SEMI-EMPIRICAL, ALL-VALENCE-ELECTRON, MOLECULAR ORBITAL THEORY

by

John Martin Sichel

A thesis submitted to the Faculty of Graduate
Studies and Research in partial fulfilment of
the requirements for the degree of
Doctor of Philosophy

Department of Chemistry
McGill University
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October 1967

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To Joan

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TABLE OF CONTENTS

PART B
CALCULATION OF PHYSICAL PROPERTIES

LIST OF TABLES

PART A

MOLECULAR ORBITAL THEORY

CHAPTER 1

INTRODUCTION

Molecular orbital theory provides an approximate description of the electronic structure of molecules. In this introductory chapter, the quantum-mechanical basis of molecular orbital theory will be described.[1-3]

According to quantum mechanics, any system is completely described by a wave function, Ψ, which is a function of the space and spin co-ordinates of all particles in the system. For time-independent or stationary states, the wave function satisfies the time-independent Schrodinger equation,[1,4]

$$\overset{o}{H}\Psi = E\Psi \tag{1.1}$$

where $\overset{o}{H}$ is the Hamiltonian operator for the system, and the wave function, Ψ, is an eigenfunction of $\overset{o}{H}$ with energy eigenvalue E.

For a molecule, the principal terms in the Hamiltonian[1] are the electronic kinetic energy ($\overset{o}{T}_e$), nuclear kinetic energy ($\overset{o}{T}_n$), internuclear potential energy ($\overset{o}{V}_{nn}$), nuclear-electronic potential energy ($\overset{o}{V}_{ne}$), and interelectronic potential energy ($\overset{o}{V}_{ee}$).

$$\overset{o}{H} = \overset{o}{T}_n + \overset{o}{T}_e + \overset{o}{V}_{nn} + \overset{o}{V}_{ne} + \overset{o}{V}_{ee} \tag{1.2}$$

Other terms, such as the interactions studied in magnetic resonance, involve much smaller energies and can be treated as perturbations.[5]

In order to solve equation (1.1) for molecules, a number of approximations are usually made in quantum chemistry. The most basic is the Born-Oppenheimer approximation,[1,2,6] in which the total wave function is expressed as a product of an electronic wave function, Ψ_e, and the nuclear wave function, Ψ_n. The electronic wave function, which is of primary chemical interest, satisfies the electronic Schrodinger equation,

$$\overset{o}{H}_e \Psi_e = E_e \Psi_e \qquad (1.3)$$

The *electronic Hamiltonian* H_e includes the electronic kinetic energy, and the nuclear-electronic and interelectronic potential energies.[1,3]

$$\overset{o}{H}_e = \overset{o}{T}_e + \overset{o}{V}_{ne} + \overset{o}{V}_{ee} \qquad (1.4)$$

From equations (1.2) and (1.4), the total Hamiltonian is

$$\overset{o}{H} = \overset{o}{H}_e + \overset{o}{T}_n + \overset{o}{V}_{nn} \qquad (1.5)$$

The electronic wave function and energy depend on the nuclear configuration, since $\overset{o}{V}_{ne}$ depends on the nuclear as well as the electronic co-ordinates. The internuclear potential energy is not included explicitly in $\overset{o}{H}_e$, but it must be included in the total energy, and will be considered further in Chapter 8.

An exact solution of equation (1.3) is impossible for any molecule with two or more electrons,[1-4] so that approximate methods of solution must be used. The basis of most approximate methods is the *variational theorem*[1,4,6], which states that for an arbitrary wave function, Ψ_e, the expectation value of the electronic energy, given by

$$E = \int \Psi_e^* \overset{o}{H}_e \Psi_e \, d\tau \Big/ \int \Psi_e^* \Psi_e \, d\tau \tag{1.6}$$

is greater than, or equal to, the lowest eigenvalue of $\overset{o}{H}_e$, which is called the ground-state energy of the molecule, E_o. The integrations extend over all possible values of the space and spin coordinates of all the electrons in the molecule. If E_o is a nondegenerate eigenvalue, as in all molecules considered in the thesis, then $E = E_o$ only when Ψ_e is the exact ground-state electronic wave function of the molecule, and E is greater than E_o in all other cases.[4]

This theorem has been applied in two different types of quantum-chemical calculation:[8]

