomic orbital ϕ_μ and the repulsion terms for an electron in ϕ_μ with all the electrons in all the other atomic orbitals ϕ_υ. This total Hamiltonian produces a set of equations known as the Hartree-Fock equations

$$F\Psi = E\Psi \quad , \tag{11}$$

where F is called the Hartree-Fock Hamiltonian. For conjugated molecules it is given as

$$F = H^{CORE} + 2J - K \quad , \tag{12}$$

where H^{CORE}, the core Hamiltonian, is the one-electron energy similar to that of the HMO theory and includes the kinetic energy of the π electrons and their potential energy in the field of the core — the nuclei and the σ electrons. The operator J is called the two-electron Coulomb energy and represents the electrostatic repulsion between all pairs of electrons. The operator K is called the two-electron exchange energy and represents an attractive interaction between pairs of electrons of parallel spin in different orbitals (exchange interaction). These two operators are defined such that

$$J(1)\psi_i(1) = \left(\sum_j \int \psi_j^*(2) \frac{e^2}{r_{12}} \psi_j(2) d\tau\right)\psi_i(1) \tag{13}$$

$$K(1)\psi_i(1) = (\Sigma_j \int \psi_j^*(2)\frac{e^2}{r_{12}}\psi_i(2)d\tau)\psi_j(1) \quad , \tag{14}$$

where ψ_i and ψ_j are the molecular orbitals interacting and the summation is taken over all the occupied orbitals.

Combining Equations (4), (5) and (6) (as in the HMO theory) and using the Hartree-Fock Hamiltonian results in a matrix having terms of the form

$$F_{\mu\upsilon} \equiv \int \phi_\mu^* (H^{CORE} + 2J - K)\phi_\upsilon d\tau \quad . \tag{15}$$

Applying Equations (13) and (14) to the matrix elements $F_{\mu\upsilon}$ gives

$$F_{\mu\upsilon} = \int \phi_\mu^* H^{CORE} \phi_\upsilon d\tau + 2 \sum_{\eta} \sum_{\zeta} \sum_{k} c_{k\eta} c_{k\zeta}$$

$$\times \left[\int \phi_\mu^*(1)\phi_\upsilon(1)\frac{e^2}{r_{12}}\phi_\eta^*(1)\phi_\zeta(2)d\tau_1 d\tau_2 \right.$$

$$\left. -\frac{1}{2}\int \phi_\mu^*(1)\phi_\eta(1)\frac{e^2}{r_{12}}\phi_\upsilon^*(2)\phi_\zeta(2)d\tau_1 d\tau_2 \right] \quad . \tag{16}$$

The equations made up of these terms are extremely complicated, but by making a further set of assumptions they can be considerably simplified.

These assumptions, known as the zero-differential-overlap (ZDO) approximation, were introduced by Pariser and Parr[21] and by Pople.[22] As in the Hückel theory atomic overlap is neglected with $S_{\mu\upsilon}$ assumed to be zero for all $\mu \neq \upsilon$ and $S_{\mu\mu}$ set equal to unity. Also, all two-electron

integrals which depend on the overlapping of charge distributions of different orbitals are neglected. That is, the Coulomb interals of (16) vanish for $\mu \neq \upsilon$ and $\eta \neq \zeta$, and the exchange integrals vanish for $\mu \neq \eta$ and $\upsilon \neq \zeta$. The nonvanishing integrals are generally called two center electron repulsion integrals and are given by

$$\gamma_{\mu\upsilon} \equiv \int |\phi_{\mu}(1)|^2 \frac{e^2}{r_{12}} |\phi_{\upsilon}(2)|^2 d\tau_1 d\tau_2 \quad . \tag{17}$$

The one-electron core integrals are usually represented by

$$H_{\mu\upsilon}^{\text{CORE}} \equiv \int \phi_{\mu}^{*} H^{\text{CORE}} \phi_{\upsilon} d\tau \quad . \tag{18}$$

At this point it is convenient to define two terms which help simplify Equation (16). The bond order $p_{\mu\upsilon}$ between atoms μ and υ for molecular orbital ψ_i is

$$p_{\mu\upsilon} \equiv \sum_i n_i c_{i\mu}^{*} c_{i\upsilon} \quad , \tag{19}$$

where n_i is the number of electrons in the MO, $c_{i\mu}$ and $c_{i\upsilon}$ are the coefficients of the μ^{th} and υ^{th} atomic orbitals, respectively, in ψ_i, and the summation is taken over all the occupied molecular orbitals. The electronic charge density q_{μ} at atom μ is defined as

$$q_{\mu} \equiv \sum_i n_i c_{i\mu}^{*} c_{i\mu} \quad . \tag{20}$$

For closed-shell molecules in which all molecular orbitals are doubly

occupied, Equations (19) and (20) reduce to

$$p_{\mu\upsilon} = 2\sum_i c_{i\mu} c_{i\upsilon} \tag{21}$$

$$q_\mu = 2\sum_i c_{i\mu}^2 \quad . \tag{22}$$

Note that $p_{\mu\mu} = q_\mu$.

Applying the above assumptions and Equations (17), (18), (21) and (22) to Equation (16) yields

$$F_{\mu\upsilon} = H_{\mu\upsilon}^{CORE} - \frac{1}{2} p_{\mu\upsilon} \gamma_{\mu\upsilon} \quad \mu \neq \upsilon \tag{23}$$

$$F_{\mu\mu} = H_{\mu\mu}^{CORE} + \frac{1}{2} q_\mu \gamma_{\mu\mu} + \sum_{\eta \neq \mu} q_\eta \gamma_{\mu\eta} \quad . \tag{24}$$

The final assumptions of the Pariser-Parr-Pople approximation involve the core elements $H_{\mu\upsilon}^{CORE}$ and $H_{\mu\mu}^{CORE}$. Similar to the HMO theory, the $H_{\mu\upsilon}^{CORE}$ are neglected for non-bonded atoms. For bonded atoms μ and υ, $H_{\mu\upsilon}^{CORE}$ are denoted by the parameters $\beta_{\mu\upsilon}$, which are called two center core integrals and are independent of the conditions of the atomic orbitals ϕ_μ and ϕ_υ. The diagonal core elements $H_{\mu\mu}^{CORE}$ are divided into two parts: a total energy α_μ of the core at atom μ and an effective potential $-\sum_{\eta \neq \mu} \gamma_{\mu\eta}$ of a distant core of one positive charge at each atom $\eta \neq \mu$. That is

$$H_{\mu\mu}^{CORE} = \alpha_{\mu} - \sum_{\eta \neq \mu} \gamma_{\mu\eta} \quad . \tag{25}$$

From these assumptions Equations (23) and (24) are modified to provide the final form of the matrix elements of the SCF theory to be

$$F_{\mu\upsilon} = \beta_{\mu\upsilon} - \frac{1}{2} p_{\mu\upsilon} \gamma_{\mu\upsilon} \qquad \mu \neq \upsilon \tag{26}$$

$$F_{\mu\mu} = \alpha_{\mu} + \frac{1}{2} q_{\mu} \gamma_{\mu\mu} + \sum_{\eta \neq \mu} (q_{\eta} - 1) \gamma_{\mu\eta} \quad . \tag{27}$$

In order to solve this set of equations it is necessary to first approximate the molecular orbitals. This specifies a set of coefficients $c_{i\mu}$ which are used to calculate the $p_{\mu\upsilon}$ and q_{μ}. Then, using empirical values for $\beta_{\mu\upsilon}$, $\gamma_{\mu\upsilon}$, α_{μ}, and $\gamma_{\mu\mu}$, new molecular orbitals are determined by solving Equation (6). This procedure is repeated until self-consistence is attained. Because of the inclusion of repulsion and exchange interaction, as well as a more complete effective one-electron core energy, the molecular orbital energies of the SCFMO theory are more accurate than those of the HMO theory.

CHAPTER III

METHOD

I. HÜCKEL METHOD

HMO calculations are made initially to obtain a first approximation to the molecular orbitals for use in the SCFMO method. For conjugated hydrocarbons the empirical values for the Coulomb integral α_o and the bond integral β_o are taken to be -6.24 eV and -3.14 eV, respectively, as determined by Wacks and Dibeler.[23] These values are modified for heteromolecules by using the relations

$$\alpha = \alpha_o + h\beta_o$$

$$\beta = k\beta_o \quad . \tag{28}$$

The parameters h and k are experimental quantities based on electronegativities and bond distances, respectively. The values used for these parameters are given in Table I for the core atoms that were considered. By expressing the matrix elements $H_{\mu\upsilon}$ in terms of β, so that $H_{\mu\upsilon}/\beta = k$, the matrix is simplified to contain just the k-values as its elements. Determining the eigenvalues and eigenvectors of this matrix gives a set of relative energies m_i in terms of β and the corresponding set of MO coefficients $c_{i\mu}$. The absolute MO energies are calculated using

$$E_i = \alpha + m_i\beta \text{ eV} \quad . \tag{29}$$

TABLE I

HMO PARAMETERS h AND k

Core Atom	Index	h	Bond	k
C^+	1	0 [13]	C - C	1.0 [13]
N^+	2	1.5 [24]	C = C	1.0 [13]
N^{++}	3	1.5 [24]	C - N	0.9 [24]
O^+	4	2.0 [24]	C≡ N	0.9 [24]
O^{++}	5	2.0 [24]	C - O	0.34 [24]
S^+	6	1.0 [25]	C = O	0.34 [24]
$C^+(C \equiv N)$	7	0 [13]	C - S	0.68 [25]
$N^+(C \equiv N)$	8	1.5 [24]	C - Se	0.68 [25]
Se^+	9	0.9 [25]	C - F	0.7 [13]
F^+	10	3.0 [13]	C - Cl	0.4 [13]
Cl^+	11	2.0 [13]	C - Br	0.3 [13]
Br^+	12	1.5 [13]		

The bond orders $p_{\mu\upsilon}$ and charge densities q_{μ} are calculated from these coefficients. The Hückel molecular orbitals are completely determined and taken as the first values in the SCFMO calculations.

II. SELF-CONSISTENT FIELD METHOD

A variable β-γ procedure as given by Kunii and Kuroda[11,12] is used to evaluate $F_{\mu\upsilon}$ and $F_{\mu\mu}$ in Equations (26) and (27). This method is suited for calculations of complex molecules since a precise molecular geometry need not be specified. The α_{μ} terms are taken as the valence state ionization potential I_{μ} of the charged core atom μ. The so-called one center electron repulsion integrals $\gamma_{\mu\mu}$ are approximated by

$$\gamma_{\mu\mu} = I_{\mu} - A_{\mu} \quad \text{eV}, \tag{30}$$

where A_{μ} is the valence state electron affinity of the μ^{th} core atom.[26] The values for the parameters α_{μ} and $\gamma_{\mu\mu}$ are given in Table II for the core atoms of interest.

The two center core integrals $\beta_{\mu\upsilon}$ and the two center electron repulsion integrals $\gamma_{\mu\upsilon}$ are adjusted at each iteration until self-consistency is attained. The $\beta_{\mu\upsilon}$ terms are approximated by Nishimoto and Forster[28,29] for bonded atoms μ and υ by the relation

$$\beta_{\mu\upsilon} = A_o + A_1 p_{\mu\upsilon} \quad \text{eV}, \tag{31}$$

where the bond orders $p_{\mu\upsilon}$ are from the MO calculations of the previous

TABLE II

SCFMO PARAMETERS α_μ AND $\gamma_{\mu\mu}$ [27]

Core Atom	α_μ	$\gamma_{\mu\mu}$
C^+	-11.16	11.13
N^+	-14.12	12.34
N^{++}	-26.70	17.44
O^+	-17.70	15.23
O^{++}	-32.90	21.53
S^{+} *	-20.00	10.84
$C^+(C \equiv N)$	-12.69	10.09
$N^+(C \equiv N)$	-16.18	11.52

*Estimated values for present work.

iteration. The empirical constants A_o and A_1 are given in Table III.

The $\gamma_{\mu\upsilon}$ terms are approximated by a relationship developed by Nishimoto and Mataga.[30,31] These integrals are estimated for a pair of bonded atoms μ and υ by

$$\gamma_{\mu\upsilon} = \frac{e^2}{a_{\mu\upsilon} + r_{\mu\upsilon}} \quad , \tag{32}$$

where $a_{\mu\upsilon}$ is a constant of the bond and $r_{\mu\upsilon}$ is the bond distance. The constants $a_{\mu\upsilon}$ are determined from the reciprocal averages

$$\frac{1}{a_{\mu\upsilon}} = \frac{1}{2}\left(\frac{1}{a_{\mu\mu}} + \frac{1}{a_{\upsilon\upsilon}}\right) \quad . \tag{33}$$

The constants $a_{\mu\mu}$ are taken as inversely proportional to the one center electron repulsion integrals $\gamma_{\mu\mu}$, such that

$$a_{\mu\mu} = \frac{e^2}{\gamma_{\mu\mu}} \quad . \tag{34}$$

This value of $a_{\mu\mu}$ is consistent with Equation (32) for $\mu = \upsilon$ and $r_{\mu\mu} = 0$. Combining Equations (33) and (34) gives

$$a_{\mu\upsilon} = \frac{2e^2}{\gamma_{\mu\mu} + \gamma_{\upsilon\upsilon}} \quad . \tag{35}$$

Eliminating the $a_{\mu\upsilon}$ from Equation (32) by using (35) results in

TABLE III

SCFMO PARAMETERS A_o AND A_1 FOR INTEGRALS $\beta_{\mu\omega}$[12]

	A_o					A_1
Bond	n^* = 1	2	3	4	≥5	all n
C - C	- 2.04	-1.90	-1.84	-1.82	- 1.81	-0.51
C - N	- 2.24	-2.09	-2.02	-2.00	- 1.98	-0.53
C - O	- 2.44	-2.27	-2.20	-2.18	- 2.17	-0.56
C - S^+	- 2.44	-2.27	-2.20	-2.18	- 2.17	-0.56
C ≡ N^+	- 2.24	-2.09	-2.02	-2.00	- 1.98	-0.53

*Number of benzene rings in molecules.

+Estimated values for present work.

$$\gamma_{\mu\upsilon} = \frac{e^2}{\frac{2e^2}{\gamma_{\mu\mu} + \gamma_{\upsilon\upsilon}} + r_{\mu\upsilon}}$$

$$\gamma_{\mu\upsilon} = \frac{1}{\frac{2}{\gamma_{\mu\mu} + \gamma_{\upsilon\upsilon}} + \frac{r_{\mu\upsilon}}{e^2}} \quad . \tag{36}$$

Converting all units to eV finally gives the relation

$$\gamma_{\mu\upsilon} = \frac{1}{\frac{2}{\gamma_{\mu\mu} + \gamma_{\upsilon\upsilon}} + 0.069362\, r_{\mu\upsilon}} \quad \text{eV} \quad , \tag{37}$$

where $r_{\mu\upsilon}$ are given in Å. The $\gamma_{\mu\upsilon}$ are adjusted at each iteration by varying the bond distances $r_{\mu\upsilon}$ according to the relation

$$r_{\mu\upsilon} = D_o + D_1 p_{\mu\upsilon} \quad \text{Å} \quad , \tag{38}$$

where the bond orders are again from the MO calculations of the previous iteration. The empirical constants D_o and D_1 are given in Table IV.

To sum up the SCFMO method, bond orders $p_{\mu\upsilon}$ and charge densities q_μ from a previous calculation are used to determine the two center core integrals $\beta_{\mu\upsilon}$ and the two center electron repulsion integrals $\gamma_{\mu\upsilon}$ (via

TABLE IV

SCFMO PARAMETERS D_o AND D_1 FOR BOND DISTANCES $r_{\mu\omega}$ [11]

Bond	D_o	D_1
C - C	1.517	-0.18
C - N	1.451	-0.18
C - O	1.410	-0.18
C - S*	1.410	-0.18
C ≡ N*	1.309	-0.18

*Estimated values for present work.

the bond distances $r_{\mu\upsilon}$). These values, along with the appropriate values for the ionization potentials α_{μ} and the one center electron repulsion integrals $\gamma_{\mu\mu}$, are used to calculate the matrix elements $F_{\mu\upsilon}$. Determining the eigenvalues and eigenvectors of the matrix gives a set of MO energies, E_i, and the corresponding set of MO coefficients, $c_{i\mu}$. New bond orders and charge densities which are to be used in the next iteration are calculated from these coefficients. The self-consistent field molecular orbitals are completely determined when sets of MO energies from successive iterations are the same within a specified fixed tolerance.

CHAPTER IV

DISCUSSION

I. COMPUTER PROGRAM

A computer program was written to perform HMO and SCFMO calculations for a number of conjugated systems. The program is written in Fortran and runs on an IBM 360/91 at the National Laboratory in Oak Ridge. A listing of the program is given in Appendix III. Besides calculating the MO energies and coefficients, the program computes the total π electron energy, the charge densities and bond orders, the bond lengths, and the free valences. Calculations have been made for some conjugated heteromolecules as well as hydrocarbons. Results of some of these calculations are contained in Appendix II.

II. KOOPMANS' THEOREM

According to Koopmans,[10] when one electron is removed from an orbital of a closed-shell molecule, the energy change corresponds to an ionization potential of the molecule and is given by

$$\delta E_i = I_i = -\epsilon_i \ , \tag{39}$$

where ϵ_i is the orbital energy associated with the molecular orbital ψ_i. Koopmans' theorem does not allow for the reorganization of the nuclei and inner electrons in the molecular ion. That is, it assumes that the

remaining electrons act exactly the same after one of their number has been removed. Actually, the remaining electrons undergo relaxation leading to considerable stabilization of the molecular ion.[32] Taking this into consideration, Equation (39) is modified to

$$I_i = -\epsilon_i - R_i \quad , \tag{40}$$

where R_i is the relaxation correction.[33] The corrections R_i do not depend strongly on energy level i, and it can be assumed that $\delta R_i = 0$. Since the SCFMO method treats electrons as moving in a field produced both by the fixed nuclei and the averaged interactions with the other electrons, Koopmans' theorem holds for SCFMO energies.[34] Thus, the relationship between the SCFMO energy and the ionization potential for a conjugated molecule is given by

$$IP = -\epsilon_{HOMO} - R \quad , \tag{41}$$

where ϵ_{HOMO} is the energy of the highest occupied molecular orbital. Many calculations show an excellent linear relationship between the negative value of the energy of the highest occupied molecular orbitals and the experimentally determined ionization potentials.

The energy required to remove an electron from the outer shell of a molecule in its ground state is by definition the ionization potential. Likewise, the energy liberated when an electron attaches to the outer shell of a molecule in its ground state is the electron affinity. As a

first approximation, it is expected that adding an extra electron would be less of a perturbation to the inner electrons than removing an electron from the outer shell of a molecule. It is therefore expected that Koopmans' theorem should accurately be applied to molecular electron affinities as well as ionization potentials. The relationship between the SCFMO energy and the electron affinity for a conjugated molecule is

$$EA = - \epsilon_{LVMO} - C \quad , \tag{42}$$

where ϵ_{LVMO} is the energy of the lowest vacant molecular orbital and C is the reorganization energy correction.

III. ELECTRON AFFINITIES

The difficulty in experimentally determining electron affinities has been an adverse factor in relating the negative value of the energy of the lowest vacant molecular orbital and the electron affinity. Kunii and Kuroda[12] have shown an excellent linear relationship for a limited number of conjugated hydrocarbons and heteromolecules. They used electron affinities for the hydrocarbons determined by Becker and Chen[35] from the electron capture method. This method is limited to determining electron affinities only in the range from $\sim$0 to $\sim$1 eV. Their electron affinities for the heteromolecules were estimated by Briegleb[36] from charge-transfer bands for molecular complexes involving the given molecule as the electron

donor. Values determined from charge-transfer spectra are generally too low for reasons which are well known.

The ground state of a molecular negative ion can be either bound or unbound. An unbound or virtual state exists when the total energy of the negative ion is greater than that of the neutral molecule, i.e., the molecule has a negative electron affinity. These states are sometimes called compound states. When the energy of the negative ion is below that of the neutral molecule, a bound state exists, i.e., the molecule has a positive electron affinity. Virtual states can be studied by electron scattering techniques, whereas bound states can be studied by photodetachment methods for simple molecules or by the collisional ionization method for polyatomic molecules. Recent experiments by Nenner and Schulz[5] utilizing electron transmission spectroscopy have provided reliable electron affinities for some virtual states. Electron affinities for bound states have been determined in current experiments by Compton and colleagues[7-9] using a collisional ionization technique. Because of the accurate beam values for electron affinities for conjugated molecules and the extensive interest in these systems, we undertook the present work using Koopmans' theorem to correlate measured electron affinities with molecular orbital energies of the lowest vacant orbital.

A correlation of the orbital energy ϵ_{LVMO} from the SCFMO calculations and the electron affinities determined by the beam experiments has been made for some conjugated systems containing carbon, nitrogen,

and oxygen atoms. The molecules used in the correlation are given in Table V along with measured electron affinities and molecular orbital energies. In Figure 1 we plot the electron affinity determined from the beam experiments versus the energy of the lowest vacant molecular orbital. The negative electron affinities were determined from the electron beam experiments, and the positive values come from the collisional ionization experiments. The solid data points represent ground states of the negative ion, while the open points represent the first excited negative ion states. A least squares fit of a straight line to the data gives the following equation:

$$EA = -0.95\ \epsilon_{LVMO} - 1.90\ eV \quad . \tag{43}$$

The error limits on this correlation are estimated to be $\pm$ 0.2 eV, the tolerance of the cesium collisional ionization data. A comparison of Equations (42) and (43) shows that our relationship is consistent with Koopmans' theorem. The slope of this line is well within experimental limits of the predicted slope of - 1. Rather than force our line to a slope of -1, we choose a least squares fit for predictive purposes.