(i) For small molecules, an approximate wave function depending on certain parameters is assumed. The energy E is minimized with respect to the parameters, and since E is an upper bound to E_o, the wave function corresponding to the minimum energy is taken as the best wave function of the assumed form.[1,2]

(ii) For larger molecules, the computation of E using the exact Hamiltonian is impossibly difficult, even with electronic computers. As in (i), an approximate wave function is assumed and the energy is minimized with respect to the parameters. Now, however, the energy is computed from an approximate Hamiltonian. Since the variational theorem applies only when E is computed from the exact Hamiltonian, the computed energy is no longer necessarily an upper bound to the true energy. The validity of the approximate Hamiltonian must therefore be verified by comparing the values of the energy and other physical properties computed from it with experiment. The word semi-empirical is used to describe theories which are based on quantum mechanics, but which employ some experimental data for "calibration."[1]

Various forms for approximate wave functions have been used in theories of molecular electronic structures. One which has proved especially suitable for quantitative calculation on a large variety of molecules[2] is based on molecular orbitals. Molecular orbital theory was originally developed by Hund,[9] Mulliken[10] and Lennard-Jones,[11] and used for qualitative descriptions of bonding and electronic spectra in small molecules.[6,9-11] Later, it was applied extensively to conjugated hydrocarbons[1,12-16] and transition metal complexes.[17-19] A general formulation of molecular orbital theory, independent of symmetry considerations, has been given by Roothaan.[20,21]

An orbital is defined as a one-electron wave function, i.e., a function of the co-ordinates of one electron.[20] In the orbital approximation, any correlation of the instantaneous motion of different electrons is neglected.[1-3] The position of each electron is assumed to be independent of the instantaneous positions of the other electrons, and to depend only on their time-average charge distribution. Orbitals have been used to describe the electronic structure of both atoms and molecules,[3,7] and the orbitals involved are called atomic and molecular orbitals respectively.

Orbitals were first used in a quantitative theory by Hartree,[22] who used them to compute atomic wave functions.[23] Hartree initially assumed that the total electronic wave function was a simple product of one-electron orbitals. The Pauli exclusion principle[4] states, however, that the total wave function of a many-electron system must be antisymmetric with respect to the interchange of the space and spin coordinates of any two electrons. Slater[24] showed that the antisymmetry requirement is satisfied by a determinantal wave function of the form

$$\Psi = \begin{vmatrix} \psi_1(1)\eta_1(1) & \psi_2(1)\eta_2(1) & \dots & \psi_N(1)\eta_N(1) \\ \psi_1(2)\eta_1(2) & \psi_2(2)\eta_2(2) & \dots & \psi_N(2)\eta_N(2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(N)\eta_1(N) & \psi_2(N)\eta_2(N) & \dots & \psi_N(N)\eta_N(N) \end{vmatrix} \qquad (1.7)$$

where $\psi_i(k)$ is the i^th^ orbital as a function of the co-ordinates of the k^th^ electron, and the η_i are spin functions (α or β). This form of wave function is called a Slater determinant and is often written in the short form,

$$\Psi = \mathrm{Det}\,|\psi_1\eta_1 \quad \psi_2\eta_2 \dots \psi_N\eta_N| \qquad (1.8)$$

Fock[25] incorporated determinantal wave functions into the Hartree method, and the resultant <u>Hartree-Fock method</u>[2,7] has been widely used to compute atomic wave functions.[7,23,26]

The wave function defined by equation (1.8) represents a specific electron <u>configuration</u>, in which specified orbitals are occupied by electrons of specified spin. A completely general wave function can be formed by a linear superposition of configurations, since the set of all possible determinantal many-electron wave functions formed from a complete set of one-electron spin-orbitals (products of orbitals and spin functions) is itself a complete set.[1,2] Chemical experience indicates, however, that the ground state of most stable molecules (provided it is a singlet ground state) can be well approximated by a single closed-shell configuration, in which each occupied orbital is doubly occupied by two electrons of opposite spin.[20] For a closed shell, the N-electron wave function, defined by equation (1.8) has the form

$$\Psi = \mathrm{Det}\left| \psi_1\alpha \quad \psi_1\beta \; \cdots \; \psi_n\beta \right| \tag{1.9}$$

where n = N/2 is the number of occupied orbitals. The use of a single determinant greatly reduces the computation required to determine the electronic wave function of a molecule, so that approximate wave functions may be determined for molecules with a greater number of electrons than would otherwise be possible. This thesis is concerned with the computation of single-determinant closed-shell wave functions for molecular ground states.

The object[20] of a molecular orbital calculation is to find the single-determinant wave function with the lowest energy, as determined by equation (1.6). The molecular orbitals themselves in equation (1.9) are arbitrary to a certain extent, since the determinant is invariant to a unitary transformation among the occupied molecular orbitals.[27] In practice, however, the wave function is usually found by solving equations which determine a set of molecular orbitals, although it is also possible to proceed by determining the one-electron density matrix directly.[28]

The Hartree-Fock equations are integro-differential equations,[2,7] whose solution is feasible for atoms, due to the simplification provided by spherical symmetry.[7,23] For molecules, this symmetry is absent and direct solution of the Hartree-Fock equations is not feasible. If, however, the molecular orbitals are expressed as linear combinations of a set of basis orbitals,[20] instead of being allowed to assume an arbitrary functional form, then the equations can be solved by the methods of linear algebra, as outlined in Chapters 2 and 5. If a mathematically complete basis were used, this would involve no further approximation since the orbitals could still have an arbitrary functional form. In practice, computation is possible only for a finite, incomplete basis, so that it is important to choose a basis which yields a good approximation to the wave function with a limited number of terms.

Many different types of basis set have been used, especially in calculations on small molecules.[29,30] The most usual basis in quantum chemistry consists of the atomic orbitals on the different atoms of the molecule. MO's composed of linear combinations of atomic orbitals are called LCAO-MO's and have several advantages:

(i) The potential acting on an electron in the neighbourhood of a nucleus is similar to that in the free atom, so that an atomic orbital on a given atom is a first approximation to a molecular orbital near that nucleus.[2,29]

(ii) The free-atom orbitals have the correct exponential behavior at the nucleus,[1,2,29] which Gaussian functions,[31] for example, do not.

(iii) Since the atomic orbitals are each associated with an individual atom, the Hamiltonian matrix elements may be evaluated semi-empirically rather than computed a priori, as discussed in Chapters 2-5.

(iv) The charge density corresponding to the computed wave function can be related[32-35] to chemical concepts such as atomic populations, overlap populations, hybridization, bond orders, and orbital promotion.

A disadvantage of atomic orbitals as a basis set is that AO's on different atoms are not necessarily orthogonal. This nonorthogonality of the basis set can be handled either by transforming to a basis of orthogonalized orbitals, as in Chapter 5, or by systematically neglecting terms due to nonorthogonality, as in Chapters 2-4.

The size of the basis set used in molecular orbital calculations varies widely. For very small molecules, basis sets with a large number of atomic orbitals on each atom are often used.[30] Because of the difficulty of using extensive basis sets for large molecules, however, a minimum basis set[34] is often used. Such a minimum basis includes a 1s orbital for each hydrogen atom in the molecule, and inner-shell and valence-shell s and p orbitals for each other atom, as well as d orbitals for transition metals.

The size of the basis may be reduced still further by considering only <u>some</u> of the electrons--usually those of principal chemical interest. Lykos and Parr[36] have shown that the electrons of a molecule may be divided into groups, which may be considered separately, if the total wave function is expressible as an antisymmetrized product of determinants built up from mutually exclusive sets of orbitals corresponding to the groups of electrons.

The electrons are initially divided into distinct groups, and the indistinguishability of the electrons is restored only in the final antisymmetrization.

The criterion which is normally used, in deciding which electrons in a molecule can be treated separately, is chemical experience. Lykos and Parr[36] treated the separation of sigma and pi electrons in planar conjugated molecules, a separation known as the pi-electron approximation. In this approximation, calculations are made involving the pi-electrons only, and the sigma electrons are considered as a "core." The detailed behaviour of the sigma electrons is assumed not to affect the conclusions derived from the calculations. This approximation is most useful for hydrocarbons, and is of doubtful validity for heterocyclic molecules, since the results of recent minimum-basis SCF-MO calculations[37] on pyridine and pyrazine, including all electrons, show that there is substantial charge transfer from carbon to nitrogen in the sigma-system, and very little in the pi-system.