From the SCFMO calculations the ground $^2E_{2u}$ state of the benzene negative ion $C_6H_6^-$ is degenerate. This degeneracy is removed upon substitution of one, two, or three (asymmetrically placed) nitrogen atoms into the ring.[37] The calculations indicate a splitting of the pyridine negative ion state, which is in good agreement with experiment (see Figure 1). Nenner and Schulz[5]

TABLE V

ELECTRON AFFINITY AND ϵ_{LVMO} VALUES

Molecule	EA (eV)	ϵ_{LVMO} (eV)
Benzene	$-1.14 \pm .05^{5}$	-0.87
Naphthalene	$-0.20 \pm .05^{5}$	-1.94
Pyridine (1st. res.)	$-0.62 \pm .05^{5}$	-1.26
Pyridine (2nd res.)	$-1.20 \pm .05^{5}$	-0.91
Pyrimidine (2nd res.)	$-0.77 \pm .05^{5}$	-1.09
Pyrazine (2nd. res.)	$-0.87 \pm .05^{5}$	-1.01
Maleic Anhydride	$1.4 \pm .2^{8}$	-3.35
Para-Benzoquinone	$1.8 \pm .2^{9}$	-3.71
TCNQ	$2.8 \pm .2^{7}$	-5.12

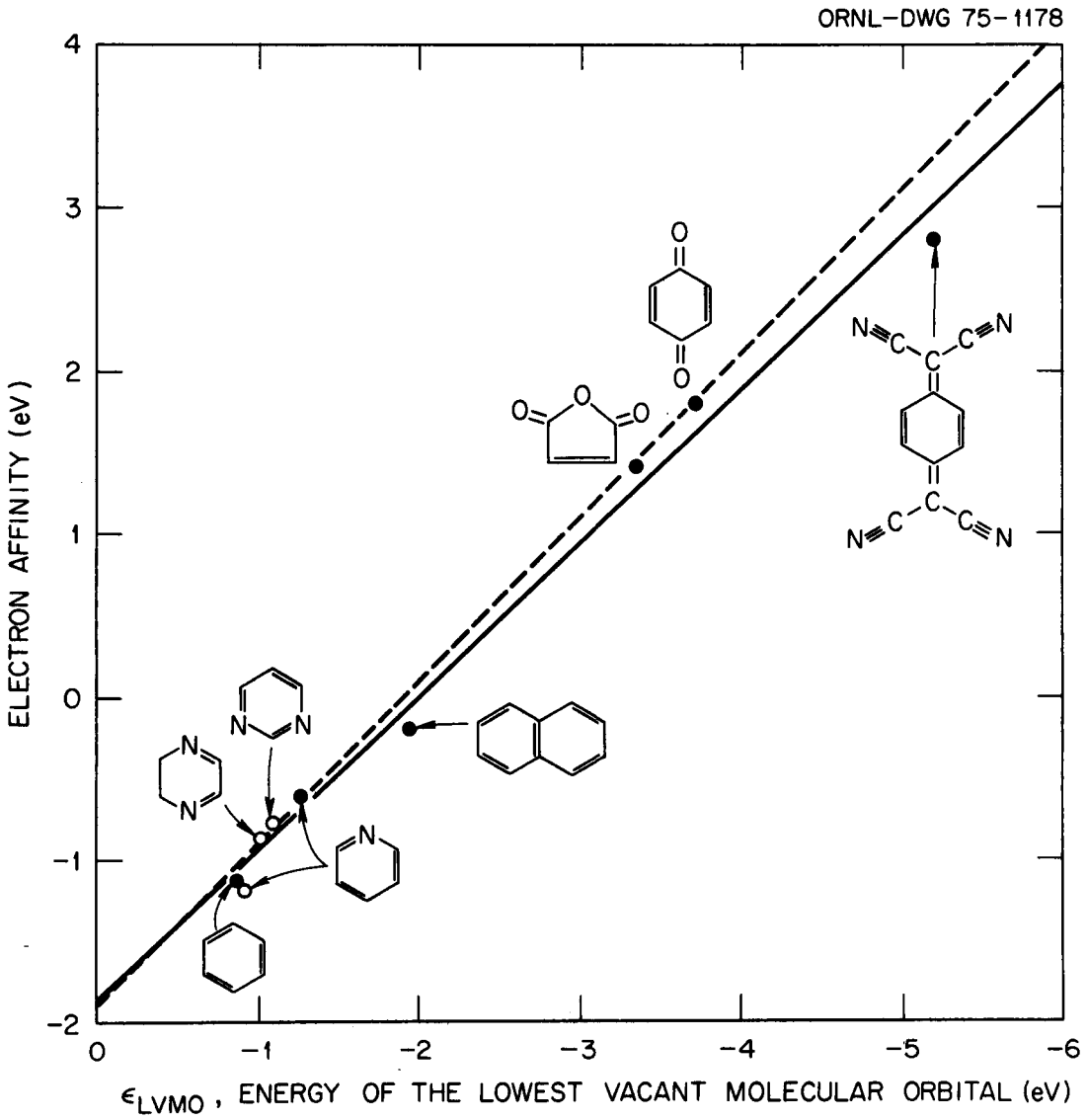


Figure 1. Correlation of the energy of the lowest vacant molecular orbital, ϵ_{LVMO}, and electron affinities determined from beam experiments.

reported only the first excited $\tilde{A}^2 A_u$ states for pyrimidine and pyrazine negative ions as the ground ^2B states were believed to be bound, and therefore was not measurable by their technique. They did estimate the electron affinities from polarographic potentials for the ground states of these two diazines and s-triazine to be slightly positive. However, our calculations predict virtual states with electron affinities of -0.52 eV for pyrimidine, -0.30 eV for pyrazine, and -0.54 eV for s-triazine.

Becker and Chen[35] have used the electron capture method to determine the electron affinities of some aromatic hydrocarbons in the range from $\sim$ 0 to $\sim$ 1 eV. Table VI contains a comparison of their electron affinity values with our predicted values. Except for azulene the electron affinity values measured by Becker and Chen are an average of 0.22 eV higher than our values. These are just within the estimated limits of error of our correlation. The values of Wentworth and Becker are in somewhat better agreement.

IV. WORK FUNCTION OF GRAPHITE

According to Matsen[40] the SCFMO theory can be used to predict the work function of graphite. It is suggested that the ionization potential and electron affinity plotted as a function of the lowest allowed energy, $h\upsilon$, should be symmetrical about the work function of graphite.[41] Also, Hush and Pople[42] suggest that the sum of the ionization potential and electron affinity should be a constant for conjugated hydrocarbons. A determination of a

TABLE VI

COMPARISON OF ELECTRON AFFINITY VALUES

Molecule	ϵ_{LVMO} (eV)	EA (eV)	EA* (eV)	EA+ (eV)
Naphthalene	-1.94	-0.06	0.15	
Anthracene	-2.52	0.49	0.55	0.42
Phenanthrene	-2.03	0.03	0.31	0.20
1.2-Benz-Anthracene	-2.44	0.42	0.66	0.46
Chrysene	-2.27	0.26	0.41	0.33
3.4-Benz-Penanthrene	-2.19	0.18	0.54	0.33
Pyrene	-2.47	0.45	0.59	0.39
Triphenylene	-1.94	-0.06	0.28	0.14
4.5-Benz-Pyrene	-2.37	0.35	0.51	
1.2-Benz-Pyrene	-2.67	0.64	0.75	
1.2,5.6-Dibenz-Anthracene	-2.39	0.37	0.64	
1.2,7.8-Dibenz-Anthracene	-2.35	0.33	0.64	
Picene	-2.31	0.29	0.52	
Azulene	-2.81	0.77	0.66	

*Average of two values of electron affinities given by Becker and Chen.[35]

+Previous experimental electron affinities by Wentworth and Becker.[38,39]

meaningful value for the work function of graphite would be a good indicator of the accuracy of the present work.

With this objective in mind, a correlation of the orbital energy ϵ_{HOMO} from the SCFMO calculations and ionization potential has been made for some of the same conjugated molecules as used in the electron affinity correlation. The values for the ionization potentials were taken from Dewar and Worley[43] and Kotov and Potapov.[44] The molecules, measured ionization potentials, and molecular orbital energies are given in Table VII. In Figure 2 we plot the measured ionization potential versus the energy of the highest occupied molecular orbital. A least squares fit to the data gives the following equation:

$$IP = -0.97\ \epsilon_{HOMO} - 0.68\ eV \quad . \tag{44}$$

Again, this relationship is consistent with Koopmans' theorem as seen by comparing Equations (41) and (44).

In terms of the SCFMO calculations the lowest allowed energy is given by

$$h\upsilon = \epsilon_{LVMO} - \epsilon_{HOMO} \quad . \tag{45}$$

Electron affinities and ionization potentials have been calculated for 28 hydrocarbons. This data is contained in Table VIII. The electron affinities and ionization potentials are plotted versus the lowest allowed energy $h\upsilon$ in Figure 3. The two sets of data fall on two excellent straight

TABLE VII

IONIZATION POTENTIAL AND ϵ_{HOMO} VALUES

Molecule	IP (eV)	ϵ_{HOMO} (eV)
Benzene	9.25[44]	-10.32
Naphthalene	8.12[44]	- 9.25
Pyridine	9.27[43]	-10.36
Pyrimidine	9.64[43]	-10.76
Pyrazine	9.29[43]	-10.39
Para-Benzoquinone	9.96[44]	-10.97
TCNQ	9.42[44]	-10.01

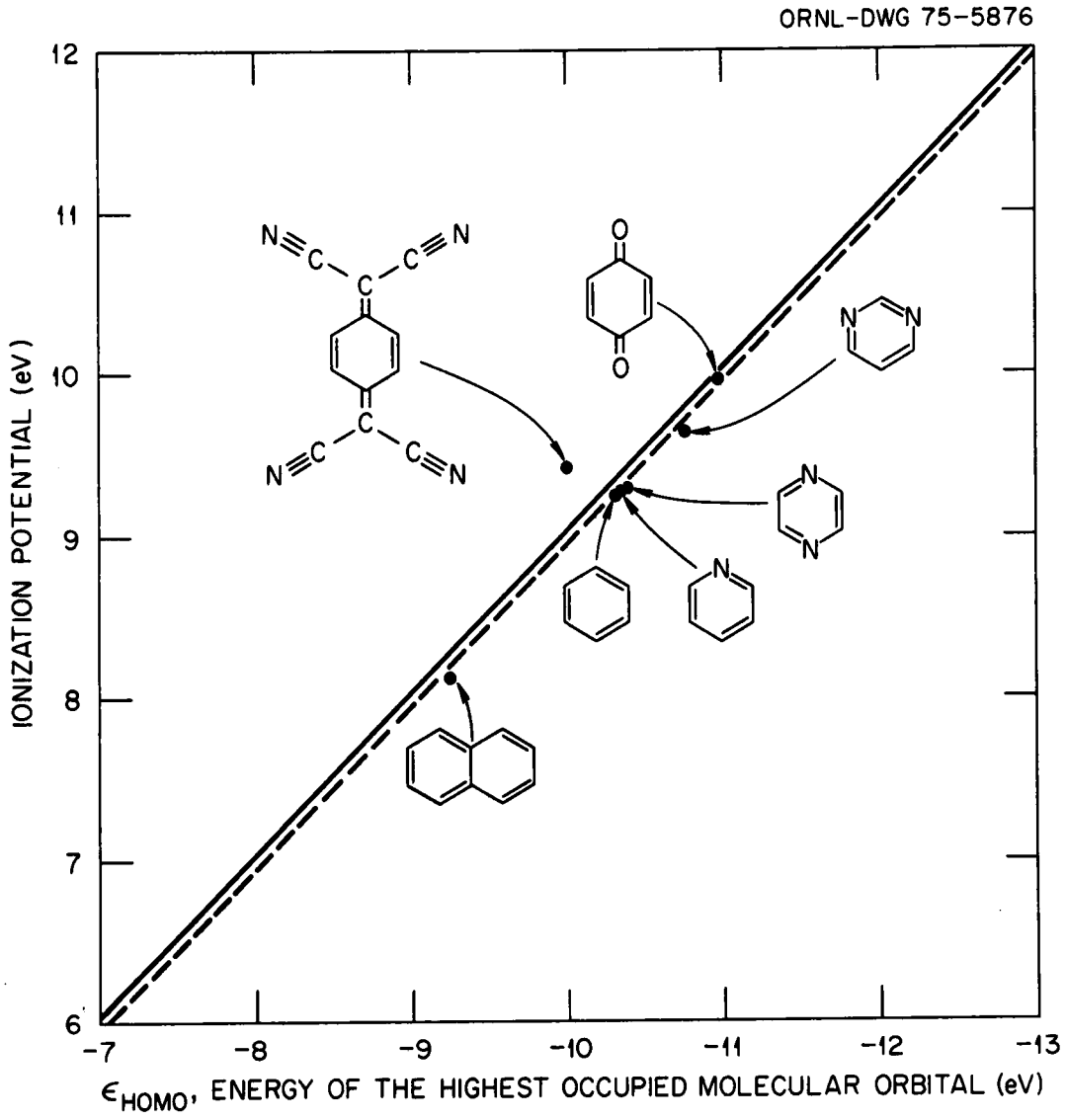


Figure 2. Correlation of the energy of the highest occupied molecular orbital, ϵ_{HOMO}, and experimentally determined ionization potentials.

TABLE VIII

ELECTRON AFFINITIES, IONIZATION POTENTIALS, AND LOWEST ENERGIES

Molecule	ϵ_{LVMO} (eV)	EA (eV)	ϵ_{HOMO} (eV)	IP (eV)	$\epsilon_{LVMO}-\epsilon_{HOMO}$ (eV)
Benzene	-0.87	-1.07	-10.32	9.33	9.45
Naphthalene	-1.94	-0.06	- 9.25	8.29	7.31
Phenanthrene	-2.03	0.03	- 9.16	8.21	7.13
Anthracene	-2.52	0.49	- 8.67	7.73	6.15
Triphenylene	-1.94	-0.06	- 9.25	8.29	7.31
3.4-Benz-Phenanthrene	-2.19	0.18	- 9.00	8.05	6.81
Chrysene	-2.27	0.26	- 8.92	7.97	6.65
1.2-Benz-Anthracene	-2.44	0.42	- 8.75	7.81	6.31
Pyrene	-2.47	0.45	- 8.72	7.78	6.25
Naphthacene	-2.88	0.84	- 8.31	7.38	5.43
3.4,5.6-Dibenz-Phenanthrene	-2.27	0.26	- 8.92	7.97	6.65
Picene	-2.31	0.29	- 8.88	7.93	6.57
1.2,7.8-Dibenz-Anthracene	-2.35	0.33	- 8.84	7.89	6.49
1.2,3.4-Dibenz-Anthracene	-2.36	0.34	- 8.83	7.89	6.47
1.2,5.6-Dibenz-Anthracene	-2.39	0.37	- 8.80	7.86	6.41
Pentaphene	-2.46	0.44	- 8.73	7.79	6.27
4.5-Benz-Pyrene	-2.37	0.35	- 8.82	7.88	6.45
1.2-Benz-Pyrene	-2.67	0.64	- 8.52	7.58	5.85
Perylene	-2.75	0.71	- 8.44	7.51	5.69
Pentacene	-3.12	1.06	- 8.07	7.15	4.95
Hexahelicene	-2.27	0.26	- 8.92	7.97	6.65
1.12-Benz-Perylene	-2.54	0.51	- 8.65	7.71	6.11
Coronene	-2.34	0.32	- 8.85	7.90	6.51

TABLE VIII (continued)

Molecule	ϵ_{LVMO} (eV)	EA (eV)	ϵ_{HOMO} (eV)	IP (eV)	$\epsilon_{LVMO}-\epsilon_{HOMO}$ (eV)
Ovalene	-2.85	0.81	-8.34	7.41	5.49
Hexacene	-3.29	1.23	-7.90	6.98	4.61
Heptacene	-3.41	1.34	-7.78	6.87	4.37
Octacene	-3.50	1.43	-7.69	6.78	4.19
Novacene	-3.57	1.49	-7.62	6.71	4.05

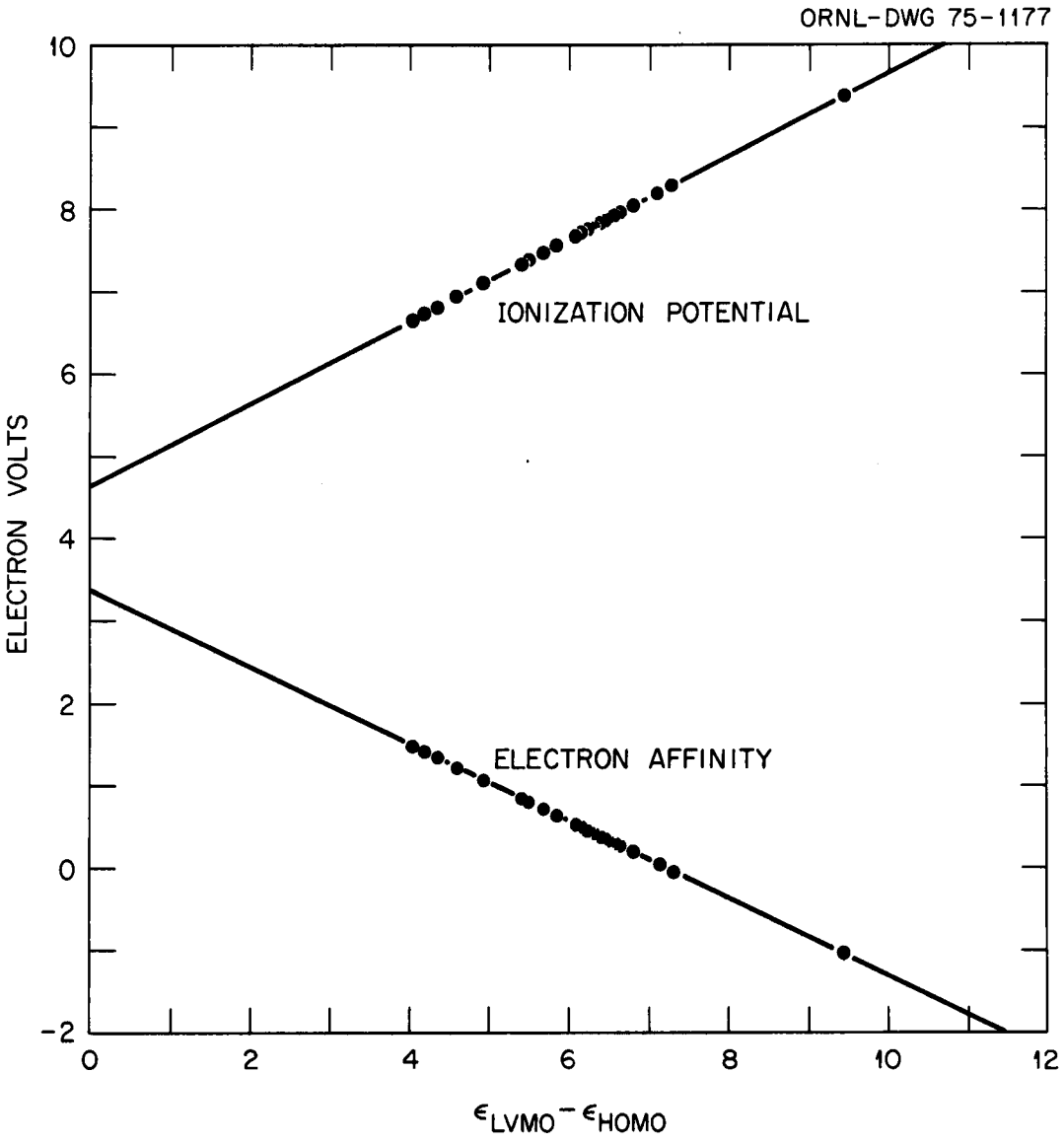


Figure 3. Correlations of electron affinity and ionization potential with lowest electronic transition energy, $\epsilon_{LVMO}-\epsilon_{HOMO}$.

lines. The equations for these lines as determined by least squares fits are

$$EA = -0.48\ h\upsilon + 3.43\ eV \quad , \tag{46}$$

and

$$IP = 0.48\ h\upsilon + 4.75\ eV \quad . \tag{47}$$

The slopes of these two lines are very close to that expected from theory, i.e., -0.5 and 0.5, respectively.[35] The small difference is due to the fact that the slopes of our correlation lines are about -0.96 rather than the theoretical value of -1.0.

By adding Equations (46) and (47) together, it can be seen that the sum of the electron affinity and ionization potential is, indeed, a constant for the conjugated hydrocarbons. Our value for the constant is

$$EA + IP = 8.18\ eV \quad .$$

According to theory, the difference in energy between the highest occupied and lowest vacant molecular orbitals should go to zero for graphite.[39] So the point $h\upsilon = 0$ represents graphite on the plot of Figure 3. The zero intercepts of the least squares lines yield a value of 3.43 eV for the electron affinity and a value of 4.75 eV for the ionization potential of graphite. These values agree very well with the values previously reported by Becker and Chen[35] of 3.02 eV and 4.71 eV, respectively, using their lowest energy transition (^1L_b) data. The molecular electronegativities, given by

$$\chi = \frac{1}{2}(EA + IP) \quad , \tag{48}$$

have a constant value of 4.09 eV for the conjugated hydrocarbons studied in this work. Therefore, the ionization potential and electron affinity plots are symmetrical about the molecular electronegativity. Matsen[40] and Hush and Pople[42] have taken the molecular electronegativity to be the work function of graphite. Further, they observe that the ionization potential equals the electron affinity at this point. This result was predicted based on Koopmans' theorem without consideration of the reorganization energy, that is IP = $-\epsilon_{HOMO}$ and EA = $-\epsilon_{LVMO}$. Of course, our semi-empirical calculations include correction for reorganization energy. By subtracting Equation (43) from Equation (44), the difference in our reorganization energy terms is 1.22 eV. This qualitatively explains the difference in ionization potential and electron affinity of 1.32 eV observed for graphite.