In this thesis, the electrons in a molecule are divided into inner-shell and valence-shell electrons. Calculations are made involving the valence-shell electrons only, and the inner-shell electrons of each atom are considered, along with the nucleus, as a "core" acting on the valence-shell electrons. The molecular orbitals occupied by the inner-shell electrons are assumed to be identical with those in the free atoms. This approximation is justified by the fact that chemical bonding can be described using the valence electrons alone, with the inner-shell electrons treated as inert. Also, the results of calculations for small molecules including all electrons show that inner-shell orbital energies are very different from valence-shell orbital energies.[2] Manne[38] has considered core-valence interactions using perturbation theory.

The title of this thesis indicates that it is concerned with the calculation of approximate electronic wave functions built up from molecular orbitals. All valence electrons are considered explicitly, and the theories used are semi-empirical, in that experimental data are used to assign some of the quantities which are difficult to compute exactly, or to correct for some of the errors inherent in the orbital approximation. Two types of theory are considered: self-consistent field molecular orbital (SCF-MO) theories (Chapters 2-4) and independent-electron theories (Chapter 5). This distinction arises from the nature of the electronic Hamiltonian equation (1.4) which may be rewritten in the form

$$\overset{o}{H}_e = \sum_i \overset{o}{H}_i + \sum_{i>j} \overset{o}{H}_{ij} \qquad (1.10)$$

The kinetic energy and the nuclear-electronic potential energy are written as a sum of one-electron energies for each electron in the molecule, while the interelectronic potential energy is expressed as a sum of two-electron terms $\overset{o}{H}_{ij}$, for each pair of electrons. The two-electron terms are difficult to handle, and are therefore not always explicitly included. In independent-electron theories (Chapter 5) a simplified Hamiltonian is used which is a sum of one-electron terms,

$$\overset{o}{h}{}^{\mathrm{eff}} = \sum_i \overset{o}{h}{}_i^{\mathrm{eff}} \qquad (1.11)$$

where $\overset{o}{h}_i^{eff}$ is an effective one-electron Hamiltonian, which includes the two-electron terms "in some average way."[1] Such methods are <u>not rigorously justifiable</u> but are popular because of their computational simplicity. SCF-MO theories, on the other hand, include the two-electron terms explicitly, as in equation (1.10), and will be discussed in Chapters 2-4.

CHAPTER 2

SELF-CONSISTENT FIELD MOLECULAR ORBITAL THEORY

In this chapter, the calculation of determinantal wave functions, of the form given by equation (1.8), is considered. For molecules of high symmetry, the form of the molecular orbitals can often be written down from symmetry considerations alone,[2,6,20] but this is not true in general. It is therefore necessary to formulate a method to find the determinantal wave function with the lowest possible energy.

In the related problem for atoms, the orbitals are general functions of unrestricted form. Minimization of the energy of the determinant, equation (1.8) leads to the integro-differential Hartree-Fock euqations,[7] which may be solved by an iterative method originally due to Hartree.[22] For atoms, it is feasible to solve such equations because of spherical symmetry.[7,22,23] However, the absence of such symmetry in molecules makes the Hartree-Fock equations in their integro-differential form intractable.[2] Roothaan[20,21] showed that, if the molecular orbitals are expressed as linear combinations of specified basis orbitals, such as atomic orbitals, then the Hartree-Fock equations can be reduced to the algebraic equations described in Section A of this chapter.

The Roothaan equations have been applied to the determination of wave functions for many small molecules,[29,30,39] as well as for atoms.[26] However, the amount of computation involved makes it difficult to solve the equations, except for very small molecules, even with the use of modern

2

electronic computers, because of the need to evaluate large numbers of electron-interaction integrals, as discussed later. Since chemists are often interested in much larger molecules than those for which Roothaan's equations can be solved, it is desirable to simplify the theory so that it can be extended to larger molecules. One way to do this is to use the "Zero Differential Overlap" (ZDO) approximation, which was introduced by Parr,[40] and forms the basis of the highly successful semi-empirical Pariser-Parr-Pople theory[41,42] of pi-electrons used to study conjugated organic molecules.[1] Recently, Pople, Santry and Segal[43-46] have considered the extension of the ZDO approximation to molecular orbital calculations involving all valence electrons, with emphasis on the ways in which the approximation can be made so as to preserve the invariance properties of the wave function.[43] This is discussed further in Sections B and C.

A. ROOTHAAN'S EQUATIONS

Roothaan originally proposed equations for the case of closed-shell molecules,[20] in which the wave function is a single Slater determinant of the form given by equation (1.9). Later, he extended these equations to open-shell molecules,[21] whose simplest description may be a linear combination of determinants of the general form given by equation (1.8). This thesis considers only the closed-shell case.

Roothaan[20] showed that for a single-determinant wave function,

$$\Psi = \mathrm{Det}\left|\psi_1\alpha \quad \psi_1\beta \; \ldots\ldots \; \psi_n\beta\right| \tag{1.9}$$

for a closed-shell molecule, in which the molecular orbitals are orthonormal linear combinations of some basis orbitals, ϕ_k, so that

$$\psi_i = \sum_{k=1}^{n} \phi_k C_{ki} \qquad (i = 1, \ldots, n) \tag{2.1}$$

the energy is a minimum when the coefficients C_{ki} satisfy the <u>secular equations</u>

$$\sum_{l=1}^{n} F_{kl} C_{li} = \sum_{l=1}^{n} S_{kl} C_{li} E_i \qquad (k,i = 1, \ldots, n) \tag{2.2}$$

In matrix form, this becomes

$$FC = SCE \tag{2.3}$$

where E is a diagonal matrix.

In these equations F_{kl} is the matrix element of the <u>Hartree-Fock Hamiltonian operator</u>, $\overset{o}{F}$, in the atomic orbital basis set,

$$F_{kl} = \int \phi_k^*(1) \overset{o}{F} \phi_l(1)\, dV_1 \tag{2.4}$$

and S_{kl} is the overlap integral,

$$S_{kl} = \int \phi_k^*(1) \phi_l(1)\, dV_1 \tag{2.5}$$

The integration extends over all space. If S_{kl} is zero, then ϕ_k and ϕ_l are said to be <u>orthogonal</u>.[4,6] Atomic orbitals on different atoms are not, in general, orthogonal to each other.

The condition that the molecular orbitals are orthonormal can be expressed in terms of the overlap integrals. The orbitals ψ_i and ψ_j are orthonormal if

$$\int \psi_i^* \psi_j \, dV = \int \Big(\sum_k \phi_k^* C_{ki}^*\Big)\Big(\sum_l \phi_l C_{lj}\Big) \, dV$$

$$= \sum_k \sum_l C_{ki}^* C_{lj} \int \phi_k^* \phi_l \, dV = \delta_{ij} \qquad (2.6)$$

On substituting equation (2.5) into equation (2.6), the orthonormality condition becomes

$$\sum_k \sum_l C_{ki}^* C_{lj} S_{kl} = \delta_{ij} \qquad (2.7)$$

or in matrix form,

$$C^+ SC = I \qquad (2.8)$$

where C^+ is the Hermitean adjoint of C, and I is the unit matrix.

E_i is the energy eigenvalue of the molecular orbital ψ_i, and can be related to a molecular ionization potential (Chapter 7). The orbital energies can be expressed in terms of the coefficients by pre-multiplying equation (2.3) by C^+:

$$C^+ FC = C^+ SCE \qquad (2.9)$$

From equations (2.8) and (2.9),

$$E = C^+ FC \qquad (2.10)$$

and the orbital energy E_i is given by

$$E_i = \sum_{k,l} C_{ki}^* C_{li} F_{kl} \qquad (2.11)$$

The secular equations (2.2) are written as linear equations,[20] so that if the matrix elements F_{kl} and S_{kl} are known, the secular equations can be solved by the methods of linear algebra. In the simplest case, the nondiagonal overlap matrix elements, S_{kl}, (for $k \neq l$) are neglected, so that S is the unit matrix, and equation (2.3) is simply an eigenvalue equation. If the nondiagonal S_{kl} are included, then equation (2.3) can be reduced to an eigenvalue equation by Lowdin's method,[47] as described in Chapter 5.

The difficulty in solving Roothaan's equations is that the Hartree-Fock Hamiltonian, $\overset{o}{F}$, includes electron-repulsion terms, which in turn depend on the molecular orbitals. This means that the matrix elements, F_{kl} , cannot be evaluated until the molecular orbitals are known. But the coefficients C_{ki} in the molecular orbitals are determined from the secular equations. The standard procedure in self-consistent field molecular orbital theory is to solve the secular equations by an *iterative method*,[20] which will be described after examining the matrix elements F_{kl}. Roothaan expressed the Hartree-Fock Hamiltonian operator in terms of integrals of operators over molecular orbitals. For computation, it is more convenient to express the matrix elements directly in terms of atomic orbitals, as done by Lennard-Jones,[27] Hall,[48] and Pople.[42] The following form is due to Pople.[42]

$$F_{kl} = H_{kl} + \sum_{r,s} P_{rs} \left\{ (kl/rs) - 1/2\,(ks/rl) \right\} \tag{2.12}$$