The graphite under consideration is an infinite two-dimensional molecule (graphite sheet). By plotting the electron affinities and ionization potentials as a function of the number of benzene rings in a hydrogen molecule, the values for graphite should be approached as the number of rings increases to infinity. In practice, however, the data points are so scattered such that an extrapolation to a large number of rings is impossible. A one-dimensional approximation for graphite can be obtained by considering only the linear chains of benzene rings. The molecules, electron affinities,

ionization potentials, and the number N of linear chain benzene rings forming the molecules are given in Table IX. The electron affinities and ionization potentials are plotted versus N in Figure 4. Various mathematical functional forms for the data were considered, and the best fit seemed to be a hyperbola. The least squares hyperbolas for the two sets of data are given by

$$EA = \frac{N - 1}{0.305N + 0.361} - 1.07 \text{ eV} , \tag{49}$$

and

$$IP = \frac{N - 1}{-0.299N - 0.348} + 9.33 \text{ eV} . \tag{50}$$

For large N, the resulting hyperbolas are asymptotic to values of 2.21 eV for the electron affinity and 5.99 eV for the ionization potential. These values agree with the results obtained by Becker and Chen[35] for the ^1L_a transition above the ^1L_b transition. Their intercept values were 2.23 eV for the electron affinity and 5.60 eV for the ionization potential. Apparently, the results of this method do not correspond to the lowest allowed energy values. However, the ionization potential and electron affinity plots are again symmetrical about the molecular electronegativity constant of 4.10 eV. Our electronegativity values agree with that of Wentworth and Becker[39] of 4.07 eV and that of Becker and Chen[35] of 4.17 eV. Mulliken[45] and Braun and Busch[46] have experimentally determined

TABLE IX

ELECTRON AFFINITY, IONIZATION POTENTIAL, AND NUMBER OF LINEAR RINGS

Molecule	EA	IP	N
Benzene	-1.07	9.33	1
Naphthalene	-0.06	8.29	2
Anthracene	0.49	7.73	3
Naphthacene	0.84	7.38	4
Pentacene	1.06	7.15	5
Hexacene	1.23	6.98	6
Heptacene	1.34	6.87	7
Octacene	1.43	6.78	8
Novacene	1.49	6.71	9

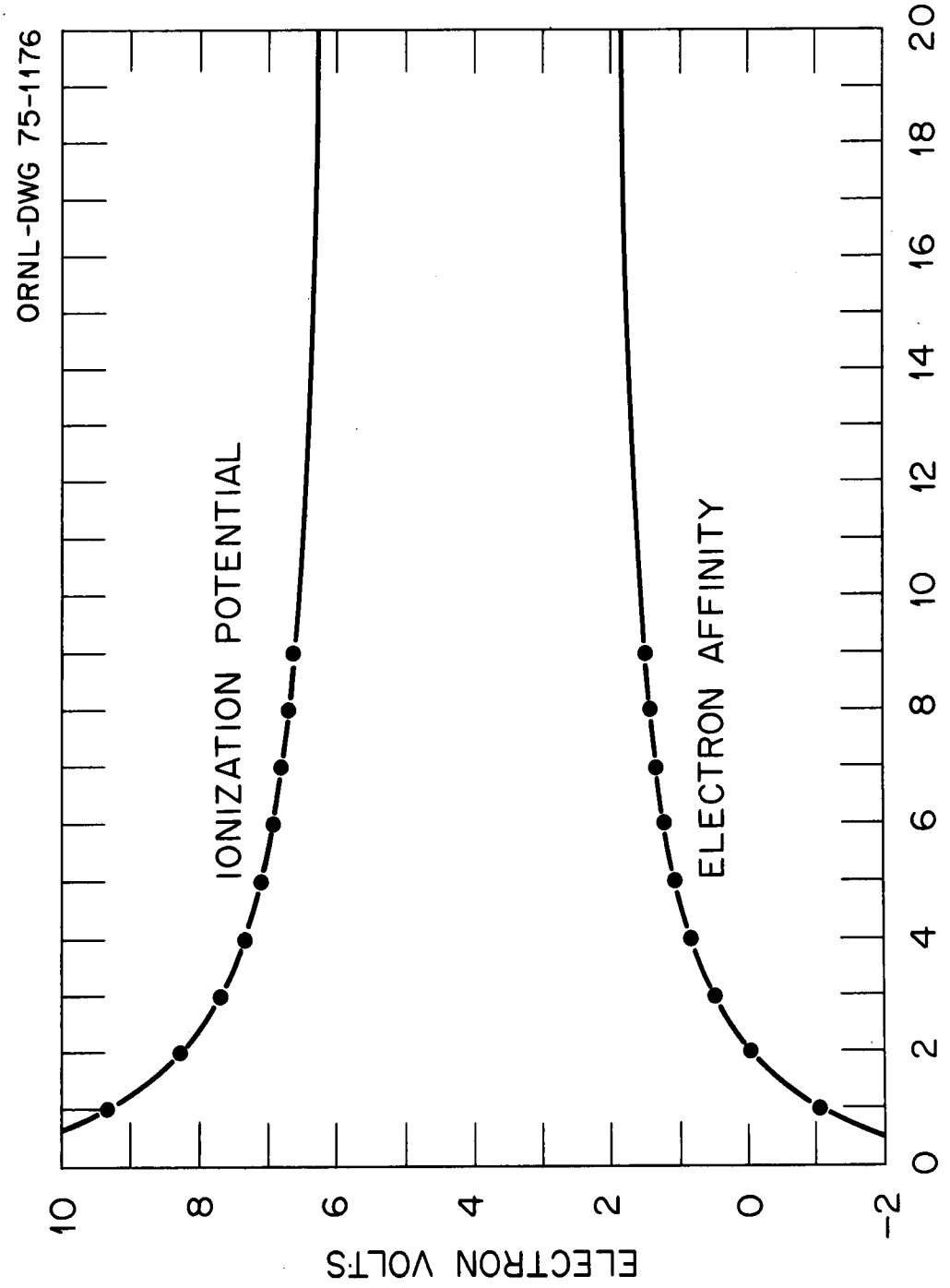


Figure 4. Plots of electron affinity and ionization potential versus the number of linear chain benzene rings.

the work function of graphite to be 4.39 eV. However, a more recent determination of the work function of pyrolytic graphite by Willis, Feuerbacher, and Fitton[47] indicates a value of 4.7 eV. It is not clear for which state of graphite these values were measured. In any event, the exact value ($\pm$ 0.1 eV) of the work function of graphite is uncertain. Our calculations obviously pertain to graphite vapor. Since the work function of graphite is a statistical quantity in that an electron is removed from the top of the Fermi level, it appears that the value should be in the range from about 3.5 eV to 4.7 eV and most probably should occur near 4.1 eV for graphite vapor.

V. EXCITED NEGATIVE ION STATES

The semi-empirical calculations presented here appear to adequately account for all electron affinities where reliable measurements exist. The splitting of the pyridine negative ion state is predicted exactly. It is interesting to consider the applicability of the present theory to excited negative ion states. Nenner and Schulz[5] have presented data on the energy position of the $\tilde{B}^2B_{2g}$, $\tilde{B}^2B_1$, and $\tilde{B}^2B_{2g}$ negative ion states of benzene, pyridine, and pyrazine, respectively. The lifetimes of these states are sufficiently short so that vibrational progressions were not observed and the resonances were rather broad ($\sim$ 1.5 eV). Using Equation (43) we calculate the 0-0 transition energies to be 3.97 eV, 3.83 eV, and 3.67 eV for benzene, pyridine, and pyrazine, respectively. These values agree

with the onsets for the states reported by Nenner and Schulz to within 0.2 eV. In each of these cases the onset was difficult to ascertain because of the broadness of the resonance. The theory, however, does seem to predict the positions of the resonances rather well. The present theory also adequately predicts resonances observed in para-benzoquinone and TCNQ.

We have calculated electron affinities and excitation energies for conjugated hydrocarbons and heteromolecules of physical and biological interest. The results of these calculations are presented in Appendix I. Our evidence indicates good agreement between calculated and experimental values for the hydrocarbons. For example, a compound state is observed as a broad and structureless dip at about 1.7 eV in the electron transmission spectra of ethylene. We calculate that the $^2B_{3u}$ state of $C_2H_4^-$ should occur at 1.61 eV. Many of the electron affinities of the heteromolecules are presented without comparison to experimental values because of the lack of reliable measurements.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. R. S. Berry and C. W. Reimann, J. Chem. Phys. 38, 1540 (1963).

2. M. W. Siegel, R. J. Celotta, J. L. Hall, J. Levine, and R. A. Bennett, Phys. Rev. 6, 607 (1972).

3. R. J. Celotta, R. J. Bennett, J. L. Hall, M. W. Siegel, and J. Levine, Phys. Rev. 6, 631 (1972).

4. L. Sanche and G. J. Schulz, J. Chem. Phys. 58, 479 (1973).

5. I. Nenner and G. J. Schulz, J. Chem. Phys. 62, 1747 (1975).

6. R. N. Compton and C. D. Cooper, J. Chem Phys. 59, 4140 (1973).

7. C. E. Klots, R. N. Compton, and V. F. Raaen, J. Chem. Phys. 60, 1177 (1974).

8. R. N. Compton, P. W. Reinhardt, and C. D. Cooper, J. Chem. Phys. 60, 2953 (1974).

9. C. D. Cooper, W. T. Naff, and R. N. Compton, submitted to J. Chem. Phys. (in press).

10. T. Koopmans, Physica 1, 104 (1934).

11. T. L. Kunii and H. Kuroda, Theoret. Chim. Acta (Berlin) 7, 220 (1967).

12. T. L. Kunii and H. Kuroda, Theoret. Chim. Acta (Berlin) 11, 97 (1968).

13. A. Streitwiesser, Jr., Molecular Orbital Theory for Organic Chemists (Wiley, New York, 1961).

14. L. Salem, The Molecular Orbital Theory of Conjugated Systems (Benjamin, New York, 1966).

15. E. Hückel, Z. Physik 70, 204 (1931).

16. E. Hückel, Z. Physik 72, 310 (1931).

17. E. Hückel, Z. Physik 76, 628 (1932).

18. C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A191, 39 (1947).

19. C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A192, 16 (1947).

20. C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

21. R. Pariser and R. G. Parr, J. Chem. Phys. 21, 446, 767 (1953).

22. J. A. Pople, Trans. Faraday Soc. 49, 1375 (1953).

23. M. E. Wacks and V. H. Dibeler, J. Chem. Phys. 31, 1557 (1959).

24. B. A. Hess, Jr., C. W. Holyoke, Jr., and L. J. Schaad, Tetrahedron 28, 3657 (1972).

25. B. A. Hess, Jr. and L. J. Schaad, J. Am. Chem. Soc. 95, 3907 (1973).

26. J. Hinge and H. H. Jaffe, J. Am. Chem. Soc. 84, 540 (1962).

27. T. Ohta, H. Kuroda, and T. L. Kunii, Theoret. Chim. Acta (Berlin) 19, 167 (1970).

28. K. Nishimoto and L. S. Forster, Theoret. Chim. Acta (Berlin) 3, 407 (1965).

29. K. Nishimoto and L. S. Forster, Theoret Chim. Acta. (Berlin) 4, 155 (1966).

30. K. Nishimoto and N. Mataga, Z. Physik Chem. (Frankfurt) 12, 353 (1957).

31. K. Nishimoto and N. Mataga, Z. Physik Chem. (Frankfurt) 13, 140 (1957).

32. M. M. Rohmer and A. Veillard, Chem. Comm. 250 (1973).

33. E. Heilbronner, The World of Quantum Chemistry, ed. R. Daudel and B. Pullman (Reidel, Boston, 1973) p. 211.

34. J. H. D. Eland, Photoelectron Spectroscopy (Wiley, New York, 1974).

35. R. S. Becker and E. Chen, J. Chem. Phys. 45, 2403 (1966).

36. G. Brieglab, Angew. Chem. 76, 326 (1964).

37. R. H. Huebner, R. N. Compton, and H. C. Schweinler, J. Chem. Phys. 2, 407 (1968).

38. W. Wentworth and R. S. Becker, J. Am. Chem. Soc. 84, 4263 (1962).

39. R. S. Becker and W. Wentworth, J. Am. Chem. Soc. 85, 2210 (1963).

40. F. A. Matsen, J. Chem. Phys. 24, 602 (1955).

41. R. M. Hedges and F. A. Matsen, J. Chem. Phys. 28, 950 (1958).

42. N. S. Hush and J. A. Pople, Trans. Faraday Soc. 51, 600 (1955).

43. M. J. S. Dewar and S. D. Worley, J. Chem Phys. 51, 263 (1969).

44. B. V. Kotov and V. K. Potapov, Khim. Vys. Energ. 6, 375 (1972).

45. R. S. Mulliken, Phys. Rev. 74, 736 (1948).

46. A. Braun and G. Busch, Helv. Phys. 20, 33 (1947).

47. R. F. Willis, B. Feuerbacher, and B. Fitton, Phys. Rev. B4, 2441 (1971).

APPENDIXES

APPENDIX I

TABLE X

ELECTRON AFFINITIES AND EXCITATION ENERGIES

Molecule	ϵ_{LVMO} (eV)	EA (eV)	ϵ_{2VMO} (eV)	1st Excited State (eV)	ϵ_{3VMO} (eV)	2nd Excited State (eV)
Acenaphthylene	- 2.81	0.77	- 1.25	- 0.71	- 0.15	- 1.76
Acridine	- 2.79	0.75	- 1.36	- 0.61	- 1.06	- 0.89
Acrylonitrile	- 3.38	1.31	- 0.47	- 1.45	-----	-----
Adenine	- 1.75	- 0.24	- 1.26	- 0.70	0.06	- 1.96
Alloxan	- 3.50	1.43	- 0.59	- 1.34	- 0.55	- 1.38
Aniline	- 1.39	- 0.58	- 1.26	- 0.70	1.52	- 3.34
Anthracene	- 2.52	0.49	- 1.32	- 0.65	- 1.03	- 0.92
Azulene	- 2.81	0.77	- 1.94	- 0.06	0.72	- 2.58
Benzene	- 0.87[a]	- 1.07	2.18	- 3.97	-----	-----
Para-benzoquinone	- 3.71	1.62	- 1.08	- 0.87	- 0.13	- 1.78
1,2-Benz-anthracene	- 2.44	0.42	- 1.83	- 0.16	- 1.22	- 0.74
1,12-Benz-perylene	- 2.54	0.51	- 1.97	- 0.03	- 1.17	- 0.79
3,4-Benz-phenanthrene	- 2.19	0.18	- 1.94	- 0.06	- 1.11	- 0.85
1,2-Benz-pyrene	- 2.67	0.64	- 1.74	- 0.25	- 1.22	- 0.74
4,5-Benz-pyrene	- 2.37	0.35	- 1.89	- 0.10	- 1.21	- 0.75
1,2,3,4-Dibenz-anthracene	- 2.36	0.34	- 1.90	- 0.10	- 1.64	- 0.34

TABLE X (Continued)

Molecule	ϵ_{LVMO} (eV)	EA (eV)	ϵ_{2VMO} (eV)	1st Excited State (eV)	ϵ_{3VMO} (eV)	2nd Excited State (eV)
1,2,5,6-Dibenz-anthracene	- 2.39	0.37	- 1.98	- 0.02	- 1.58	- 0.40
1,2,7,8-Dibenz-anthracene	- 2.35	0.33	- 2.07	0.07	- 1.38	- 0.59
3,4,5,6-Dibenz-phenanthrene	- 2.27	0.26	- 2.02	0.02	- 1.58	- 0.40
Biphenyl	- 1.78	- 0.21	- 1.00[a]	- 0.95	- 0.27	- 1.64
Biphenylene	- 1.65	- 0.33	- 1.27	- 0.69	- 0.83	- 1.11
1,3 Butadiene	- 1.46	- 0.51	1.07	- 2.92	-----	-----
Carbazole	- 1.63	- 0.35	- 1.24	- 0.72	- 0.40	- 1.52
Chrysene	- 2.27	0.26	- 1.75	- 0.24	- 1.38	- 0.59
Coronene	- 2.34[a]	0.32	- 1.18[a]	- 0.78	- 0.92	- 1.03
Cytosine	- 1.97	- 0.03	- 0.84	- 1.10	1.40	- 3.23
Ethylene	- 0.31	- 1.61	-----	-----	-----	-----
Fluoranthene	- 2.66	0.63	- 1.30	- 0.67	- 1.25	- 0.71
Fulvalene	- 3.82	1.73	- 0.41	- 1.51	0.79[a]	- 2.65
Fumaronitrile	- 4.38	2.26	- 2.38	0.36	0.07	- 1.97
Furan	0.53	- 2.40	0.80	- 2.66	-----	-----
Glyoxal	- 2.99	0.94	0.07	- 1.97	-----	-----
Guanine	- 1.10	- 0.86	- 0.54	- 1.39	0.35	- 2.23
HCN	- 3.17	1.11	-----	-----	-----	-----
Heptacene	- 3.41	1.34	- 2.62	0.59	- 1.81	- 0.18

TABLE X (Continued)

Molecule	ϵ_{LVMO} (eV)	EA (eV)	ϵ_{2VMO} (eV)	1st Excited State (eV)	ϵ_{3VMO} (eV)	2nd Excited State (eV)
Heptafulvalene	- 2.19[a]	0.18	- 1.93	- 0.07	0.55	- 2.42
Hexacene	- 3.29	1.23	- 2.37	0.35	- 1.47	- 0.50
Hexahelicene	- 2.27	0.26	- 2.20	0.19	- 1.61	- 0.37
Imidazole	0.11	- 2.00	0.67	- 2.54	-----	-----
Isoquinoline	- 2.07	0.07	- 1.34	- 0.63	- 0.30	- 1.62
Maleic Anhydride	- 3.35	1.28	0.73	- 2.59	0.94	- 2.79
Maleimide	- 3.21	1.15	0.73	- 2.59	0.81	- 2.67
Naphthacene	- 2.88	0.84	- 1.62	- 0.36	- 1.39	- 0.58
Naphthalene	- 1.94	- 0.06	- 1.18	- 0.78	- 0.22	- 1.69
1,5-Naphthyridine	- 2.45	0.43	- 1.24	- 0.72	- 0.57	- 1.36
1,6-Naphthyridine	- 2.31	0.29	- 1.35	- 0.62	- 0.46	- 1.46
1,7-Naphthyridine	- 2.36	0.34	- 1.38	- 0.59	- 0.46	- 1.46
1,8-Naphthyridine	- 2.43	0.41	- 1.23	- 0.73	- 0.51	- 1.42
2,6-Naphthyridine	- 2.27	0.26	- 1.45	- 0.52	- 0.41	- 1.51
2,7-Naphthyridine	- 2.15	0.14	- 1.53	- 0.45	- 0.36	- 1.56
Novacene	- 3.57	1.49	- 2.96	0.91	- 2.31	0.29
Octacene	- 3.50	1.43	- 2.81	0.77	- 2.08	0.08
Ovalene	- 2.85	0.81	- 2.23	0.22	- 1.72	- 0.27

TABLE X (Continued)

Molecule	ϵ_{LVMO} (eV)	EA (eV)	ϵ_{2VMO} (eV)	1st Excited State (eV)	ϵ_{3VMO} (eV)	2nd Excited State (eV)
Oxazole	0.37	- 2.25	0.54	- 2.41	-----	-----
Parabanic Acid	- 2.95	0.90	0.50	- 2.38	0.87	- 2.73
Para-Phenylenediamine	- 1.75	- 0.24	- 1.55	- 0.43	0.98	- 2.83
Pentacene	- 3.12	1.06	- 2.05	0.05	- 1.42	- 0.55
Pentaphene	- 2.46	0.44	- 2.29	0.28	- 1.34	- 0.63
Perylene	- 2.75	0.71	- 1.25[a]	- 0.71	- 1.18	- 0.78
Phenanthrene	- 2.03	0.03	- 1.72	- 0.27	- 0.82	- 1.12
Phenazine	- 3.12	1.06	- 1.40	- 0.57	- 1.14	- 0.82
Phenol	- 1.31	- 0.66	- 1.12	- 0.84	1.64	- 3.46
Picene	- 2.31	0.29	- 1.99	- 0.01	- 1.54	- 0.44
Purine	- 1.92	- 0.08	- 0.93	- 1.02	0.51	- 2.38
Pyrazine	- 1.68	- 0.30	- 1.01	- 0.94	1.87	- 3.68
Pyrene	- 2.47	0.45	- 1.60	- 0.38	- 1.01	- 0.94
Pyridine	- 1.26	- 0.70	- 0.91	- 1.04	2.03	- 3.83
Pyrimidine	- 1.45	- 0.52	- 1.09	- 0.86	1.89	- 3.70
Pyrrole	0.52	- 2.39	0.70	- 2.57	-----	-----
Quinazoline	- 2.32	0.30	- 1.33	- 0.64	- 0.43	- 1.49
Quinoline	- 2.21	0.20	- 1.21	- 0.75	- 0.37	- 1.55

TABLE X (Continued)

Molecule	ϵ_{LVMO} (eV)	EA (eV)	ϵ_{2VMO} (eV)	1st Excited State (eV)	ϵ_{3VMO} (eV)	2nd Excited State (eV)
Quinoxaline	- 2.54	0.51	- 1.27	- 0.69	- 0.50	- 1.43
Styrene	- 1.59	- 0.39	- 0.85	- 1.09	0.39	- 2.27
TCNE	- 5.21	3.05	- 3.20[a]	1.14	- 1.90	- 0.10
TCNQ	- 5.12	2.96	- 2.92[a]	0.87	- 2.48	0.46
s-Triazine	- 1.43[a]	- 0.54	1.75	- 3.56	-----	-----
Triphenylene	- 1.94[a]	- 0.06	- 1.37	- 0.60	- 0.45[a]	- 1.47
Uracil	- 1.86	- 0.13	- 0.23	- 1.68	2.01	- 3.81
Vinylene Carbonate	- 0.32	- 1.60	1.55	- 3.37	-----	-----
Vinylidene Cyanide	- 3.74	1.65	- 2.94	0.89	0.23	- 2.12

[a]This orbital is degenerate.