All the molecular orbitals have been expanded in terms of atomic orbitals, and the summation extends over all atomic orbitals in the basis set. H_{kl} is the matrix element of the one-electron *core Hamiltonian* for an electron in the field of the atomic cores, consisting of the nuclei and any inner-shell, or sigma, electrons not considered explicitly in the problem. This

Hamiltonian consists of the kinetic energy plus the potential energy due to all the atomic cores in the molecule, so that the form of the one-electron core matrix elements is

$$H_{kl} = \int \phi_k^* \overset{o}{H}_{core}\, \phi_l \; d\,V = \int \phi_k^* \, (-1/2\, \nabla^2 + \sum_A V_A)\, \phi_l \; d\,V \qquad (2.13)$$

V_A is the potential of the atom A; the summation extends over all the atoms in the molecule, and the integration extends over all space. The matrix P is defined by the expansion of the one-electron density matrix in terms of the basis orbitals:[28]

$$\rho = 2 \sum_{i=1} \psi_i^* \psi_i = \sum_k \sum_l (2 \sum_{i=1} c_{ki}^* \, c_{li})\, \phi_k^* \, \phi_l = \sum_k \sum_l P_{kl}\, \phi_k^* \, \phi_l \qquad (2.14)$$

where i is summed over the doubly occupied molecular orbitals, and k and are summed over the basis orbitals, so that

$$P_{kl} = 2 \sum_i c_{ki}^* \, c_{li} \qquad (2.15)$$

The quantities (kl /rs) are electron-interaction integrals between two electrons with specified charge distributions,[27,42,48]

$$(kl\ /rs) = \iint \phi_k^* \,(1)\, \phi_l(1) \frac{1}{r_{12}}\, \phi_r^* \,(2)\, \phi_s \,(2)\; d\,V_1 \; d\,V_2 \qquad (2.16)$$

where r_{12} is the distance between the two electrons. In the most general case, k, l , r and s refer to orbitals of four different atoms, and the integral given by equation (2.16) is called a <u>four-centre integral</u>.[2]

Equations (2.12) to (2.16) complete the specification of the terms in Roothaan's equations. If equations (2.12) and (2.15) are substituted into equations (2.2), the resulting equations for the coefficients are cubic simultaneous equations,[48] so that the methods of linear algebra cannot be used. It is therefore more convenient to solve the linear equations (2.2). The standard method of solution of Roothaan's equations is the iterative procedure[20] shown in Figure (2.1):

(i) The quantities S_{kl} , H_{kl} and (kr/l s), as defined by equations (2.5), (2.13) and (2.16) respectively, are initially computed, since they do not depend on the coefficients C_{ki}.

(ii) An initial F-matrix, F_o, is assigned arbitrarily.

(iii) The matrix equation (2.3) is solved to find the LCAO coefficients, C_{ki}.

(iv) The P-matrix is computed from equation (2.15).

(v) A new F-matrix is computed from equation (2.12).