APPENDIX II

SAMPLE HMO AND SCFMO CALCULATIONS

```
********** BENZENE **********

NO. OF ATOMS=  6

NO. OF PI ELECTRONS=  6

NO. OF BONDS=  6

NO. OF RINGS=  1

ALPHA=  -6.2400      BETA=  -3.1400

OVERLAP INTEGRAL=  0.0

HAMILTONIAN MATRIX AND BOND TYPE

  1  1  0.0   0   1  2  1.00  1   1  3  0.0   0   1  4  0.0   0   1  5  0.0   0   1  6  1.00  1
  2  2  0.0   0   2  3  1.00  1   2  4  0.0   0   2  5  0.0   0   2  6  0.0   0
  3  3  0.0   0   3  4  1.00  1   3  5  0.0   0   3  6  0.0   0
  4  4  0.0   0   4  5  1.00  1   4  6  0.0   0
  5  5  0.0   0   5  6  1.00  1
  6  6  0.0   0

HUCKEL MO

ENERGIES AND COEFFICIENTS

  1  E=  2.000000D 00 BETA
     E= -1.252000D 01 EV
     1  1   4.082483D-01      2  1   4.082483D-01      3  1   4.082483D-01      4  1   4.082483D-01
     5  1   4.082483D-01      6  1   4.082483D-01

  2  E=  1.000000D 00 BETA
     E= -9.380000D 00 EV
     1  2   2.232015D-01      2  2  -3.495238D-01      3  2  -5.727253D-01      4  2  -2.232015D-01
     5  2   3.495238D-01      6  2   5.727253D-01

  3  E=  1.000000D 00 BETA
     E= -9.380000D 00 EV
     1  3  -5.324607D-01      2  3  -4.595285D-01      3  3   7.293224D-02      4  3   5.324607D-01
     5  3   4.595285D-01      6  3  -7.293224D-02

  4  E= -1.000000D 00 BETA
     E= -3.100000D 00 EV
     1  4  -2.319616D-01      2  4  -3.418897D-01      3  4   5.738513D-01      4  4  -2.319616D-01
     5  4  -3.418897D-01      6  4   5.738513D-01

  5  E= -1.000000D 00 BETA
     E= -3.100000D 00 EV
     1  5  -5.287033D-01      2  5   4.652363D-01      3  5   6.346704D-02      4  5  -5.287033D-01
     5  5   4.652363D-01      6  5   6.346704D-02

  6  E= -2.000000D 00 BETA
     E=  4.000000D-02 EV
     1  6  -4.082483D-01      2  6   4.082483D-01      3  6  -4.082483D-01      4  6   4.082483D-01
     5  6  -4.082483D-01      6  6   4.082483D-01
```

```
TOTAL PI ENERGY

     E=  8.000000D 00 BETA
     E= -3.136000D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

  1  Q=  1.000000D 00
    1  2   6.666667D-01     1  3   0.0              1  4  -3.333333D-01     1  5   0.0
    1  6   6.666667D-01

  2  Q=  1.000000D 00
    2  3   6.666667D-01     2  4   0.0              2  5  -3.333333D-01     2  6   0.0

  3  Q=  1.000000D 00
    3  4   6.666667D-01     3  5   0.0              3  6  -3.333333D-01

  4  Q=  1.000000D 00
    4  5   6.666667D-01     4  6   0.0

  5  Q=  1.000000D 00
    5  6   6.666667D-01

  6  Q=  1.000000D 00

FREE VALENCES

  1  F=  3.987175D-01
  2  F=  3.987175D-01
  3  F=  3.987175D-01
  4  F=  3.987175D-01
  5  F=  3.987175D-01
  6  F=  3.987175D-01

SELF-CONSISTENT FIELD MO

SCF CONVERGED IN  2 ITERATIONS

ENERGIES AND COEFFICIENTS

  1  E= -1.336550D 01 EV
    1  1   4.082483D-01     2  1   4.082483D-01     3  1   4.082483D-01     4  1   4.082483D-01
    5  1   4.082483D-01     6  1   4.082483D-01

  2  E= -1.031937D 01 EV
    1  2  -9.321333D-03     2  2  -5.045955D-01     3  2  -4.952742D-01     4  2   9.321333D-03
    5  2   5.045955D-01     6  2   4.952742D-01

  3  E= -1.031937D 01 EV
    1  3  -5.772750D-01     2  3  -2.805650D-01     3  3   2.967100D-01     4  3   5.772750D-01
    5  3   2.805650D-01     6  3  -2.967100D-01

  4  E= -8.706346D-01 EV
    1  4   5.510704D-01     2  4  -1.264009D-01     3  4  -4.246695D-01     4  4   5.510704D-01
    5  4  -1.264009D-01     6  4  -4.246695D-01

  5  E= -8.706346D-01 EV
```

```
    1  5  -1.722054D-01      2  5   5.633437D-01      3  5  -3.911383D-01      4  5  -1.722054D-01
    5  5   5.633437D-01      6  5  -3.911383D-01

  6  E=  2.175503D 00 EV
    1  6   4.082483D-01      2  6  -4.082483D-01      3  6   4.082483D-01      4  6  -4.082483D-01
    5  6   4.082483D-01      6  6  -4.082483D-01

TOTAL PI ENERGY

     E= -6.800847D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

  1  Q=  1.000000D 00
    1  2   6.666667D-01      1  3   0.0               1  4  -3.333333D-01      1  5   0.0
    1  6   6.666667D-01

  2  Q=  1.000000D 00
    2  3   6.666667D-01      2  4   0.0               2  5  -3.333333D-01      2  6   0.0

  3  Q=  1.000000D 00
    3  4   6.666667D-01      3  5   0.0               3  6  -3.333333D-01

  4  Q=  1.000000D 00
    4  5   6.666667D-01      4  6   0.0

  5  Q=  1.000000D 00
    5  6   6.666667D-01

  6  Q=  1.000000D 00

BOND LENGTHS

    1  2  R=  1.396999D 00
    1  6  R=  1.396999D 00
    2  3  R=  1.396999D 00
    3  4  R=  1.396999D 00
    4  5  R=  1.396999D 00
    5  6  R=  1.396999D 00

FREE VALENCES

  1  F=  3.987175D-01
  2  F=  3.987175D-01
  3  F=  3.987175D-01
  4  F=  3.987175D-01
  5  F=  3.987175D-01
  6  F=  3.987175D-01
```

********** NAPHTHALENE **********

NO. OF ATOMS= 10

NO. OF PI ELECTRONS= 10

NO. OF BONDS= 11

NO. OF RINGS= 2

ALPHA= -6.2400 BETA= -3.1400

OVERLAP INTEGRAL= 0.0

HAMILTONIAN MATRIX AND BOND TYPE

```
 1  1  0.0   0   1  2  1.00  1   1  3  0.0   0   1  4  0.0   0   1  5  0.0   0   1  6  0.0   0   1  7  0.0   0   1  8  0.0   0
 1  9  1.00  1   1 10  0.0   0
 2  2  0.0   0   2  3  1.00  1   2  4  0.0   0   2  5  0.0   0   2  6  0.0   0   2  7  0.0   0   2  8  0.0   0   2  9  0.0   0
 2 10  0.0   0
 3  3  0.0   0   3  4  1.00  1   3  5  0.0   0   3  6  0.0   0   3  7  0.0   0   3  8  0.0   0   3  9  0.0   0   3 10  0.0   0
 4  4  0.0   0   4  5  0.0   0   4  6  0.0   0   4  7  0.0   0   4  8  0.0   0   4  9  0.0   0   4 10  1.00  1
 5  5  0.0   0   5  6  1.00  1   5  7  0.0   0   5  8  0.0   0   5  9  0.0   0   5 10  1.00  1
 6  6  0.0   0   6  7  1.00  1   6  8  0.0   0   6  9  0.0   0   6 10  0.0   0
 7  7  0.0   0   7  8  1.00  1   7  9  0.0   0   7 10  0.0   0
 8  8  0.0   0   8  9  1.00  1   8 10  0.0   0
 9  9  0.0   0   9 10  1.00  1
10 10  0.0   0
```

HUCKEL MO

ENERGIES AND COEFFICIENTS

```
 1  E=  2.302776D 00 BETA
    E= -1.347072D 01 EV
    1  1   3.005516D-01     2  1   2.307009D-01     3  1   2.307009D-01     4  1   3.005516D-01
    5  1   3.005516D-01     6  1   2.307009D-01     7  1   2.307009D-01     8  1   3.005516D-01
    9  1   4.614019D-01    10  1   4.614019D-01

 2  E=  1.618034D 00 BETA
    E= -1.132063D 01 EV
    1  2  -2.628656D-01     2  2  -4.253254D-01     3  2  -4.253254D-01     4  2  -2.628656D-01
    5  2   2.628656D-01     6  2   4.253254D-01     7  2   4.253254D-01     8  2   2.628656D-01
    9  2   0.0             10  2   0.0

 3  E=  1.302776D 00 BETA
    E= -1.033072D 01 EV
    1  3  -3.995857D-01     2  3  -1.735235D-01     3  3   1.735235D-01     4  3   3.995857D-01
    5  3   3.995857D-01     6  3   1.735235D-01     7  3  -1.735235D-01     8  3  -3.995857D-01
    9  3  -3.470470D-01    10  3   3.470470D-01

 4  E=  1.000000D 00 BETA
    E= -9.380000D 00 EV
    1  4   0.0             2  4  -4.082483D-01     3  4  -4.082483D-01     4  4   0.0
    5  4   0.0             6  4  -4.082483D-01     7  4  -4.082483D-01     8  4   0.0
    9  4   4.082483D-01    10  4   4.082483D-01

 5  E=  6.180340D-01 BETA
    E= -8.180627D 00 EV
```

```
  1  5  -4.253254D-01     2  5  -2.628656D-01     3  5   2.628656D-01     4  5   4.253254D-01
  5  5  -4.253254D-01     6  5  -2.628656D-01     7  5   2.628656D-01     8  5   4.253254D-01
  9  5   0.0             10  5   0.0

 6  E= -6.180340D-01 BETA
    E= -4.299373D 00 EV
  1  6   4.253254D-01     2  6  -2.628656D-01     3  6  -2.628656D-01     4  6   4.253254D-01
  5  6  -4.253254D-01     6  6   2.628656D-01     7  6   2.628656D-01     8  6  -4.253254D-01
  9  6   0.0             10  6   0.0

 7  E= -1.000000D 00 BETA
    E= -3.100000D 00 EV
  1  7   0.0             2  7   4.082483D-01     3  7  -4.082483D-01     4  7   0.0
  5  7   0.0             6  7  -4.082483D-01     7  7   4.082483D-01     8  7   0.0
  9  7  -4.082483D-01    10  7   4.082483D-01

 8  E= -1.302776D 00 BETA
    E= -2.149284D 00 EV
  1  8  -3.995857D-01     2  8   1.735235D-01     3  8   1.735235D-01     4  8  -3.995857D-01
  5  8  -3.995857D-01     6  8   1.735235D-01     7  8   1.735235D-01     8  8  -3.995857D-01
  9  8   3.470470D-01    10  8   3.470470D-01

 9  E= -1.618034D 00 BETA
    E= -1.159373D 00 EV
  1  9  -2.628656D-01     2  9   4.253254D-01     3  9  -4.253254D-01     4  9   2.628656D-01
  5  9  -2.628656D-01     6  9   4.253254D-01     7  9  -4.253254D-01     8  9   2.628656D-01
  9  9   0.0             10  9   0.0

10  E= -2.302776D 00 BETA
    E=  9.907155D-01 EV
  1 10  -3.005516D-01     2 10   2.307009D-01     3 10  -2.307009D-01     4 10   3.005516D-01
  5 10   3.005516D-01     6 10  -2.307009D-01     7 10   2.307009D-01     8 10  -3.005516D-01
  9 10   4.614019D-01    10 10  -4.614019D-01

TOTAL PI ENERGY

     E=  1.368324D 01 BETA
     E= -4.920537D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

 1  Q=  1.000000D 00
   1  2   7.245637D-01     1  3   0.0             1  4  -3.622818D-01     1  5   8.493175D-02
   1  6   0.0             1  7  -1.698635D-01     1  8   0.0             1  9   5.547002D-01
   1 10   0.0

 2  Q=  1.000000D 00
   2  3   6.031651D-01     2  4   0.0             2  5   0.0             2  6   1.559516D-01
   2  7   0.0             2  8  -1.698635D-01     2  9   0.0             2 10  -2.408833D-01

 3  Q=  1.000000D 00
   3  4   7.245637D-01     3  5  -1.698635D-01     3  6   0.0             3  7   1.559516D-01
   3  8   0.0             3  9  -2.408833D-01     3 10   0.0

 4  Q=  1.000000D 00
   4  5   0.0             4  6  -1.698635D-01     4  7   0.0             4  8   8.493175D-02
   4  9   0.0             4 10   5.547002D-01

 5  Q=  1.000000D 00
```

```
    5  6   7.245637D-01      5  7   0.0               5  8  -3.622818D-01      5  9   0.0
    5 10   5.547002D-01

  6  Q=  1.000000D 00
    6  7   6.031651D-01      6  8   0.0               6  9  -2.408833D-01      6 10   0.0

  7  Q=  1.000000D 00
    7  8   7.245637D-01      7  9   0.0               7 10  -2.408833D-01

  8  Q=  1.000000D 00
    8  9   5.547002D-01      8 10   0.0

  9  Q=  1.000000D 00
    9 10   5.182334D-01

 10  Q=  1.000000D 00

FREE VALENCES

  1  F=  4.527869D-01
  2  F=  4.043220D-01
  3  F=  4.043220D-01
  4  F=  4.527869D-01
  5  F=  4.527869D-01
  6  F=  4.043220D-01
  7  F=  4.043220D-01
  8  F=  4.527869D-01
  9  F=  1.044170D-01
 10  F=  1.044170D-01

SELF-CONSISTENT FIELD NO

SCF CONVERGED IN 19 ITERATIONS

ENERGIES AND COEFFICIENTS

  1  E= -1.370459D 01 EV
    1  1   3.021637D-01      2  1   2.499173D-01      3  1   2.499173D-01      4  1   3.021637D-01
    5  1   3.021637D-01      6  1   2.499173D-01      7  1   2.499173D-01      8  1   3.021637D-01
    9  1   4.387218D-01     10  1   4.387218D-01

  2  E= -1.198979D 01 EV
    1  2  -2.718828D-01      2  2  -4.196186D-01      3  2  -4.196186D-01      4  2  -2.718828D-01
    5  2   2.718828D-01      6  2   4.196186D-01      7  2   4.196186D-01      8  2   2.718828D-01
    9  2   0.0              10  2   0.0

  3  E= -1.097338D 01 EV
    1  3  -3.983678D-01      2  3  -1.891372D-01      3  3   1.891372D-01      4  3   3.983678D-01
    5  3   3.983678D-01      6  3   1.891372D-01      7  3  -1.891372D-01      8  3  -3.983678D-01
    9  3  -3.332574D-01     10  3   3.332574D-01

  4  E= -1.000631D 01 EV
    1  4   4.358323D-04      2  4  -3.895747D-01      3  4  -3.895747D-01      4  4   4.358323D-04
    5  4   4.358323D-04      6  4  -3.895747D-01      7  4  -3.895747D-01      8  4   4.358323D-04
    9  4   4.432411D-01     10  4   4.432411D-01

  5  E= -9.253300D 00 EV
```

```
   1  5  -4.196186D-01     2  5  -2.718828D-01     3  5   2.718828D-01     4  5   4.196186D-01
   5  5  -4.196186D-01     6  5  -2.718828D-01     7  5   2.718828D-01     8  5   4.196186D-01
   9  5   0.0             10  5   0.0

 6  E= -1.936701D 00 EV
   1  6   4.196186D-01     2  6  -2.718828D-01     3  6  -2.718828D-01     4  6   4.196186D-01
   5  6  -4.196186D-01     6  6   2.718828D-01     7  6   2.718828D-01     8  6  -4.196186D-01
   9  6   0.0             10  6   0.0

 7  E= -1.183694D 00 EV
   1  7   4.358323D-04     2  7   3.895747D-01     3  7  -3.895747D-01     4  7  -4.358323D-04
   5  7  -4.358323D-04     6  7  -3.895747D-01     7  7   3.895747D-01     8  7   4.358323D-04
   9  7  -4.432411D-01    10  7   4.432411D-01

 8  E= -2.166195D-01 EV
   1  8   3.983678D-01     2  8  -1.891372D-01     3  8  -1.891372D-01     4  8   3.983678D-01
   5  8   3.983678D-01     6  8  -1.891372D-01     7  8  -1.891372D-01     8  8   3.983678D-01
   9  8  -3.332574D-01    10  8  -3.332574D-01

 9  E=  7.997919D-01 EV
   1  9  -2.718828D-01     2  9   4.196186D-01     3  9  -4.196186D-01     4  9   2.718828D-01
   5  9  -2.718828D-01     6  9   4.196186D-01     7  9  -4.196186D-01     8  9   2.718828D-01
   9  9   0.0             10  9   0.0

10  E=  2.514592D 00 EV
   1 10   3.021637D-01     2 10  -2.499173D-01     3 10   2.499173D-01     4 10  -3.021637D-01
   5 10  -3.021637D-01     6 10   2.499173D-01     7 10  -2.499173D-01     8 10   3.021637D-01
   9 10  -4.387218D-01    10 10   4.387218D-01

TOTAL PI ENERGY

     E= -1.118547D 02 EV

ELECTRON DENSITIES AND BOND ORDERS

 1  Q=  1.000000D 00
   1  2   7.577329D-01     1  3   0.0             1  4  -3.391065D-01     1  5   6.953141D-02
   1  6   0.0             1  7  -1.549637D-01     1  8   0.0             1  9   5.310360D-01
   1 10   0.0

 2  Q=  1.000000D 00
   2  3   5.612275D-01     2  4   0.0             2  5   0.0             2  6   1.525896D-01
   2  7   0.0             2  8  -1.549637D-01     2  9   0.0             2 10  -2.521254D-01

 3  Q=  1.000000D 00
   3  4   7.577329D-01     3  5  -1.549637D-01     3  6   0.0             3  7   1.525896D-01
   3  8   0.0             3  9  -2.521254D-01     3 10   0.0

 4  Q=  1.000000D 00
   4  5   0.0             4  6  -1.549637D-01     4  7   0.0             4  8   6.953141D-02
   4  9   0.0             4 10   5.310360D-01

 5  Q=  1.000000D 00
   5  6   7.577329D-01     5  7   0.0             5  8  -3.391065D-01     5  9   0.0
   5 10   5.310360D-01

 6  Q=  1.000000D 00
   6  7   5.612275D-01     6  8   0.0             6  9  -2.521254D-01     6 10   0.0
```

```
  7  Q=  1.000000D 00
     7  8    7.577329D-01      7  9    0.0               7 10  -2.521254D-01

  8  Q=  1.000000D 00
     8  9    5.310360D-01      8 10    0.0

  9  Q=  1.000000D 00
     9 10    5.557580D-01

 10  Q=  1.000000D 00

BOND LENGTHS

     1  2  R=  1.380607D 00
     1  9  R=  1.421413D 00
     2  3  R=  1.415978D 00
     3  4  R=  1.380607D 00
     4 10  R=  1.421413D 00
     5  6  R=  1.380607D 00
     5 10  R=  1.421413D 00
     6  7  R=  1.415978D 00
     7  8  R=  1.380607D 00
     8  9  R=  1.421413D 00
     9 10  R=  1.416963D 00

FREE VALENCES

   1  F=  4.432819D-01
   2  F=  4.130904D-01
   3  F=  4.130904D-01
   4  F=  4.432819D-01
   5  F=  4.432819D-01
   6  F=  4.130904D-01
   7  F=  4.130904D-01
   8  F=  4.432819D-01
   9  F=  1.142207D-01
  10  F=  1.142207D-01
```

********** PYRIDINE **********

NO. OF ATOMS= 6

NO. OF PI ELECTRONS= 6

NO. OF BONDS= 6

NO. OF RINGS= 1

ALPHA= -6.2400 BETA= -3.1400

OVERLAP INTEGRAL= 0.0

HAMILTONIAN MATRIX AND BOND TYPE

```
 1  1  0.0   0   1  2  0.90  2   1  3  0.0   0   1  4  0.0   0   1  5  0.0   0   1  6  0.90  2
 2  2  0.0   0   2  3  1.00  1   2  4  0.0   0   2  5  0.0   0   2  6  0.0   0
 3  3  0.0   0   3  4  1.00  1   3  5  0.0   0   3  6  0.0   0
 4  4  0.0   0   4  5  1.00  1   4  6  0.0   0
 5  5  0.0   0   5  6  1.00  1
 6  6  0.0   0
```

HUCKEL MO

ENERGIES AND COEFFICIENTS

```
 1  E=  1.938502D 00 BETA
    E= -1.290900D 01 EV
    1  1   3.617361D-01     2  1   3.895702D-01     3  1   4.296202D-01     4  1   4.432496D-01
    5  1   4.296202D-01     6  1   3.895702D-01

 2  E=  1.000000D 00 BETA
    E= -1.006033D 01 EV
    1  2   0.0              2  2  -5.000000D-01     3  2  -5.000000D-01     4  2   0.0
    5  2   5.000000D-01     6  2   5.000000D-01

 3  E=  9.285519D-01 BETA
    E= -9.843464D 00 EV
    1  3  -6.075747D-01     2  3  -3.134248D-01     3  3   2.557860D-01     4  3   5.509354D-01
    5  3   2.557860D-01     6  3  -3.134248D-01

 4  E= -9.285519D-01 BETA
    E= -4.206536D 00 EV
    1  4  -6.075747D-01     2  4   3.134248D-01     3  4   2.557860D-01     4  4  -5.509354D-01
    5  4   2.557860D-01     6  4   3.134248D-01

 5  E= -1.000000D 00 BETA
    E= -3.989667D 00 EV
    1  5   0.0              2  5  -5.000000D-01     3  5   5.000000D-01     4  5   0.0
    5  5  -5.000000D-01     6  5   5.000000D-01

 6  E= -1.938502D 00 BETA
    E= -1.140999D 00 EV
    1  6  -3.617361D-01     2  6   3.895702D-01     3  6  -4.296202D-01     4  6   4.432496D-01
    5  6  -4.296202D-01     6  6   3.895702D-01
```

```
TOTAL PI ENERGY

     E=  7.734108D 00 BETA
     E= -3.050060D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

  1  Q=  1.000000D 00
    1  2   6.627011D-01     1  3   0.0              1  4  -3.487901D-01     1  5   0.0
    1  6   6.627011D-01

  2  Q=  1.000000D 00
    2  3   6.743950D-01     2  4   0.0              2  5  -3.256050D-01     2  6   0.0

  3  Q=  1.000000D 00
    3  4   6.627011D-01     3  5   0.0              3  6  -3.256050D-01

  4  Q=  1.000000D 00
    4  5   6.627011D-01     4  6   0.0

  5  Q=  1.000000D 00
    5  6   6.743950D-01

  6  Q=  1.000000D 00

FREE VALENCES

  1  F=  4.066486D-01
  2  F=  3.949547D-01
  3  F=  3.949547D-01
  4  F=  4.066486D-01
  5  F=  3.949547D-01
  6  F=  3.949547D-01

SELF-CONSISTENT FIELD MO

SCF CONVERGED IN 10 ITERATIONS

ENERGIES AND COEFFICIENTS

  1  E= -1.406419D 01 EV
    1  1   5.710594D-01     2  1   4.220050D-01     3  1   3.355201D-01     4  1   3.042488D-01
    5  1   3.355201D-01     6  1   4.220050D-01

  2  E= -1.113395D 01 EV
    1  2  -5.363861D-01     2  2  -1.589042D-01     3  2   3.786939D-01     4  2   6.123485D-01
    5  2   3.786939D-01     6  2  -1.589042D-01

  3  E= -1.035620D 01 EV
    1  3   2.350710D-14     2  3  -4.861574D-01     3  3  -5.134695D-01     4  3  -2.421937D-14
    5  3   5.134695D-01     6  3   4.861574D-01

  4  E= -1.257152D 00 EV
    1  4   5.088344D-01     2  4  -3.464742D-01     3  4  -2.681956D-01     4  4   5.976128D-01
    5  4  -2.681956D-01     6  4  -3.464742D-01

  5  E= -9.133075D-01 EV
```

```
   1  5   1.819870D-14      2  5  -5.134695D-01      3  5   4.861574D-01      4  5   2.170901D-14
   5  5  -4.861574D-01      6  5   5.134695D-01

  6  E=  2.032931D 00 EV
   1  6  -3.567473D-01      2  6   4.202581D-01      3  6  -4.148353D-01      4  6   4.187134D-01
   5  6  -4.148353D-01      6  6   4.202581D-01

TOTAL PI ENERGY

     E= -7.110869D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

  1  Q=  1.227638D 00
   1  2   6.524479D-01      1  3  -2.304849D-02      1  4  -3.094222D-01      1  5  -2.304849D-02
   1  6   6.524479D-01

  2  Q=  8.793756D-01
   2  3   6.620842D-01      2  4   6.217944D-02      2  5  -3.364239D-01      2  6  -6.602063D-02

  3  Q=  1.039267D 00
   3  4   6.679484D-01      3  5  -1.533630D-02      3  6  -3.364239D-01

  4  Q=  9.350760D-01
   4  5   6.679484D-01      4  6   6.217944D-02

  5  Q=  1.039267D 00
   5  6   6.620842D-01

  6  Q=  8.793756D-01

BOND LENGTHS

   1  2  R=  1.333559D 00
   1  6  R=  1.333559D 00
   2  3  R=  1.397824D 00
   3  4  R=  1.396769D 00
   4  5  R=  1.396769D 00
   5  6  R=  1.397824D 00

FREE VALENCES

  1  F=  4.271551D-01
  2  F=  4.175188D-01
  3  F=  4.020182D-01
  4  F=  3.961539D-01
  5  F=  4.020182D-01
  6  F=  4.175188D-01
```

********** PYRIMIDINE **********

NO. OF ATOMS= 6

NO. OF PI ELECTRONS= 6

NO. OF BONDS= 6

NO. OF RINGS= 1

ALPHA= -6.2400 BETA= -3.1400

OVERLAP INTEGRAL= 0.0

HAMILTONIAN MATRIX AND BOND TYPE

```
 1  1  0.0   0   1  2  0.90  2   1  3  0.0   0   1  4  0.0   0   1  5  0.0   0   1  6  0.90  2
 2  2  0.0   0   2  3  1.00  1   2  4  0.0   0   2  5  0.0   0   2  6  0.0   0
 3  3  0.0   0   3  4  1.00  1   3  5  0.0   0   3  6  0.0   0
 4  4  0.0   0   4  5  0.90  2   4  6  0.0   0
 5  5  0.0   0   5  6  0.90  2
 6  6  0.0   0
```

HUCKEL MO

ENERGIES AND COEFFICIENTS

```
 1  E=  1.872384D 00 BETA
    E= -1.329733D 01 EV
    1  1   3.818639D-01     2  1   4.273386D-01     3  1   4.564646D-01     4  1   4.273386D-01
    5  1   3.818639D-01     6  1   3.671015D-01

 2  E=  9.613811D-01 BETA
    E= -1.062737D 01 EV
    1  2   3.227692D-01     2  2  -2.595799D-01     3  2  -5.400371D-01     4  2  -2.595799D-01
    5  2   3.227692D-01     6  2   6.043480D-01

 3  E=  9.000000D-01 BETA
    E= -1.044760D 01 EV
    1  3  -5.000000D-01     2  3  -5.000000D-01     3  3   0.0              4  3   5.000000D-01
    5  3   5.000000D-01     6  3   0.0

 4  E= -9.000000D-01 BETA
    E= -5.172400D 00 EV
    1  4  -5.000000D-01     2  4   5.000000D-01     3  4   0.0              4  4  -5.000000D-01
    5  4   5.000000D-01     6  4   0.0

 5  E= -9.613811D-01 BETA
    E= -4.992630D 00 EV
    1  5  -3.227692D-01     2  5  -2.595799D-01     3  5   5.400371D-01     4  5  -2.595799D-01
    5  5  -3.227692D-01     6  5   6.043480D-01

 6  E= -1.872384D 00 BETA
    E= -2.322665D 00 EV
    1  6  -3.818639D-01     2  6   4.273386D-01     3  6  -4.564646D-01     4  6   4.273386D-01
    5  6  -3.818639D-01     6  6   3.671015D-01
```

```
TOTAL PI ENERGY

     E=  7.467451D 00 BETA
     E= -2.969461D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

  1  Q=  1.000000D 00
    1  2   6.588016D-01     1  3   0.0              1  4  -3.411984D-01     1  5   0.0
    1  6   6.704954D-01

  2  Q=  1.000000D 00
    2  3   6.704954D-01     2  4   0.0              2  5  -3.411984D-01     2  6   0.0

  3  Q=  1.000000D 00
    3  4   6.704954D-01     3  5   0.0              3  6  -3.176031D-01

  4  Q=  1.000000D 00
    4  5   6.588016D-01     4  6   0.0

  5  Q=  1.000000D 00
    5  6   6.704954D-01

  6  Q=  1.000000D 00

FREE VALENCES

  1  F=  4.027538D-01
  2  F=  4.027538D-01
  3  F=  3.910599D-01
  4  F=  4.027538D-01
  5  F=  4.027538D-01
  6  F=  3.910599D-01

SELF-CONSISTENT FIELD MO

SCF CONVERGED IN 12 ITERATIONS

ENERGIES AND COEFFICIENTS

  1  E= -1.459238D 01 EV
    1  1   4.917771D-01     2  1   3.460515D-01     3  1   3.043098D-01     4  1   3.460515D-01
    5  1   4.917771D-01     6  1   4.291885D-01

  2  E= -1.179256D 01 EV
    1  2  -5.720698D-01     2  2  -4.156154D-01     3  2   1.696860D-14     4  2   4.156154D-01
    5  2   5.720698D-01     6  2  -1.089606D-14

  3  E= -1.076315D 01 EV
    1  3   2.518542D-01     2  3  -3.389135D-01     3  3  -6.684799D-01     4  3  -3.389135D-01
    5  3   2.518542D-01     6  3   4.433384D-01

  4  E= -1.450992D 00 EV
    1  4   4.156154D-01     2  4  -5.720698D-01     3  4   1.131539D-14     4  4   5.720698D-01
    5  4  -4.156154D-01     6  4   1.330810D-14

  5  E= -1.093564D 00 EV
```

```
    1  5  -2.524199D-01      2  5  -2.820769D-01      3  5   5.312963D-01      4  5  -2.820769D-01
    5  5  -2.524199D-01      6  5   6.566261D-01

  6  E=  1.890050D 00 EV
    1  6  -3.619515D-01      2  6   4.310668D-01      3  6  -4.222019D-01      4  6   4.310668D-01
    5  6  -3.619515D-01      6  6   4.336940D-01

TOTAL PI ENERGY

     E= -7.429618D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

  1  Q=  1.265078D 00
    1  2   6.451690D-01      1  3  -3.741372D-02      1  4  -3.058751D-01      1  5  -4.397714D-02
    1  6   6.454434D-01

  2  Q=  8.147003D-01
    2  3   6.637274D-01      2  4   1.237557D-01      2  5  -3.058751D-01      2  6  -3.464071D-03

  3  Q=  1.078940D 00
    3  4   6.637274D-01      3  5  -3.741372D-02      3  6  -3.315132D-01

  4  Q=  8.147003D-01
    4  5   6.451690D-01      4  6  -3.464071D-03

  5  Q=  1.265078D 00
    5  6   6.454434D-01

  6  Q=  7.615034D-01

BOND LENGTHS

    1  2  R=  1.334869D 00
    1  6  R=  1.334819D 00
    2  3  R=  1.397528D 00
    3  4  R=  1.397528D 00
    4  5  R=  1.334869D 00
    5  6  R=  1.334819D 00

FREE VALENCES

  1  F=  4.414384D-01
  2  F=  4.231545D-01
  3  F=  4.045961D-01
  4  F=  4.231545D-01
  5  F=  4.414384D-01
  6  F=  4.411640D-01
```

********** PYRAZINE **********

NO. OF ATOMS= 6

NO. OF PI ELECTRONS= 6

NO. OF BONDS= 6

NO. OF RINGS= 1

ALPHA= -6.2400 BETA= -3.1400

OVERLAP INTEGRAL= 0.0

HAMILTONIAN MATRIX AND BOND TYPE

```
 1  1  0.0   0   1  2  0.90  2   1  3  0.0   0   1  4  0.0   0   1  5  0.0   0   1  6  0.90  2
 2  2  0.0   0   2  3  1.00  1   2  4  0.0   0   2  5  0.0   0   2  6  0.0   0
 3  3  0.0   0   3  4  0.90  2   3  5  0.0   0   3  6  0.0   0
 4  4  0.0   0   4  5  0.90  2   4  6  0.0   0
 5  5  0.0   0   5  6  1.00  1
 6  6  0.0   0
```

HUCKEL MO

ENERGIES AND COEFFICIENTS

```
 1  E=  1.867479D 00 BETA
    E= -1.328296D 01 EV
    1  1   3.982348D-01     2  1   4.131640D-01     3  1   4.131640D-01     4  1   3.982348D-01
    5  1   4.131640D-01     6  1   4.131640D-01

 2  E=  1.000000D 00 BETA
    E= -1.074067D 01 EV
    1  2   0.0              2  2  -5.000000D-01     3  2  -5.000000D-01     4  2   0.0
    5  2   5.000000D-01     6  2   5.000000D-01

 3  E=  8.674794D-01 BETA
    E= -1.035229D 01 EV
    1  3  -5.843022D-01     2  3  -2.815945D-01     3  3   2.815945D-01     4  3   5.843022D-01
    5  3   2.815945D-01     6  3  -2.815945D-01

 4  E= -8.674794D-01 BETA
    E= -5.267707D 00 EV
    1  4  -5.843022D-01     2  4   2.815945D-01     3  4   2.815945D-01     4  4  -5.843022D-01
    5  4   2.815945D-01     6  4   2.815945D-01

 5  E= -1.000000D 00 BETA
    E= -4.879333D 00 EV
    1  5   0.0              2  5  -5.000000D-01     3  5   5.000000D-01     4  5   0.0
    5  5  -5.000000D-01     6  5   5.000000D-01

 6  E= -1.867479D 00 BETA
    E= -2.337040D 00 EV
    1  6  -3.982348D-01     2  6   4.131640D-01     3  6  -4.131640D-01     4  6   3.982348D-01
    5  6  -4.131640D-01     6  6   4.131640D-01
```

```
TOTAL PI ENERGY

     E=  7.469918D 00 BETA
     E= -2.970184D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

  1  Q=  1.000000D 00
     1  2   6.581452D-01     1  3   0.0              1  4  -3.656362D-01     1  5   0.0
     1  6   6.581452D-01

  2  Q=  1.000000D 00
     2  3   6.828181D-01     2  4   0.0              2  5  -3.171819D-01     2  6   0.0

  3  Q=  1.000000D 00
     3  4   6.581452D-01     3  5   0.0              3  6  -3.171819D-01

  4  Q=  1.000000D 00
     4  5   6.581452D-01     4  6   0.0

  5  Q=  1.000000D 00
     5  6   6.828181D-01

  6  Q=  1.000000D 00

FREE VALENCES

  1  F=  4.157604D-01
  2  F=  3.910875D-01
  3  F=  3.910875D-01
  4  F=  4.157604D-01
  5  F=  3.910875D-01
  6  F=  3.910875D-01

SELF-CONSISTENT FIELD MO

SCF CONVERGED IN 10 ITERATIONS

ENERGIES AND COEFFICIENTS

  1  E= -1.458191D 01 EV
     1  1   4.687231D-01     2  1   3.743652D-01     3  1   3.743652D-01     4  1   4.687231D-01
     5  1   3.743652D-01     6  1   3.743652D-01

  2  E= -1.214285D 01 EV
     1  2  -6.039827D-01     2  2  -2.600047D-01     3  2   2.600047D-01     4  2   6.039827D-01
     5  2   2.600047D-01     6  2  -2.600047D-01

  3  E= -1.038744D 01 EV
     1  3   0.0              2  3  -5.000000D-01     3  3  -5.000000D-01     4  3   0.0
     5  3   5.000000D-01     6  3   5.000000D-01

  4  E= -1.679609D 00 EV
     1  4  -5.294324D-01     2  4   3.314373D-01     3  4   3.314373D-01     4  4  -5.294324D-01
     5  4   3.314373D-01     6  4   3.314373D-01

  5  E= -1.008793D 00 EV
```

```
   1  5   0.0              2  5  -5.000000D-01     3  5   5.000000D-01     4  5   0.0
   5  5  -5.000000D-01     6  5   5.000000D-01

 6  E=  1.873843D 00 EV
   1  6  -3.677022D-01     2  6   4.270803D-01     3  6  -4.270803D-01     4  6   3.677022D-01
   5  6  -4.270803D-01     6  6   4.270803D-01

TOTAL PI ENERGY

     E= -7.422440D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

 1  Q=  1.168993D 00
   1  2   6.650239D-01     1  3   3.687058D-02     1  4  -2.901875D-01     1  5   3.687058D-02
   1  6   6.650239D-01

 2  Q=  9.155035D-01
   2  3   6.450938D-01     2  4   3.687058D-02     2  5  -3.549062D-01     2  6  -8.449646D-02

 3  Q=  9.155035D-01
   3  4   6.650239D-01     3  5  -8.449646D-02     3  6  -3.549062D-01

 4  Q=  1.168993D 00
   4  5   6.650239D-01     4  6   3.687058D-02

 5  Q=  9.155035D-01
   5  6   6.450938D-01

 6  Q=  9.155035D-01

BOND LENGTHS

   1  2  R=  1.331295D 00
   1  6  R=  1.331295D 00
   2  3  R=  1.400882D 00
   3  4  R=  1.331295D 00
   4  5  R=  1.331295D 00
   5  6  R=  1.400882D 00

FREE VALENCES

 1  F=  4.020029D-01
 2  F=  4.219331D-01
 3  F=  4.219331D-01
 4  F=  4.020029D-01
 5  F=  4.219331D-01
 6  F=  4.219331D-01
```

******** MALEIC ANHYDRIDE *********

NO. OF ATOMS= 7

NO. OF PI ELECTRONS= 7

NO. OF BONDS= 7

NO. OF RINGS= 1

ALPHA= -5.0900 BETA= -3.2500

OVERLAP INTEGRAL= 0.0

HAMILTONIAN MATRIX AND BOND TYPE

```
 1  1  0.0   0   1  2  0.34  3   1  3  0.0   0   1  4  0.0   0   1  5  0.34  3   1  6  0.0   0   1  7  0.0   0
 2  2  0.0   0   2  3  1.00  1   2  4  0.0   0   2  5  0.0   0   2  6  0.0   0   2  7  0.34  3
 3  3  0.0   0   3  4  1.00  1   3  5  0.0   0   3  6  0.0   0   3  7  0.0   0
 4  4  0.0   0   4  5  1.00  1   4  6  0.0   0   4  7  0.0   0
 5  5  0.0   0   5  6  0.34  3   5  7  0.0   0
 6  6  0.0   0   6  7  0.0   0
 7  7  0.0   0
```

HUCKEL MO

ENERGIES AND COEFFICIENTS

```
 1  E=  1.679093D 00 BETA
    E= -1.127468D 01 EV
    1  1   1.578438D-01     2  1   3.897566D-01     3  1   5.739371D-01     4  1   5.739371D-01
    5  1   3.897566D-01     6  1   7.892192D-02     7  1   7.892192D-02

 2  E=  7.341257D-01 BETA
    E= -9.361794D 00 EV
    1  2   0.0              2  2  -5.685066D-01     3  2  -3.278347D-01     4  2   3.278347D-01
    5  2   5.685066D-01     6  2   2.632958D-01     7  2  -2.632958D-01

 3  E=  2.277559D-01 BETA
    E= -8.336757D 00 EV
    1  3  -6.899698D-01     2  3  -2.310951D-01     3  3   2.992513D-01     4  3   2.992513D-01
    5  3  -2.310951D-01     6  3  -3.449849D-01     7  3  -3.449849D-01

 4  E= -9.540448D-19 BETA
    E= -7.875714D 00 EV
    1  4  -5.773503D-01     2  4   0.0              3  4   0.0              4  4   0.0
    5  4   0.0              6  4   5.773503D-01     7  4   5.773503D-01

 5  E= -9.613370D-02 BETA
    E= -7.681112D 00 EV
    1  5   0.0              2  5   1.842238D-01     3  5   2.038176D-01     4  5  -2.038176D-01
    5  5  -1.842238D-01     6  5   6.515520D-01     7  5  -6.515520D-01

 6  E= -9.068487D-01 BETA
    E= -6.039993D 00 EV
    1  6  -4.070549D-01     2  6   5.428489D-01     3  6  -2.846838D-01     4  6  -2.846838D-01
    5  6   5.428489D-01     6  6  -2.035275D-01     7  6  -2.035275D-01

 7  E= -1.637992D 00 BETA
    E= -4.559950D 00 EV
```

```
  1  7   0.0              2  7  -3.779707D-01     3  7   5.924380D-01     4  7  -5.924380D-01
  5  7   3.779707D-01     6  7  -7.845584D-02     7  7   7.845584D-02

TOTAL PI ENERGY

     E=  5.281949D 00 BETA
     E= -1.856789D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

  1  Q=  1.335279D 00
     1  2   4.419386D-01     1  3  -2.317638D-01     1  4  -2.317638D-01     1  5   4.419386D-01
     1  6   1.676396D-01     1  7   1.676396D-01

  2  Q=  1.057030D 00
     2  3   6.818329D-01     2  4  -6.367185D-02     2  5  -2.357692D-01     2  6  -7.840152D-02
     2  7   5.203401D-01

  3  Q=  1.052861D 00
     3  4   6.229591D-01     3  5  -6.367185D-02     3  6  -2.885169D-01     3  7   5.675309D-02

  4  Q=  1.052861D 00
     4  5   6.818329D-01     4  6   5.675309D-02     4  7  -2.885169D-01

  5  Q=  1.057030D 00
     5  6   5.203401D-01     5  7  -7.840152D-02

  6  Q=  7.224692D-01
     6  7   4.451704D-01

  7  Q=  7.224692D-01

FREE VALENCES

  1  F=  8.481736D-01
  2  F=  8.793924D-02
  3  F=  4.272588D-01
  4  F=  4.272588D-01
  5  F=  8.793924D-02
  6  F=  1.211711D 00
  7  F=  1.211711D 00

SELF-CONSISTENT FIELD NO

SCF CONVERGED IN 31 ITERATIONS

ENERGIES AND COEFFICIENTS

  1  E= -1.617066D 01 EV
     1  1   5.944962D-01     2  1   4.160792D-01     3  1   2.139506D-01     4  1   2.139506D-01
     5  1   4.160792D-01     6  1   3.230950D-01     7  1   3.230950D-01

  2  E= -1.376226D 01 EV
     1  2   0.0              2  2  -3.799090D-01     3  2  -1.011152D-01     4  2   1.011152D-01
     5  2   3.799090D-01     6  2   5.877456D-01     7  2  -5.877456D-01

  3  E= -1.155142D 01 EV
     1  3  -4.187099D-01     2  3  -1.634024D-03     3  3   6.410582D-01     4  3   6.410582D-01
     5  3  -1.634024D-03     6  3  -3.718473D-02     7  3  -3.718473D-02
```

```
 4  E= -9.613924D 00 EV
   1  4   -5.402693D-01      2  4    1.101308D-02      3  4  -1.429134D-01      4  4  -1.429134D-01
   5  4    1.101308D-02      6  4    5.775024D-01      7  4   5.775024D-01

 5  E= -3.345943D 00 EV
   1  5    0.0               2  5   -4.060336D-01      3  5  -4.665614D-01      4  5   4.665614D-01
   5  5    4.060336D-01      6  5   -3.427202D-01      7  5   3.427202D-01

 6  E=  7.323986D-01 EV
   1  6    0.0               2  6    4.368132D-01      3  6  -5.216284D-01      4  6   5.216284D-01
   5  6   -4.368132D-01      6  6    1.926084D-01      7  6  -1.926084D-01

 7  E=  9.354091D-01 EV
   1  7   -4.235155D-01      2  7    5.716241D-01      3  7  -1.511465D-01      4  7  -1.511465D-01
   5  7    5.716241D-01      6  7   -2.464101D-01      7  7  -2.464101D-01

TOTAL PI ENERGY

     E= -9.258262D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

 1  Q=  1.349378D 00
   1  2    4.901333D-01      1  3   -2.052375D-01      1  4  -2.052375D-01      1  5   4.901333D-01
   1  6    1.032899D-01      1  7    1.032899D-01

 2  Q=  6.350322D-01
   2  3    2.512010D-01      2  4    9.754272D-02      2  5   5.770868D-02      2  6  -1.712319D-01
   2  7    7.219275D-01

 3  Q=  9.543338D-01
   3  4    9.134367D-01      3  5    9.754272D-02      3  6  -1.108152D-01      3  7   1.269048D-01

 4  Q=  9.543338D-01
   4  5    2.512010D-01      4  6    1.269048D-01      4  7  -1.108152D-01

 5  Q=  6.350322D-01
   5  6    7.219275D-01      5  7   -1.712319D-01

 6  Q=  1.235945D 00
   6  7   -1.458345D-01

 7  Q=  1.235945D 00

BOND LENGTHS

    1  2  R=  1.321776D 00
    1  5  R=  1.321776D 00
    2  3  R=  1.471783D 00
    2  7  R=  1.280053D 00
    3  4  R=  1.352581D 00
    4  5  R=  1.471783D 00
    5  6  R=  1.280053D 00

FREE VALENCES

 1  F=  7.517841D-01
 2  F=  2.687889D-01
```

```
3  P=  5.674131D-01
4  P=  5.674131D-01
5  P=  2.687889D-01
6  P=  1.010123D 00
7  P=  1.010123D 00
```

******** P-BENZOQUINONE ***********

NO. OF ATOMS= 8

NO. OF PI ELECTRONS= 8

NO. OF BONDS= 8

NO. OF RINGS= 1

ALPHA= -6.2400 BETA= -3.1400

OVERLAP INTEGRAL= 0.0

HAMILTONIAN MATRIX AND BOND TYPE

```
 1  1  0.0   0   1  2  0.34  3   1  3  0.0   0   1  4  0.0   0   1  5  0.0   0   1  6  0.0   0   1  7  0.0   0   1  8  0.0   0
 2  2  0.0   0   2  3  1.00  1   2  4  0.0   0   2  5  0.0   0   2  6  0.0   0   2  7  0.0   0   2  8  1.00  1
 3  3  0.0   0   3  4  1.00  1   3  5  0.0   0   3  6  0.0   0   3  7  0.0   0   3  8  0.0   0
 4  4  0.0   0   4  5  1.00  1   4  6  0.0   0   4  7  0.0   0   4  8  0.0   0
 5  5  0.0   0   5  6  0.34  3   5  7  1.00  1   5  8  0.0   0
 6  6  0.0   0   6  7  0.0   0   6  8  0.0   0
 7  7  0.0   0   7  8  1.00  1
 8  8  0.0   0
```

HUCKEL MO

ENERGIES AND COEFFICIENTS

```
 1  E=  2.019327D 00 BETA
    E= -1.310447D 01 EV
    1  1   6.928016D-02     2  1   4.114684D-01     3  1   4.036669D-01     4  1   4.036669D-01
    5  1   4.114684D-01     6  1   6.928016D-02     7  1   4.036669D-01     8  1   4.036669D-01

 2  E=  1.072694D 00 BETA
    E= -1.062250D 01 EV
    1  2  -1.790983D-01     2  2  -5.650519D-01     3  2  -2.726171D-01     4  2   2.726171D-01
    5  2   5.650519D-01     6  2   1.790983D-01     7  2   2.726171D-01     8  2  -2.726171D-01

 3  E=  1.000000D 00 BETA
    E= -1.043190D 01 EV
    1  3   0.0              2  3   0.0              3  3  -5.000000D-01     4  3  -5.000000D-01
    5  3   0.0              6  3   0.0              7  3   5.000000D-01     8  3   5.000000D-01

 4  E=  5.336733D-02 BETA
    E= -7.949924D 00 EV
    1  4  -6.805322D-01     2  4  -1.068182D-01     3  4   1.128402D-01     4  4   1.128402D-01
    5  4  -1.068182D-01     6  4  -6.805322D-01     7  4   1.128402D-01     8  4   1.128402D-01

 5  E= -5.336733D-02 BETA
    E= -7.670076D 00 EV
    1  5  -6.805322D-01     2  5   1.068182D-01     3  5   1.128402D-01     4  5  -1.128402D-01
    5  5  -1.068182D-01     6  5   6.805322D-01     7  5  -1.128402D-01     8  5   1.128402D-01

 6  E= -1.000000D 00 BETA
    E= -5.188100D 00 EV
    1  6   0.0              2  6   0.0              3  6  -5.000000D-01     4  6   5.000000D-01
    5  6   0.0              6  6   0.0              7  6  -5.000000D-01     8  6   5.000000D-01
```

```
 7  E= -1.072694D 00 BETA
    E= -4.997504D 00 EV
   1  7   1.790983D-01     2  7  -5.650519D-01     3  7   2.726171D-01     4  7   2.726171D-01
   5  7  -5.650519D-01     6  7   1.790983D-01     7  7   2.726171D-01     8  7   2.726171D-01

 8  E= -2.019327D 00 BETA
    E= -2.515528D 00 EV
   1  8   6.928016D-02     2  8  -4.114684D-01     3  8   4.036669D-01     4  8  -4.036669D-01
   5  8   4.114684D-01     6  8  -6.928016D-02     7  8  -4.036669D-01     8  8   4.036669D-01

TOTAL PI ENERGY

    E=  8.290776D 00 BETA
    E= -2.954758D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

 1  Q=  1.000000D 00
   1  2   4.047993D-01     1  3   0.0               1  4  -1.953010D-01     1  5   0.0
   1  6   8.716952D-01     1  7  -1.953010D-01     1  8   0.0

 2  Q=  1.000000D 00
   2  3   6.161713D-01     2  4   0.0               2  5  -2.771344D-01     2  6   0.0
   2  7   0.0              2  8   6.161713D-01

 3  Q=  1.000000D 00
   3  4   7.027196D-01     3  5   0.0               3  6  -1.953010D-01     3  7  -2.972804D-01
   3  8   0.0

 4  Q=  1.000000D 00
   4  5   6.161713D-01     4  6   0.0               4  7   0.0               4  8  -2.972804D-01

 5  Q=  1.000000D 00
   5  6   4.047993D-01     5  7   6.161713D-01     5  8   0.0

 6  Q=  1.000000D 00
   6  7   0.0              6  8  -1.953010D-01

 7  Q=  1.000000D 00
   7  8   7.027196D-01

 8  Q=  1.000000D 00

FREE VALENCES

 1  F=  1.327252D 00
 2  F=  9.490900D-02
 3  F=  4.131599D-01
 4  F=  4.131599D-01
 5  F=  9.490900D-02
 6  F=  1.327252D 00
 7  F=  4.131599D-01
 8  F=  4.131599D-01
```

SELF-CONSISTENT FIELD MO

SCF CONVERGED IN 17 ITERATIONS

ENERGIES AND COEFFICIENTS

```
1  E= -1.479525D 01 EV
   1  1   3.885262D-01     2  1   4.159713D-01     3  1   2.966608D-01     4  1   2.966608D-01
   5  1   4.159713D-01     6  1   3.885262D-01     7  1   2.966608D-01     8  1   2.966608D-01

2  E= -1.376442D 01 EV
   1  2  -5.313570D-01     2  2  -4.359976D-01     3  2  -1.174007D-01     4  2   1.174007D-01
   5  2   4.359976D-01     6  2   5.313570D-01     7  2   1.174007D-01     8  2  -1.174007D-01

3  E= -1.133550D 01 EV
   1  3   0.0              2  3   0.0              3  3  -5.000000D-01     4  3  -5.000000D-01
   5  3   0.0              6  3   0.0              7  3   5.000000D-01     8  3   5.000000D-01

4  E= -1.096951D 01 EV
   1  4  -4.881492D-01     2  4  -5.683170D-02     3  4   3.595000D-01     4  4   3.595000D-01
   5  4  -5.683170D-02     6  4  -4.881492D-01     7  4   3.595000D-01     8  4   3.595000D-01

5  E= -3.706314D 00 EV
   1  5   4.219053D-01     2  5  -3.416531D-01     3  5  -3.203662D-01     4  5   3.203662D-01
   5  5   3.416531D-01     6  5  -4.219053D-01     7  5   3.203662D-01     8  5  -3.203662D-01

6  E= -1.082271D 00 EV
   1  6   0.0              2  6   0.0              3  6  -5.000000D-01     4  6   5.000000D-01
   5  6   0.0              6  6   0.0              7  6  -5.000000D-01     8  6   5.000000D-01

7  E= -1.265494D-01 EV
   1  7   3.328028D-01     2  7  -5.689798D-01     3  7   1.809754D-01     4  7   1.809754D-01
   5  7  -5.689798D-01     6  7   3.328028D-01     7  7   1.809754D-01     8  7   1.809754D-01

8  E=  1.896054D 00 EV
   1  8  -1.991372D-01     2  8   4.395217D-01     3  8  -3.654895D-01     4  8   3.654895D-01
   5  8  -4.395217D-01     6  8   1.991372D-01     7  8   3.654895D-01     8  8  -3.654895D-01
```

TOTAL PI ENERGY

E= -1.017294D 02 EV

ELECTRON DENSITIES AND BOND ORDERS

```
1  Q=  1.343165D 00
   1  2   8.420569D-01     1  3   4.305110D-03     1  4  -2.452217D-01     1  5  -8.462451D-02
   1  6   2.138040D-01     1  7  -2.452217D-01     1  8   4.305110D-03

2  Q=  7.327116D-01
   2  3   3.083156D-01     2  4   1.035699D-01     2  5  -2.766385D-02     2  6  -8.462451D-02
   2  7   1.035699D-01     2  8   3.083156D-01

3  Q=  9.620616D-01
   3  4   9.069299D-01     3  5   1.035699D-01     3  6  -2.452217D-01     3  7  -9.307007D-02
   3  8  -3.793836D-02

4  Q=  9.620616D-01
   4  5   3.083156D-01     4  6   4.305110D-03     4  7  -3.793836D-02     4  8  -9.307007D-02
```

```
  5  Q=  7.327116D-01
    5  6   8.420569D-01      5  7   3.083156D-01      5  8   1.035699D-01

  6  Q=  1.343165D 00
    6  7   4.305110D-03      6  8  -2.452217D-01

  7  Q=  9.620616D-01
    7  8   9.069299D-01

  8  Q=  9.620616D-01

BOND LENGTHS

    1  2  R=  1.258430D 00
    2  3  R=  1.461502D 00
    2  8  R=  1.461502D 00
    3  4  R=  1.353752D 00
    4  5  R=  1.461502D 00
    5  6  R=  1.258430D 00
    5  7  R=  1.461502D 00
    7  8  R=  1.353752D 00

FREE VALENCES

  1  F=  8.899939D-01
  2  F=  2.733627D-01
  3  F=  5.168053D-01
  4  F=  5.168053D-01
  5  F=  2.733627D-01
  6  F=  8.899939D-01
  7  F=  5.168053D-01
  8  F=  5.168053D-01
```

********** TCNQ **********

NO. OF ATOMS= 16

NO. OF PI ELECTRONS= 16

NO. OF BONDS= 16

NO. OF RINGS= 1

ALPHA= -6.2400 BETA= -3.1400

OVERLAP INTEGRAL= 0.0

HAMILTONIAN MATRIX AND BOND TYPE

1	1	0.0	0	1	2	0.90	5	1	3	0.0	0	1	4	0.0	0	1	5	0.0	0	1	6	0.0	0	1	7	0.0	0	1	8	0.0	0
1	9	0.0	0	1	10	0.0	0	1	11	0.0	0	1	12	0.0	0	1	13	0.0	0	1	14	0.0	0	1	15	0.0	0	1	16	0.0	0
2	2	0.0	0	2	3	1.00	1	2	4	0.0	0	2	5	0.0	0	2	6	0.0	0	2	7	0.0	0	2	8	0.0	0	2	9	0.0	0
2	10	0.0	0	2	11	0.0	0	2	12	0.0	0	2	13	0.0	0	2	14	0.0	0	2	15	0.0	0	2	16	0.0	0				
3	3	0.0	0	3	4	1.00	1	3	5	0.0	0	3	6	1.00	1	3	7	0.0	0	3	8	0.0	0	3	9	0.0	0	3	10	0.0	0
3	11	0.0	0	3	12	0.0	0	3	13	0.0	0	3	14	0.0	0	3	15	0.0	0	3	16	0.0	0								
4	4	0.0	0	4	5	0.90	5	4	6	0.0	0	4	7	0.0	0	4	8	0.0	0	4	9	0.0	0	4	10	0.0	0	4	11	0.0	0
4	12	0.0	0	4	13	0.0	0	4	14	0.0	0	4	15	0.0	0	4	16	0.0	0												
5	5	0.0	0	5	6	0.0	0	5	7	0.0	0	5	8	0.0	0	5	9	0.0	0	5	10	0.0	0	5	11	0.0	0	5	12	0.0	0
5	13	0.0	0	5	14	0.0	0	5	15	0.0	0	5	16	0.0	0																
6	6	0.0	0	6	7	1.00	1	6	8	0.0	0	6	9	0.0	0	6	10	0.0	0	6	11	0.0	0	6	12	0.0	0	6	13	0.0	0
6	14	0.0	0	6	15	0.0	0	6	16	1.00	1																				
7	7	0.0	0	7	8	1.00	1	7	9	0.0	0	7	10	0.0	0	7	11	0.0	0	7	12	0.0	0	7	13	0.0	0	7	14	0.0	0
7	15	0.0	0	7	16	0.0	0																								
8	8	0.0	0	8	9	1.00	1	8	10	0.0	0	8	11	0.0	0	8	12	0.0	0	8	13	0.0	0	8	14	0.0	0	8	15	0.0	0
8	16	0.0	0																												
9	9	0.0	0	9	10	0.0	0	9	11	0.0	0	9	12	1.00	1	9	13	0.0	0	9	14	0.0	0	9	15	1.00	1	9	16	0.0	0
10	10	0.0	0	10	11	0.90	5	10	12	0.0	0	10	13	0.0	0	10	14	0.0	0	10	15	0.0	0	10	16	0.0	0				
11	11	0.0	0	11	12	1.00	1	11	13	0.0	0	11	14	0.0	0	11	15	0.0	0	11	16	0.0	0								
12	12	0.0	0	12	13	1.00	1	12	14	0.0	0	12	15	0.0	0	12	16	0.0	0												
13	13	0.0	0	13	14	0.90	5	13	15	0.0	0	13	16	0.0	0																
14	14	0.0	0	14	15	0.0	0	14	16	0.0	0																				
15	15	0.0	0	15	16	1.00	1																								
16	16	0.0	0																												

HUCKEL MO

ENERGIES AND COEFFICIENTS

1 E= 2.307562D 00 BETA
E= -1.448210D 01 EV

1	1	6.189276D-02	2	1	1.586904D-01	3	1	3.104845D-01	4	1	1.586904D-01
5	1	6.189276D-02	6	1	3.990814D-01	7	1	3.052103D-01	8	1	3.052103D-01
9	1	3.990814D-01	10	1	6.189276D-02	11	1	1.586904D-01	12	1	3.104845D-01
13	1	1.586904D-01	14	1	6.189276D-02	15	1	3.052103D-01	16	1	3.052103D-01

2 E= 2.001490D 00 BETA
E= -1.354506D 01 EV

1	2	-1.228209D-01	2	2	-2.731385D-01	3	2	-4.361452D-01	4	2	-2.731385D-01
5	2	-1.228209D-01	6	2	-3.266629D-01	7	2	-1.088336D-01	8	2	1.088336D-01
9	2	3.266629D-01	10	2	1.228209D-01	11	2	2.731385D-01	12	2	4.361452D-01
13	2	2.731385D-01	14	2	1.228209D-01	15	2	1.088336D-01	16	2	-1.088336D-01

```
3  E=  1.534362D 00 BETA
   E= -1.211495D 01 EV
  1  3    1.790919D-01     2  3   3.053242D-01     3  3   3.072949D-01     4  3   3.053242D-01
  5  3    1.790919D-01     6  3  -1.391468D-01     7  3  -2.603982D-01     8  3  -2.603982D-01
  9  3   -1.391468D-01    10  3   1.790919D-01    11  3   3.053242D-01    12  3   3.072949D-01
 13  3    3.053242D-01    14  3   1.790919D-01    15  3  -2.603982D-01    16  3  -2.603982D-01

4  E=  1.000000D 00 BETA
   E= -1.047900D 01 EV
  1  4    0.0              2  4   0.0              3  4   0.0              4  4   0.0
  5  4    0.0              6  4   0.0              7  4   5.000000D-01     8  4   5.000000D-01
  9  4    0.0             10  4   0.0             11  4   0.0             12  4   0.0
 13  4    0.0             14  4   0.0             15  4  -5.000000D-01    16  4  -5.000000D-01

5  E=  9.595532D-01 BETA
   E= -1.035517D 01 EV
  1  5   -2.186440D-01     2  5  -2.331117D-01     3  5  -2.690349D-02     4  5  -2.331117D-01
  5  5   -2.186440D-01     6  5   4.404081D-01     7  5   2.247492D-01     8  5  -2.247492D-01
  9  5   -4.404081D-01    10  5   2.186440D-01    11  5   2.331117D-01    12  5   2.690349D-02
 13  5    2.331117D-01    14  5   2.186440D-01    15  5  -2.247492D-01    16  5   2.247492D-01

6  E=  9.000000D-01 BETA
   E= -1.017285D 01 EV
  1  6    2.044919D-02     2  6   2.044919D-02     3  6   0.0              4  6  -2.044919D-02
  5  6   -2.044919D-02     6  6   0.0              7  6   0.0              8  6   0.0
  9  6    0.0             10  6  -4.995817D-01    11  6  -4.995817D-01    12  6   0.0
 13  6    4.995817D-01    14  6   4.995817D-01    15  6   0.0             16  6   0.0

7  E=  9.000000D-01 BETA
   E= -1.017285D 01 EV
  1  7   -4.995817D-01     2  7  -4.995817D-01     3  7   0.0              4  7   4.995817D-01
  5  7    4.995817D-01     6  7   0.0              7  7   0.0              8  7   0.0
  9  7    0.0             10  7  -2.044919D-02    11  7  -2.044919D-02    12  7   0.0
 13  7    2.044919D-02    14  7   2.044919D-02    15  7   0.0             16  7   0.0

8  E=  1.191191D-01 BETA
   E= -7.782183D 00 EV
  1  8    3.888511D-01     2  8   5.146624D-02     3  8  -3.438354D-01     4  8   5.146624D-02
  5  8    3.888511D-01     6  8  -1.438899D-01     7  8   1.633477D-01     8  8   1.633477D-01
  9  8   -1.438899D-01    10  8   3.888511D-01    11  8   5.146624D-02    12  8  -3.438354D-01
 13  8    5.146624D-02    14  8   3.888511D-01    15  8   1.633477D-01    16  8   1.633477D-01

9  E= -1.191191D-01 BETA
   E= -7.052817D 00 EV
  1  9   -3.888511D-01     2  9   5.146624D-02     3  9   3.438354D-01     4  9   5.146624D-02
  5  9   -3.888511D-01     6  9  -1.438899D-01     7  9  -1.633477D-01     8  9   1.633477D-01
  9  9    1.438899D-01    10  9   3.888511D-01    11  9  -5.146624D-02    12  9  -3.438354D-01
 13  9   -5.146624D-02    14  9   3.888511D-01    15  9   1.633477D-01    16  9  -1.633477D-01

10  E= -9.000000D-01 BETA
    E= -4.662150D 00 EV
   1 10   -4.896205D-01     2 10   4.896205D-01     3 10   0.0              4 10  -4.896205D-01
   5 10    4.896205D-01     6 10   0.0              7 10   0.0              8 10   0.0
   9 10    0.0             10 10  -1.013495D-01    11 10   1.013495D-01    12 10   0.0
  13 10   -1.013495D-01    14 10   1.013495D-01    15 10   0.0             16 10   0.0

11  E= -9.000000D-01 BETA
    E= -4.662150D 00 EV
```

```
   1 11   1.013495D-01     2 11  -1.013495D-01     3 11   0.0              4 11   1.013495D-01
   5 11  -1.013495D-01     6 11   0.0              7 11   0.0              8 11   0.0
   9 11   0.0             10 11  -4.896205D-01    11 11   4.896205D-01    12 11   0.0
  13 11  -4.896205D-01    14 11   4.896205D-01    15 11   0.0             16 11   0.0

12  E= -9.595532D-01 BETA
    E= -4.479828D 00 EV
   1 12  -2.186440D-01     2 12   2.331117D-01     3 12  -2.690349D-02     4 12   2.331117D-01
   5 12  -2.186440D-01     6 12  -4.404081D-01     7 12   2.247492D-01     8 12   2.247492D-01
   9 12  -4.404081D-01    10 12  -2.186440D-01    11 12   2.331117D-01    12 12  -2.690349D-02
  13 12   2.331117D-01    14 12  -2.186440D-01    15 12   2.247492D-01    16 12   2.247492D-01

13  E= -1.000000D 00 BETA
    E= -4.356000D 00 EV
   1 13   0.0              2 13   0.0              3 13   0.0              4 13   0.0
   5 13   0.0              6 13   0.0              7 13   5.000000D-01     8 13  -5.000000D-01
   9 13   0.0             10 13   0.0             11 13   0.0             12 13   0.0
  13 13   0.0             14 13   0.0             15 13   5.000000D-01    16 13  -5.000000D-01

14  E= -1.534362D 00 BETA
    E= -2.720052D 00 EV
   1 14   1.790919D-01     2 14  -3.053242D-01     3 14   3.072949D-01     4 14  -3.053242D-01
   5 14   1.790919D-01     6 14   1.391468D-01     7 14  -2.603982D-01     8 14   2.603982D-01
   9 14  -1.391468D-01    10 14  -1.790919D-01    11 14   3.053242D-01    12 14  -3.072949D-01
  13 14   3.053242D-01    14 14  -1.790919D-01    15 14   2.603982D-01    16 14  -2.603982D-01

15  E= -2.001490D 00 BETA
    E= -1.289940D 00 EV
   1 15   1.228209D-01     2 15  -2.731385D-01     3 15   4.361452D-01     4 15  -2.731385D-01
   5 15   1.228209D-01     6 15  -3.266629D-01     7 15   1.088336D-01     8 15   1.088336D-01
   9 15  -3.266629D-01    10 15   1.228209D-01    11 15  -2.731385D-01    12 15   4.361452D-01
  13 15  -2.731385D-01    14 15   1.228209D-01    15 15   1.088336D-01    16 15   1.088336D-01

16  E= -2.307562D 00 BETA
    E= -3.528988D-01 EV
   1 16  -6.189276D-02     2 16   1.586904D-01     3 16  -3.104845D-01     4 16   1.586904D-01
   5 16  -6.189276D-02     6 16   3.990814D-01     7 16  -3.052103D-01     8 16   3.052103D-01
   9 16  -3.990814D-01    10 16   6.189276D-02    11 16  -1.586904D-01    12 16   3.104845D-01
  13 16  -1.586904D-01    14 16   6.189276D-02    15 16   3.052103D-01    16 16  -3.052103D-01

TOTAL PI ENERGY

     E=  1.944417D 01 BETA
     E= -6.694583D 01 EV

ELECTRON DENSITIES AND BOND ORDERS

  1  Q=  1.000000D 00
   1  2   8.380623D-01     1  3   0.0              1  4  -1.619377D-01     1  5   0.0
   1  6  -2.246862D-01     1  7   0.0              1  8   1.430921D-01     1  9   0.0
   1 10   2.484394D-01     1 11   0.0              1 12  -2.378001D-01     1 13   0.0
   1 14   2.484394D-01     1 15   1.430921D-01     1 16   0.0

  2  Q=  1.000000D 00
   2  3   5.015983D-01     2  4   0.0              2  5  -1.619377D-01     2  6   0.0
   2  7  -9.066010D-02     2  8   0.0              2  9   5.376019D-02     2 10   0.0
   2 11  -1.578292D-02     2 12   0.0              2 13  -1.578292D-02     2 14   0.0
   2 15   0.0              2 16  -9.066010D-02
```

```
3  Q=  1.000000D 00
   3  4   5.015983D-01     3  5   0.0              3  6   5.224957D-01     3  7   0.0
   3  8  -1.656828D-01     3  9   0.0              3 10  -2.378001D-01     3 11   0.0
   3 12   2.362144D-01     3 13   0.0              3 14  -2.378001D-01     3 15  -1.656828D-01
   3 16   0.0

4  Q=  1.000000D 00
   4  5   8.380623D-01     4  6   0.0              4  7  -9.066010D-02     4  8   0.0
   4  9   5.376019D-02     4 10   0.0              4 11  -1.578292D-02     4 12   0.0
   4 13  -1.578292D-02     4 14   0.0              4 15   0.0              4 16  -9.066010D-02

5  Q=  1.000000D 00
   5  6  -2.246862D-01     5  7   0.0              5  8   1.430921D-01     5  9   0.0
   5 10   2.484394D-01     5 11   0.0              5 12  -2.378001D-01     5 13   0.0
   5 14   2.484394D-01     5 15   1.430921D-01     5 16   0.0

6  Q=  1.000000D 00
   6  7   5.381331D-01     6  8   0.0              6  9  -2.026716D-01     6 10   0.0
   6 11   5.376019D-02     6 12   0.0              6 13   5.376019D-02     6 14   0.0
   6 15   0.0              6 16   5.381331D-01

7  Q=  1.000000D 00
   7  8   7.505721D-01     7  9   0.0              7 10   1.430921D-01     7 11   0.0
   7 12  -1.656828D-01     7 13   0.0              7 14   1.430921D-01     7 15  -2.494279D-01
   7 16   0.0

8  Q=  1.000000D 00
   8  9   5.381331D-01     8 10   0.0              8 11  -9.066010D-02     8 12   0.0
   8 13  -9.066010D-02     8 14   0.0              8 15   0.0              8 16  -2.494279D-01

9  Q=  1.000000D 00
   9 10  -2.246862D-01     9 11   0.0              9 12   5.224957D-01     9 13   0.0
   9 14  -2.246862D-01     9 15   5.381331D-01     9 16   0.0

10  Q=  1.000000D 00
  10 11   8.380623D-01    10 12   0.0             10 13  -1.619377D-01    10 14   0.0
  10 15   0.0             10 16   1.430921D-01

11  Q=  1.000000D 00
  11 12   5.015983D-01    11 13   0.0             11 14  -1.619377D-01    11 15  -9.066010D-02
  11 16   0.0

12  Q=  1.00000CD 00
  12 13   5.015983D-01    12 14   0.0             12 15   0.0             12 16  -1.656828D-01

13  Q=  1.000000D 00
  13 14   8.380623D-01    13 15  -9.066010D-02    13 16   0.0

14  Q=  1.000000D 00
  14 15   0.0             14 16   1.430921D-01

15  Q=  1.000000D 00
  15 16   7.505721D-01

16  Q=  1.000000D 00
```

FREE VALENCES

```
 1  F=  8.939885D-01
 2  F=  3.923902D-01
 3  F=  2.063586D-01
 4  F=  3.923902D-01
 5  F=  8.939885D-01
 6  F=  1.332890D-01
 7  F=  4.433456D-01
 8  F=  4.433456D-01
 9  F=  1.332890D-01
10  F=  8.939885D-01
11  F=  3.923902D-01
12  F=  2.063586D-01
13  F=  3.923902D-01
14  F=  8.939885D-01
15  F=  4.433456D-01
16  F=  4.433456D-01
```

SELF-CONSISTENT FIELD MO

SCF CONVERGED IN 22 ITERATIONS

ENERGIES AND COEFFICIENTS

```
 1  E= -1.535840D 01 EV
   1  1   2.546719D-01    2  1   2.855301D-01    3  1   3.150891D-01    4  1   2.855301D-01
   5  1   2.546719D-01    6  1   2.437008D-01    7  1   1.558177D-01    8  1   1.558177D-01
   9  1   2.437008D-01   10  1   2.546719D-01   11  1   2.855301D-01   12  1   3.150891D-01
  13  1   2.855301D-01   14  1   2.546719D-01   15  1   1.558177D-01   16  1   1.558177D-01

 2  E= -1.518389D 01 EV
   1  2  -2.941133D-01    2  2  -3.167062D-01    3  2  -3.114505D-01    4  2  -3.167062D-01
   5  2  -2.941133D-01    6  2  -1.615031D-01    7  2  -4.064724D-02    8  2   4.064724D-02
   9  2   1.615031D-01   10  2   2.941133D-01   11  2   3.167062D-01   12  2   3.114505D-01
  13  2   3.167062D-01   14  2   2.941133D-01   15  2   4.064724D-02   16  2  -4.064724D-02

 3  E= -1.401876D 01 EV
   1  3  -5.563562D-01    2  3  -4.254334D-01    3  3   0.0             4  3   4.254334D-01
   5  3   5.563562D-01    6  3   0.0             7  3   0.0             8  3   0.0
   9  3   0.0            10  3   7.732062D-02   11  3   5.912539D-02   12  3   0.0
  13  3  -5.912539D-02   14  3  -7.732062D-02   15  3   0.0            16  3   0.0

 4  E= -1.401876D 01 EV
   1  4  -7.732062D-02    2  4  -5.912539D-02    3  4   0.0             4  4   5.912539D-02
   5  4   7.732062D-02    6  4   0.0             7  4   0.0             8  4   0.0
   9  4   0.0            10  4  -5.563562D-01   11  4  -4.254334D-01   12  4   0.0
  13  4   4.254334D-01   14  4   5.563562D-01   15  4   0.0            16  4   0.0

 5  E= -1.379925D 01 EV
   1  5   2.215474D-01    2  5   1.558559D-01    3  5  -3.770893D-02    4  5   1.558559D-01
   5  5   2.215474D-01    6  5  -3.400513D-01    7  5  -3.436529D-01    8  5  -3.436529D-01
   9  5  -3.400513D-01   10  5   2.215474D-01   11  5   1.558559D-01   12  5  -3.770893D-02
  13  5   1.558559D-01   14  5   2.215474D-01   15  5  -3.436529D-01   16  5  -3.436529D-01

 6  E= -1.195641D 01 EV
```

1	6	-2.540943D-01	2	6	-5.361840D-02	3	6	3.039829D-01	4	6	-5.361840D-02
5	6	-2.540943D-01	6	6	4.648017D-01	7	6	1.683391D-01	8	6	-1.683391D-01
9	6	-4.648017D-01	10	6	2.540943D-01	11	6	5.361840D-02	12	6	-3.039829D-01
13	6	5.361840D-02	14	6	2.540943D-01	15	6	-1.683391D-01	16	6	1.683391D-01

7 E= -1.114810D 01 EV

1	7	0.0	2	7	0.0	3	7	0.0	4	7	0.0
5	7	0.0	6	7	0.0	7	7	-5.000000D-01	8	7	-5.000000D-01
9	7	0.0	10	7	0.0	11	7	0.0	12	7	0.0
13	7	0.0	14	7	0.0	15	7	5.000000D-01	16	7	5.000000D-01

8 E= -9.992332D 00 EV

1	8	2.948108D-01	2	8	-9.326224D-02	3	8	-4.513351D-01	4	8	-9.326224D-02
5	8	2.948108D-01	6	8	-9.446225D-02	7	8	2.192613D-01	8	8	2.192613D-01
9	8	-9.446225D-02	10	8	2.948108D-01	11	8	-9.326224D-02	12	8	-4.513351D-01
13	8	-9.326224D-02	14	8	2.948108D-01	15	8	2.192613D-01	16	8	2.192613D-01

9 E= -5.123058D 00 EV

1	9	-2.637395D-01	2	9	1.890995D-01	3	9	3.275184D-01	4	9	1.890995D-01
5	9	-2.637395D-01	6	9	-3.072546D-01	7	9	-2.093943D-01	8	9	2.093943D-01
9	9	3.072546D-01	10	9	2.637395D-01	11	9	-1.890995D-01	12	9	-3.275184D-01
13	9	-1.890995D-01	14	9	2.637395D-01	15	9	2.093943D-01	16	9	-2.093943D-01

10 E= -2.924838D 00 EV

1	10	-6.933147D-02	2	10	9.066752D-02	3	10	0.0	4	10	-9.066752D-02
5	10	6.933147D-02	6	10	0.0	7	10	0.0	8	10	0.0
9	10	0.0	10	10	4.238897D-01	11	10	-5.543375D-01	12	10	0.0
13	10	5.543375D-01	14	10	-4.238897D-01	15	10	0.0	16	10	0.0

11 E= -2.924838D 00 EV

1	11	4.238897D-01	2	11	-5.543375D-01	3	11	0.0	4	11	5.543375D-01
5	11	-4.238897D-01	6	11	0.0	7	11	0.0	8	11	0.0
9	11	0.0	10	11	6.933147D-02	11	11	-9.066752D-02	12	11	0.0
13	11	9.066752D-02	14	11	-6.933147D-02	15	11	0.0	16	11	0.0

12 E= -2.480481D 00 EV

1	12	1.931522D-01	2	12	-2.752111D-01	3	12	7.077306D-02	4	12	-2.752111D-01
5	12	1.931522D-01	6	12	4.220798D-01	7	12	-2.130047D-01	8	12	-2.130047D-01
9	12	4.220798D-01	10	12	1.931522D-01	11	12	-2.752111D-01	12	12	7.077306D-02
13	12	-2.752111D-01	14	12	1.931522D-01	15	12	-2.130047D-01	16	12	-2.130047D-01

13 E= -1.187959D 00 EV

1	13	0.0	2	13	0.0	3	13	0.0	4	13	0.0
5	13	0.0	6	13	0.0	7	13	-5.000000D-01	8	13	5.000000D-01
9	13	0.0	10	13	0.0	11	13	0.0	12	13	0.0
13	13	0.0	14	13	0.0	15	13	-5.000000D-01	16	13	5.000000D-01

14 E= -7.369119D-01 EV

1	14	1.660944D-01	2	14	-3.145202D-01	3	14	3.668583D-01	4	14	-3.145202D-01
5	14	1.660944D-01	6	14	3.961694D-02	7	14	-2.353984D-01	8	14	2.353984D-01
9	14	-3.961694D-02	10	14	-1.660944D-01	11	14	3.145202D-01	12	14	-3.668583D-01
13	14	3.145202D-01	14	14	-1.660944D-01	15	14	2.353984D-01	16	14	-2.353984D-01

15 E= 5.866977D-01 EV

1	15	1.088017D-01	2	15	-2.444228D-01	3	15	4.365601D-01	4	15	-2.444228D-01
5	15	1.088017D-01	6	15	-3.713497D-01	7	15	1.190674D-01	8	15	1.190674D-01
9	15	-3.713497D-01	10	15	1.088017D-01	11	15	-2.444228D-01	12	15	4.365601D-01
13	15	-2.444228D-01	14	15	1.088017D-01	15	15	1.190674D-01	16	15	1.190674D-01

```
16  E=  1.918953D 00 EV
   1 16  -4.227976D-02     2 16   1.101846D-01     3 16  -2.621825D-01     4 16   1.101846D-01
   5 16  -4.227976D-02     6 16   4.023696D-01     7 16  -3.474929D-01     8 16   3.474929D-01
   9 16  -4.023696D-01    10 16   4.227976D-02    11 16  -1.101846D-01    12 16   2.621825D-01
  13 16  -1.101846D-01    14 16   4.227976D-02    15 16   3.474929D-01    16 16  -3.474929D-01

TOTAL PI ENERGY

     E= -2.109518D 02 EV

ELECTRON DENSITIES AND BOND ORDERS

  1  Q=  1.334863D 00
   1  2   8.555739D-01     1  3  -9.361403D-02     1  4  -1.094824D-01     1  5   7.282060D-02
   1  6  -2.234509D-01     1  7  -5.263036D-03     1  8   1.180134D-01     1  9   5.896209D-02
   1 10   9.957576D-02     1 11  -5.404080D-02     1 12  -1.510597D-01     1 13  -5.404080D-02
   1 14   9.957576D-02     1 15   1.180134D-01     1 16  -5.263036D-03

  2  Q=  8.043669D-01
   2  3   4.170440D-01     2  4   6.640952D-02     2  5  -1.094824D-01     2  6   1.032436D-01
   2  7  -5.134260D-02     2  8  -6.673123D-02     2  9  -1.664823D-03     2 10  -5.404080D-02
   2 11   2.267714D-02     2 12   8.768708D-02     2 13   2.267714D-02     2 14  -5.404080D-02
   2 15  -6.673123D-02     2 16  -5.134260D-02

  3  Q=  9.876270D-01
   3  4   4.170440D-01     3  5  -9.361403D-02     3  6   6.476731D-01     3  7   5.385350D-02
   3  8  -2.014738D-01     3  9  -1.186948D-01     3 10  -1.510597D-01     3 11   8.768708D-02
   3 12   2.299989D-01     3 13   8.768708D-02     3 14  -1.510597D-01     3 15  -2.014738D-01
   3 16   5.385350D-02

  4  Q=  8.043669D-01
   4  5   8.555739D-01     4  6   1.032436D-01     4  7  -5.134260D-02     4  8  -6.673123D-02
   4  9  -1.664823D-03     4 10  -5.404080D-02     4 11   2.267714D-02     4 12   8.768708D-02
   4 13   2.267714D-02     4 14  -5.404080D-02     4 15  -6.673123D-02     4 16  -5.134260D-02

  5  Q=  1.334863D 00
   5  6  -2.234509D-01     5  7  -5.263036D-03     5  8   1.180134D-01     5  9   5.896209D-02
   5 10   9.957576D-02     5 11  -5.404080D-02     5 12  -1.510597D-01     5 13  -5.404080D-02
   5 14   9.957576D-02     5 15   1.180134D-01     5 16  -5.263036D-03

  6  Q=  8.521438D-01
   6  7   4.378591D-01     6  8   9.862325D-02     6  9  -1.163516D-01     6 10   5.896209D-02
   6 11  -1.664823D-03     6 12  -1.186948D-01     6 13  -1.664823D-03     6 14   5.896209D-02
   6 15   9.862325D-02     6 16   4.378591D-01

  7  Q=  9.408845D-01
   7  8   8.209234D-01     7  9   9.862325D-02     7 10   1.180134D-01     7 11  -6.673123D-02
   7 12  -2.014738D-01     7 13  -6.673123D-02     7 14   1.180134D-01     7 15  -1.790766D-01
   7 16  -5.911552D-02

  8  Q=  9.408845D-01
   8  9   4.378591D-01     8 10  -5.263036D-03     8 11  -5.134260D-02     8 12   5.385350D-02
   8 13  -5.134260D-02     8 14  -5.263036D-03     8 15  -5.911552D-02     8 16  -1.790766D-01

  9  Q=  8.521438D-01
   9 10  -2.234509D-01     9 11   1.032436D-01     9 12   6.476731D-01     9 13   1.032436D-01
   9 14  -2.234509D-01     9 15   4.378591D-01     9 16   9.862325D-02
```

```
 10  Q=  1.334863D 00
   10 11   8.555739D-01     10 12  -9.361403D-02     10 13  -1.094824D-01     10 14   7.282060D-02
   10 15  -5.263036D-03     10 16   1.180134D-01

 11  Q=  8.043669D-01
   11 12   4.170440D-01     11 13   6.640952D-02     11 14  -1.094824D-01     11 15  -5.134260D-02
   11 16  -6.673123D-02

 12  Q=  9.876270D-01
   12 13   4.170440D-01     12 14  -9.361403D-02     12 15   5.385350D-02     12 16  -2.014738D-01

 13  Q=  8.043669D-01
   13 14   8.555739D-01     13 15  -5.134260D-02     13 16  -6.673123D-02

 14  Q=  1.334863D 00
   14 15  -5.263036D-03     14 16   1.180134D-01

 15  Q=  9.408845D-01
   15 16   8.209234D-01

 16  Q=  9.408845D-01

BOND LENGTHS

    1  2  R=  1.154996D 00
    2  3  R=  1.441931D 00
    3  4  R=  1.441931D 00
    3  6  R=  1.400418D 00
    4  5  R=  1.154996D 00
    6  7  R=  1.438185D 00
    6 16  R=  1.438185D 00
    7  8  R=  1.369233D 00
    8  9  R=  1.438185D 00
    9 12  R=  1.400418D 00
    9 15  R=  1.438185D 00
   10 11  R=  1.154996D 00
   11 12  R=  1.441931D 00
   12 13  R=  1.441931D 00
   13 14  R=  1.154996D 00
   15 16  R=  1.369233D 00

FREE VALENCES

  1  F=  8.764769D-01
  2  F=  4.594328D-01
  3  F=  2.502896D-01
  4  F=  4.594328D-01
  5  F=  8.764769D-01
  6  F=  2.086595D-01
  7  F=  4.732683D-01
  8  F=  4.732683D-01
  9  F=  2.086595D-01
 10  F=  8.764769D-01
 11  F=  4.594328D-01
 12  F=  2.502896D-01
 13  F=  4.594328D-01
 14  F=  8.764769D-01
 15  F=  4.732683D-01
 16  F=  4.732683D-01
```

APPENDIX III

MOLECULAR ORBITAL CALCULATION PROGRAM

```
C     MOLECULAR ORBITAL CALCULATION PROGRAM
C     THIS PROGRAM CALCULATES MOLECULAR ORBITALS USING HUCKEL MO THEORY
C     AND SELF-CONSISTENT FIELD MO THEORY.
C     INPUT DATA IS NUMBER AND TYPE OF ATOMS IN THE MOLECULE, NUMBER OF
C     PI ELECTRONS, NUMBER AND TYPE OF BONDS, NUMBER OF BENZENE-LIKE
C     RINGS IN THE MOLECULE, EMPIRICAL PARAMETERS ALPHA AND BETA FOR
C     CARBON, AND OVERLAP INTEGRAL.
C     OUTPUT CONSISTS OF THE HAMILTONIAN MATRIX, MO ENERGIES AND
C     COEFFICIENTS, TOTAL PI ENERGY, ELECTRON CHARGE DENSITIES AND BOND
C     ORDERS, BOND LENGTHS, AND FREE VALENCES.
C     HMO CALCULATIONS CAN BE MADE FOR MOLECULES HAVING C,N,O,S,SE,F,
C     CL,BR ATOMS.
C     SCFMO CALCULATIONS CAN BE MADE FOR MOLECULES HAVING C,N,O ATOMS.
C     MAIN PROGRAM READS INPUT DATA, SETS UP HAMILTONIAN MATRIX, AND
C     CALLS SUBROUTINES HMO AND SCFMO.
C     WRITTEN BY J.M.YOUNKIN FOR OAK RIDGE NATIONAL LABORATORY.
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON H(40,40),UC(40,40),P(40,40),IA(40),IB(40,40),NE(40)
   10 IFL=0
C     READ TITLE CARD.
      READ (5,20,END=1000)
   20 FORMAT (80H
     1                    )
      WRITE (6,20)
C     READ NUMBER OF ATOMS N, NUMBER OF PI ELECTRONS NEL, NUMBER OF
C     BONDS NB, NUMBER OF BENZENE RINGS NR, WRITE FLAG IWR, ALPHA, BETA,
C     AND OVERLAP INTEGRAL S.
      READ (5,30) N,NEL,NB,NR,IWR,A0,B0,S
   30 FORMAT (5I3,3F10.0)
C     READ TYPES OF ATOMS IA(I).
      READ(5,40) (IA(I),I=1,N)
   40 FORMAT (40I2)
      DO 50 I=1,N
      DO 50 J=I,N
      IB(I,J)=0
      IB(J,I)=IB(I,J)
      H(I,J)=0.0D0
   50 H(J,I)=H(I,J)
      WRITE (6,60) N,NEL,NB,NR,A0,B0,S
   60 FORMAT ('0NO. OF ATOMS=',I3/'0NO. OF PI ELECTRONS=',I3/'0NO. OF BO
     1NDS=',I3/'0NO. OF RINGS=',I3/'0ALPHA=',F9.4,5X,'BETA=',F9.4/'0OVER
     2LAP INTEGRAL=',F9.4)
      WRITE (6,70)
   70 FORMAT ('0HAMILTONIAN MATRIX AND BOND TYPE'/)
      LINE=45
C     READ K-VALUES OF HAMILTONIAN MATRIX H(I,J).
      READ (5,80) (I,J,H(I,J),K=1,NB)
   80 FORMAT (8(2I3,F4.0))
C     COMPUTE TYPES OF BONDS IB(I,J).
      DO 90 I=1,N
```

```
      DO 90 J=I,N
      IF(H(I,J).EQ.0.0D0)GO TO 90
      IF(IA(I).LE.8.AND.IA(J).LE.8)GO TO 85
      IFL=1
   85 ICON=IA(I)+IA(J)
      IB(I,J)=(ICON+1)/2
      IF(ICON.EQ.8)IB(I,J)=1
      IF(ICON.EQ.15)IB(I,J)=5
C     SET UP AND WRITE HAMILTONIAN MATRIX.
      DO 110 I=1,N
      NUM=N-I
      LINE=LINE-NUM/8-1
      IF(LINE.GT.0)GO TO 95
      WRITE (6,93)
   93 FORMAT (1H1)
      LINE=59-NUM/8
   95 WRITE (6,100) (I,J,H(I,J),IB(I,J),J=I,N)
  100 FORMAT (8(I4,I3,F6.2,I3))
      DO 110 J=I,N
      H(J,I)=H(I,J)
  110 IB(J,I)=IB(I,J)
C     COMPUTE NUMBER OF PI ELECTRONS IN EACH ORBITAL NE(I).
      NO=NEL
      DO 130 I=1,NEL
      IF(NO.LE.2)GO TO 120
      NE(I)=2
      NO=NO-2
      GO TO 130
  120 NE(I)=NO
      NO=0
  130 CONTINUE
C     CALL SUBROUTINES HMO AND SCFMO.
      CALL HMO(N,NB,A0,B0,S,LINE,&10)
      IF(IFL.EQ.1)GO TO 10
      CALL SCFMO(N,NR,IWR,S,LINE,&10)
      GO TO 10
 1000 STOP
      END
```

```
      SUBROUTINE HMO(N,NB,A0,B0,S,LINE,*)
C     SUBROUTINE HMO CALCULATES HUCKEL MOLECULAR ORBITALS.
C     THIS ROUTINE DETERMINES EIGENVALUES AND EIGENVECTORS OF
C     HAMILTONIAN MATRIX, SORTS THEM INTO ORDER, CALCULATES AN AVERAGE
C     ALPHA AND BETA FOR A HETEROMOLECULE, COMPUTES ENERGY LEVELS IN EV,
C     AND CALCULATES TOTAL PI ENERGY, ELECTRON DENSITIES, BOND ORDERS,
C     AND FREE VALENCES.
C     IT CALLS SUBROUTINES MATDAG AND BONDEN.
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 YR
      DIMENSION UCT(40),X(20)
      COMMON H(40,40),UC(40,40),P(40,40),IA(40),IB(40,40),NE(40)
      DATA X/0.0,1.5,1.5,2.0,2.0,1.0,0.0,1.5,0.9,3.0,2.0,1.5,8*0.0/
      A=0
      B=0
      YR=3.0E-16
      NITT=10
      LINE=LINE-7
      IF(LINE.GT.0)GO TO 5
      WRITE (6,3)
    3 FORMAT (1H1)
      LINE=53
    5 WRITE(6,10)
   10 FORMAT('0HUCKEL MO')
      DO 15 I=1,N
      DO 15 J=I,N
   15 P(I,J)=H(I,J)
C     DIAGONALIZE HAMILTONIAN MATRIX AND DETERMINE EIGENVALUES AND
C     EIGENVECTORS IN SUBROUTINE MATDAG.
      CALL MATDAG(H,UC,N,YR,NITER,NITT,40)
      IF(NITER.LT.NITT)GO TO 30
      WRITE(6,20)
   20 FORMAT('0',5X,'MATRIX DID NOT CONVERGE IN HMO')
      RETURN 1
C     SORT EIGENVALUES H(J,J) AND THEIR EIGENVECTORS UC(I,J) INTO ORDER.
   30 NM1=N-1
      DO 60 J=1,NM1
      BIG=H(J,J)
      M=J
      JP1=J+1
      DO 40 K=JP1,N
      IF(BIG.GE.H(K,K))GO TO 40
      BIG=H(K,K)
      M=K
   40 CONTINUE
      IF(M.EQ.J)GO TO 60
      TEMP=H(J,J)
      H(J,J)=H(M,M)
      H(M,M)=TEMP
      DO 50 I=1,N
```

```
      UCT(I)=UC(I,J)
      UC(I,J)=UC(I,M)
   50 UC(I,M)=UCT(I)
   60 CONTINUE
C     COMPUTE AN AVERAGE ALPHA AND BETA FOR A HETEROMOLECULE.
      DO 65 I=1,N
      A=A+A0+X(IA(I))*B0
      DO 65 J=I,N
   65 B=B+P(I,J)*B0
      A=A/N
      B=B/NB
      WRITE (6,70)
   70 FORMAT ('0ENERGIES AND COEFFICIENTS')
      LINE=LINE+3
      PIEN=0.0D0
      DO 100 J=1,N
      DO 80 I=1,N
      IF(DABS(UC(I,J)).LT.1.0D-14)UC(I,J)=0.0D0
   80 CONTINUE
C     CALCULATE ENERGIES H(J,J) AND PIEN IN EV.
      H(J,J)=H(J,J)/(1.0D0+S*H(J,J))
      EV=A+H(J,J)*B
      PIEN=PIEN+NE(J)*H(J,J)
      LINE=LINE-3
      IF(LINE.GT.0)GO TO 85
      WRITE (6,3)
      LINE=57
   85 WRITE (6,90) J,H(J,J),EV
   90 FORMAT ('0',I3,'  E=',1PD14.6,' BETA'/4X,'  E=',1PD14.6,' EV')
      H(J,J)=EV
      LINE=LINE-(N-1)/4-1
      IF(LINE.GT.0)GO TO 100
      WRITE (6,3)
      LINE=59-(N-1)/4
  100 WRITE (6,110) (I,J,UC(I,J),I=1,N)
  110 FORMAT (4(I6,I3,1PD15.6))
      EV=A+PIEN*B
      LINE=LINE-5
      IF(LINE.GT.0)GO TO 115
      WRITE (6,3)
      LINE=55
  115 WRITE(6,120)PIEN,EV
  120 FORMAT('0TOTAL PI ENERGY'/'0',3X,'  E=',1PD14.6,' BETA'/4X,'  E=',
     1 1PD14.6,' EV')
C     CALCULATE ELECTRON DENSITIES P(I,I) AND BOND ORDERS P(I,J) IN
C     SUBROUTINE BONDEN.
      CALL BONDEN(N)
      LINE=LINE-4
      IF(LINE.GT.0)GO TO 125
      WRITE (6,3)
```

```
      LINE=56
  125 WRITE(6,130)
  130 FORMAT('0ELECTRON DENSITIES AND BOND ORDERS')
      LINE=LINE+2
      DO 160 I=1,N
      DO 140 J=1,N
      IF(DABS(P(I,J)).LT. 1.0D-14)P(I,J)=0.0D0
  140 CONTINUE
      LINE=LINE-2
      IF(LINE.GT.0)GO TO 145
      WRITE (6,3)
      LINE=58
  145 WRITE(6,150)I,P(I,I)
  150 FORMAT('0',I3,'  Q=',1PD14.6)
      IF(I.GE.N)GO TO 160
      IP1=I+1
      NUM=N-IP1
      LINE=LINE-NUM/4-1
      IF(LINE.GT.0)GO TO 155
      WRITE (6,3)
      LINE=59-NUM/4
  155 WRITE(6,110)(I,J,P(I,J),J=IP1,N)
  160 CONTINUE
      LINE=LINE-4
      IF(LINE.GT.0)GO TO 165
      WRITE (6,3)
      LINE=56
  165 WRITE(6,170)
  170 FORMAT('0FREE VALENCES'/)
      LINE=LINE+1
C     CALCULATE FREE VALENCES UCT(I).
      DO 190 I=1,N
      UCT(I)=0.0D0
      DO 180 J=1,N
      IF(IB(I,J).EQ.0)GO TO 180
      UCT(I)=UCT(I)+P(I,J)
  180 CONTINUE
      UCT(I)=DSQRT(3.0D0)-UCT(I)
      LINE=LINE-1
      IF(LINE.GT.0)GO TO 190
      WRITE (6,3)
      LINE=59
  190 WRITE(6,200)I,UCT(I)
  200 FORMAT(' ',I3,'  F=',1PD14.6)
      RETURN
      END
```

```
      SUBROUTINE SCFMO(N,NR,IWR,S,LINE,*)
C     SUBROUTINE SCFMO CALCULATES SELF-CONSISTENT FIELD MOLECULAR
C     ORBITALS.
C     IT USES A VARIABLE BETA-GAMMA TECHNIQUE TO COMPUTE THE PARISER-
C     PARR-POPLE APPROXIMATION TO THE HARTREE-FOCK EQUATIONS. BETA
C     REPRESENTS THE TWO CENTER CORE INTEGRALS AND GAMMA REPRESENTS THE
C     TWO CENTER ELECTRON REPULSION INTEGRALS. EMPIRICAL PARAMETERS ARE
C     USED TO CALCULATE BETA AND GAMMA FROM BOND ORDERS AND POTENTIALS.
C     THE ROUTINE THEN DETERMINES EIGENVALUES AND EIGENVECTORS OF THE
C     HARTREE-FOCK MATRIX, SORTS THEM INTO ORDER, AND CALCULATES TOTAL
C     PI ENERGY, ELECTRON DENSITIES, BOND ORDERS, BOND LENGTHS, AND
C     FREE VALENCES. THIS IS AN ITERATIVE PROCEDURE USING THE HMO
C     RESULTS AS THE INITIAL GUESS AND ACHIEVING SELF-CONSISTENCY WHEN
C     RESULTS FROM SUCCESSIVE ITERATIONS AGREE WITHIN TOLERANCE.
C     IT CALLS SUBROUTINES MATDAG AND BONDEN.
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 YR
      DIMENSION UCT(40),VAL(40),A0(5,10),A1(10),D0(10),D1(10),G(10),
     1 POT(10)
      COMMON H(40,40),UC(40,40),P(40,40),IA(40),IB(40,40),NB(40)
      DATA A0/-2.04,-1.90,-1.84,-1.82,-1.81,-2.24,-2.09,-2.02,-2.00,
     1 -1.98,-2.44,-2.27,-2.20,-2.18,-2.17,-2.44,-2.27,-2.20,-2.18,
     2 -2.17,-2.24,-2.09,-2.02,-2.00,-1.98,25*0.0/
      DATA A1/-0.51,-0.53,-0.56,-0.56,-0.53,5*0.0/
      DATA D0/1.517,1.451,1.410,1.410,1.309,5*0.0/
      DATA D1/-0.18,-0.18,-0.18,-0.18,-0.18,5*0.0/
      DATA G/11.13,12.34,17.44,15.23,21.53,10.84,10.09,11.52,2*0.0/
      DATA POT/-11.16,-14.12,-26.70,-17.70,-32.90,-20.00,-12.69,-16.18,
     1 2*0.0/
      YR=3.0E-16
      NITT=10
      ITER=0
      IFL=0
      LINE=LINE-8
      IF(LINE.GT.0)GO TO 5
      WRITE (6,3)
    3 FORMAT (1H1)
      LINE=52
    5 WRITE(6,10)
   10 FORMAT('0SELF-CONSISTENT FIELD MO')
      LINE=LINE+6
      IF(NR.GT.5)NR=5
   20 ITER=ITER+1
C     SAVE ENERGIES H(I,I) FROM PREVIOUS ITERATION IN VAL(I).
C     STORE POTENTIAL DIFFERENCES G(I) IN UC(I,I).
      DO 30 I=1,N
      VAL(I)=H(I,I)
   30 UC(I,I)=G(IA(I))
      NM1=N-1
      DO 40 I=1,NM1
```

```
      IP1=I+1
      DO 40 J=IP1,N
      IF(IB(I,J).NE.0)GO TO 32
      UC(I,J)=3.0D0
      GO TO 34
C     CALCULATE BOND LENGTHS UC(I,J) USING PARAMETERS D0 AND D1 AND
C     BOND ORDERS P(I,J) FROM PREVIOUS ITERATION.
   32 UC(I,J)=D0(IB(I,J))+D1(IB(I,J))*P(I,J)
C     CALCULATE GAMMAS UC(I,J).
   34 UC(I,J)=1.0D0/(2.0D0/(UC(I,I)+UC(J,J))+0.069362D0*UC(I,J))
      UC(J,I)=UC(I,J)
      IF(IB(I,J).NE.0)GO TO 36
      H(I,J)=0.0D0
      GO TO 38
C     CALCULATE BETAS H(I,J) USING PARAMETERS A0 AND A1 AND BOND ORDERS
C     FROM PREVIOUS ITERATION.
   36 H(I,J)=A0(NR,IB(I,J))+A1(IB(I,J))*P(I,J)
C     CALCULATE NON-DIAGONAL ELEMENTS H(I,J) OF HARTREE-FOCK MATRIX.
   38 H(I,J)=H(I,J)-0.5D0*P(I,J)*UC(I,J)
   40 H(J,I)=H(I,J)
C     CALCULATE DIAGONAL ELEMENTS H(I,I) OF HARTREE-FOCK MATRIX USING
C     POTENTIALS POT(I) AND ELECTRON DENSITIES P(I,I) FROM PREVIOUS
C     ITERATION.
      DO 60 I=1,N
      H(I,I)=0.0D0
      DO 50 J=1,N
      IF(I.EQ.J)GO TO 50
      H(I,I)=H(I,I)+(P(J,J)-1.0D0)*UC(I,J)
   50 CONTINUE
   60 H(I,I)=H(I,I)+0.5D0*P(I,I)*UC(I,I)+POT(IA(I))
C     DIAGONALIZE HARTREE-FOCK MATRIX AND DETERMINE EIGENVALUES AND
C     EIGENVECTORS IN SUBROUTINE MATDAG.
      CALL MATDAG(H,UC,N,YR,NITER,NITT,40)
      IF(NITER.LT.NITT)GO TO 80
      WRITE(6,70)
   70 FORMAT('0',5X,'MATRIX DID NOT CONVERGE IN SCFMO')
      RETURN 1
C     SORT EIGENVALUES H(J,J) AND THEIR EIGENVECTORS UC(I,J) INTO
C     ASCENDING ORDER.
   80 DO 110 J=1,NM1
      SMALL=H(J,J)
      M=J
      JP1=J+1
      DO 90 K=JP1,N
      IF(SMALL.LE.H(K,K))GO TO 90
      SMALL=H(K,K)
      M=K
   90 CONTINUE
      IF(M.EQ.J)GO TO 110
      TEMP=H(J,J)
```

```
      H(J,J)=H(M,M)
      H(M,M)=TEMP
      DO 100 I=1,N
      UCT(I)=UC(I,J)
      UC(I,J)=UC(I,M)
  100 UC(I,M)=UCT(I)
  110 CONTINUE
      PIEN=0.0D0
      DO 130 J=1,N
      DO 120 I=1,N
      IF(DABS(UC(I,J)).LT.1.0D-14)UC(I,J)=0.0D0
  120 CONTINUE
      H(J,J)=H(J,J)/(1.0D0+S*H(J,J))
  130 PIEN=PIEN+NE(J)*H(J,J)
C     CALCULATE NEW ELECTRON DENSITIES P(I,I) AND BOND ORDERS P(I,J) IN
C     SUBROUTINE BONDEN.
      CALL BONDEN(N)
      DO 140 I=1,N
      DO 140 J=1,N
      IF(DABS(P(I,J)).LT.1.0D-14)P(I,J)=0.0D0
  140 CONTINUE
C     CHECK ENERGIES H(I,I) OF CURRENT ITERATION WITH ENERGIES VAL(I)
C     FROM PREVIOUS ITERATION. CONVERGENCE ATTAINED WHEN THE MAXIMUM
C     DIFFERENCE IS LESS THAN THE TOLERANCE 1.0D-05.
      DO 150 I=1,N
      DIFF=DABS(H(I,I)-VAL(I))
      IF(DIFF.GT.1.0D-05)GO TO 160
  150 CONTINUE
      IFL=1
      LINE=LINE-6
      IF(LINE.GT.0)GO TO 153
      WRITE (6,3)
      LINE=54
  153 WRITE(6,155)ITER
  155 FORMAT('0SCF CONVERGED IN ',I2,' ITERATIONS')
      GO TO 190
C     GO TO NEXT ITERATION IF NECESSARY. MAXIMUM OF 50 ITERATIONS ARE
C     ALLOWED.
  160 IF(ITER.LT.50)GO TO 180
      IFL=1
      LINE=LINE-6
      IF(LINE.GT.0)GO TO 165
      WRITE (6,3)
      LINE=54
  165 WRITE(6,170)DIFF
  170 FORMAT('0SCF DID NOT CONVERGE IN 50 ITERATIONS, DIFF =',1PD14.6)
      GO TO 190
C     RESULTS FROM EVERY TENTH ITERATION CAN BE PRINTED BY MAKING
C     WRITE FLAG IWR NON-ZERO.
  180 IF(IWR.EQ.0)GO TO 20
```

```
      IF((ITER-((ITER/10)*10)).GT.0) GO TO 20
      LINE=LINE-6
      IF(LINE.GT.0)GO TO 183
      WRITE (6,3)
      LINE=54
  183 WRITE(6,185) ITER
  185 FORMAT('0ITERATION NUMBER ',I2)
  190 WRITE (6,200)
  200 FORMAT ('0ENERGIES AND COEFFICIENTS')
      LINE=LINE+2
      DO 220 J=1,N
      LINE=LINE-2
      IF(LINE.GT.0)GO TO 205
      WRITE (6,3)
      LINE=58
  205 WRITE (6,210) J,H(J,J)
  210 FORMAT ('0',I3,'  E=',1PD14.6,' EV')
      LINE=LINE-(N-1)/4-1
      IF(LINE.GT.0)GO TO 220
      WRITE (6,3)
      LINE=59-(N-1)/4
  220 WRITE (6,230) (I,J,OC(I,J),I=1,N)
  230 FORMAT (4(I6,I3,1PD15.6))
      LINE=LINE-4
      IF(LINE.GT.0)GO TO 233
      WRITE (6,3)
      LINE=56
  233 WRITE (6,235) PIEN
  235 FORMAT ('0TOTAL PI ENERGY'/'0',3X,'  E=',1PD14.6,' EV')
      LINE=LINE-4
      IF(LINE.GT.0)GO TO 237
      WRITE (6,3)
      LINE=56
  237 WRITE(6,240)
  240 FORMAT('0ELECTRON DENSITIES AND BOND ORDERS')
      LINE=LINE+2
      DO 260 I=1,N
      LINE=LINE-2
      IF(LINE.GT.0)GO TO 245
      WRITE (6,3)
      LINE=58
  245 WRITE(6,250)I,P(I,I)
  250 FORMAT('0',I3,'  Q=',1PD14.6)
      IF(I.GE.N) GO TO 260
      IP1=I+1
      NUM=N-IP1
      LINE=LINE-NUM/4-1
      IF(LINE.GT.0)GO TO 255
      WRITE (6,3)
      LINE=59-NUM/4
```

```
  255 WRITE(6,230) (I,J,P(I,J),J=IP1,N)
  260 CONTINUE
      LINE=LINE-4
      IF(LINE.GT.0)GO TO 263
      WRITE (6,3)
      LINE=56
  263 WRITE (6,265)
  265 FORMAT ('0BOND LENGTHS'/)
      LINE=LINE+1
C     CALCULATE BOND LENGTHS BOLEN.
      DO 273 I=1,NM1
      IP1=I+1
      DO 273 J=IP1,N
      IF(IB(I,J).EQ.0)GO TO 273
      BOLEN=DO(IB(I,J))+D1(IB(I,J))*P(I,J)
      LINE=LINE-1
      IF(LINE.GT.0)GO TO 268
      WRITE (6,3)
      LINE=59
  268 WRITE (6,270) I,J,BOLEN
  270 FORMAT (I6,I3,'  R=',1PD14.6)
  273 CONTINUE
      LINE=LINE-4
      IF(LINE.GT.0)GO TO 275
      WRITE (6,3)
      LINE=56
  275 WRITE (6,278)
  278 FORMAT ('0FREE VALENCES'/)
      LINE=LINE+1
C     CALCULATE FREE VALENCES UCT(I).
      DO 290 I=1,N
      UCT(I)=0.0D0
      DO 280 J=1,N
      IF(IB(I,J).EQ.0)GO TO 280
      UCT(I)=UCT(I)+P(I,J)
  280 CONTINUE
      UCT(I)=DSQRT(3.0D0)-UCT(I)
      LINE=LINE-1
      IF(LINE.GT.0)GO TO 290
      WRITE (6,3)
      LINE=59
  290 WRITE (6,300) I,UCT(I)
  300 FORMAT (' ',I3,'  F=',1PD14.6)
      IF(IFL.EQ.0)GO TO 20
      RETURN
      END
```

```
      SUBROUTINE BONDEN(N)
C     SUBROUTINE BONDEN CALCULATES BOND ORDERS P(I,J) AND ELECTRON
C     DENSITIES P(I,I). THESE QUANTITIES ARE DEFINED IN TERMS OF THE
C     NUMBER OF PI ELECTRONS IN EACH ORBITAL NE(K) AND THE COEFFICIENTS
C     UC(I,K) OF THE ORBITAL.
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON H(40,40),UC(40,40),P(40,40),IA(40),IB(40,40),NE(40)
      DO 10 I=1,N
      DO 10 J=I,N
      P(I,J)=0.0D0
   10 P(J,I)=P(I,J)
      NM1=N-1
      DO 20 I=1,NM1
      IP1=I+1
      DO 20 J=IP1,N
      DO 20 K=1,N
      P(I,J)=P(I,J)+NE(K)*UC(I,K)*UC(J,K)
   20 P(J,I)=P(I,J)
      DO 30 I=1,N
      DO 30 K=1,N
   30 P(I,I)=P(I,I)+NE(K)*UC(I,K)**2
      RETURN
      END
```

```
      SUBROUTINE MATDAG(B,D,N,YR,NITER,NITT,ID)
C     SUBROUTINE MATDAG SOLVES FOR EIGENVALUES AND ORTHOGONAL EIGEN-
C     VECTORS OF REAL SYMMETRIC MATRICES. IT USES THE JACOBI ITERATIVE
C     METHOD. THIS METHOD HAS ADVANTAGES OVER OTHERS WHEN THE MATRIX IS
C     ALMOST DIAGONAL OR WHEN THERE ARE SEVERAL CLOSE OR EQUAL EIGEN-
C     VALUES.
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION B(ID,1),D(ID,1)
      REAL*4 YR
      NITER=0
      DO 20 I=1,N
      DO 20 J=1,N
      IF(I.NE.J)GO TO 10
      D(I,I)=1.0
      GO TO 20
   10 D(I,J)=0.0
   20 CONTINUE
      NN=N-1
   30 DO 90 K=1,NN
      MO=K+1
      DO 90 M=MO,N
      IF(DABS(B(K,M)).LE.YR)GO TO 90
      BY=(B(K,K)-B(M,M))/(2.0*B(K,M))
      IF(BY.GE.0.0)GO TO 40
      SIG=-1.0
      GO TO 50
   40 SIG=1.0
   50 COT=BY+(SIG*DSQRT(BY*BY+1.0))
      S=SIG/DSQRT(COT*COT+1.0)
      C=S*COT
   60 DO 70 I=1,N
      BKI=B(K,I)
      BMI=B(M,I)
      B(K,I)=C*BKI+S*BMI
   70 B(M,I)=-S*BKI+C*BMI
      DO 80 I=1,N
      BIK=B(I,K)
      BIM=B(I,M)
      DIK=D(I,K)
      DIM=D(I,M)
      B(I,K)=C*BIK+S*BIM
      B(I,M)=-S*BIK+C*BIM
      D(I,K)=C*DIK+S*DIM
   80 D(I,M)=-S*DIK+C*DIM
   90 CONTINUE
      BMAX=0.0
      DO 100 I=1,NN
      IO=I+1
      DO 100 J=IO,N
      BM=DABS(B(I,J))
```

```
      IF(BMAX.GE.BM)GO TO 100
      BMAX=BM
  100 CONTINUE
      IF(BMAX.LE.YR)GO TO 110
      NITER=NITER+1
      IF(NITER.LT.NITT)GO TO 30
  110 RETURN
      END
```

VITA

John Michael (Mike) Younkin was born in Maryville, Tennessee on March 8, 1946. He attended public schools in Blount County and Alcoa High School. He graduated valedictorian of his class from Suitland Senior High School in Suitland, Maryland in 1964.

Later that year Mike entered the University of Tennessee to study engineering. While at UT he was a member of Phi Eta Sigma (freshman honorary society), Tau Beta Pi (engineering honorary society), Association of Collegiate Engineers, and the American Nuclear Society. He graduated Magna Cum Laude in 1968 with a Bachelor of Science degree in Nuclear Engineering.

Upon graduation Mike was employed by Union Carbide Corporation in Oak Ridge as an engineer at the Y-12 plant. At that time he also entered the Graduate School at UT. In 1975 he obtained the Master of Science degree in Physics. He was elected to membership in Sigma Pi Sigma (physics honorary society) and is a member of the Society of Physics Students.

Mike is married to the former Barbara Gritzner. They reside in Oak Ridge with their two children.