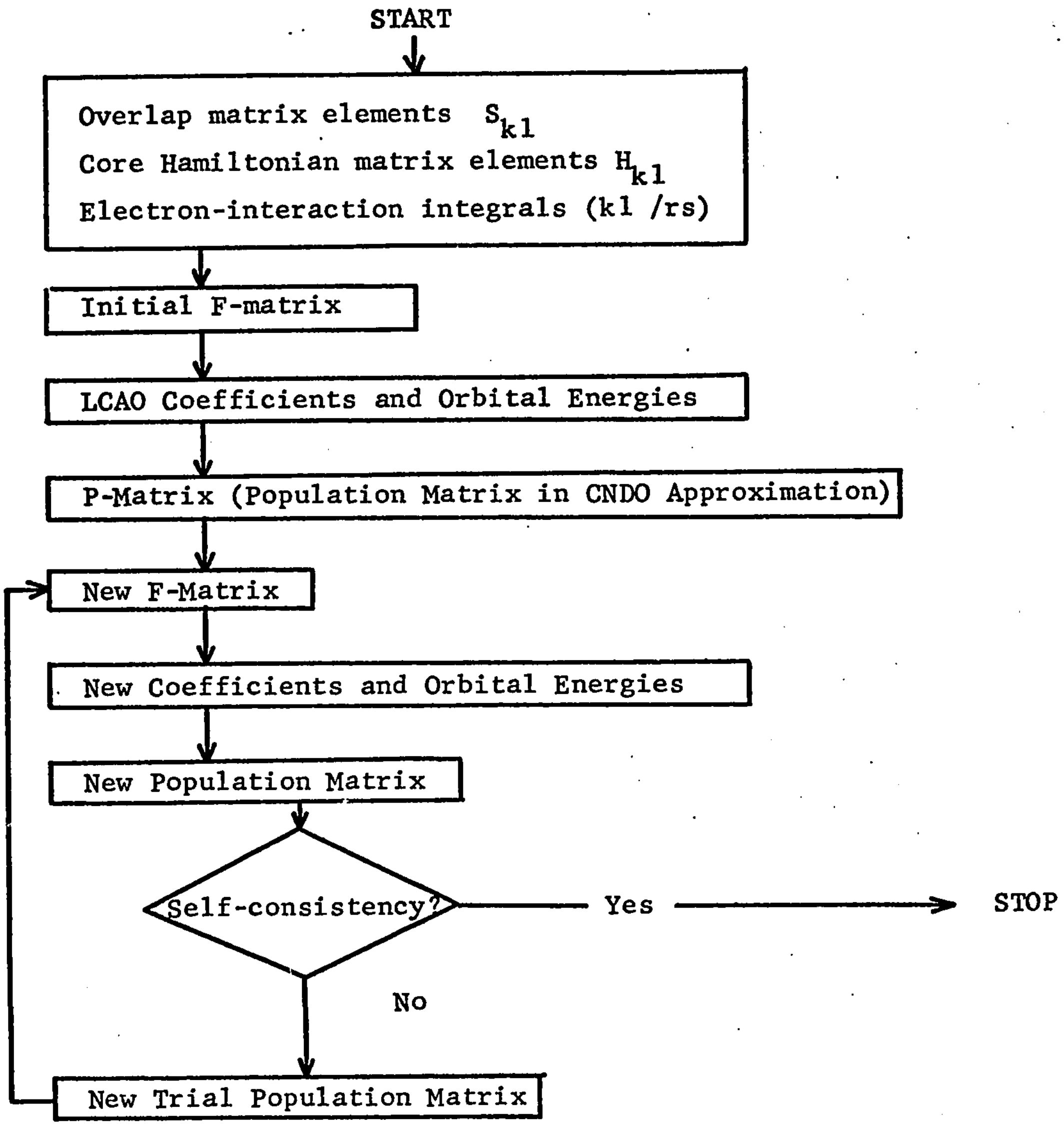
(vi) The C and P matrices are found from the new F.

(vii) The new P-matrix is compared with the previous one. If they do not agree within a specified tolerance, another trial P-matrix is assigned using the previously computed matrix as a guide, and the iterative cycle (Steps v-vii) is repeated.

(viii) After a number of iterations, it will usually be found that two successive P-matrices are identical. The calculation is then said to have converged to self-consistency, and the final result corresponds to a solution of Roothaan's equations.

This iterative method of solution is essentially the same as that

FIGURE 2.1 - ITERATIVE SOLUTION OF ROOTHAAN'S EQUATIONS



used by Hartree[22] for atoms. Each P-matrix corresponds to a charge distribution, and each Hamiltonian matrix to an electrostatic potential field. The physical significance of the iterative cycle, therefore, is that the potential field of successive charge distributions is found, and used to generate new charge distributions. When the calculation has converged, the potential field generates the same charge distribution which produces it. But this is the only physically possible situation, so that the self-consistent field represents a physical solution to the problem.

There is, unfortunately, no rigorous proof that this method of solution will converge in every case. However, the computer programme used to perform the calculations described in this thesis (Appendix C) was found to converge for most molecules considered. The method of selection of the density matrix for each iteration is arbitrary, and different procedures may affect the rate at which the calculation converges, or may even cause it to diverge, but they will not affect the results if, in fact, the calculation does converge, since each solution of the Roothaan equations corresponds to a possible electronic configuration of the molecule, and most molecules with closed-shell ground states do not have low-lying excited states. Adams[49] has shown that the question may be more complicated for open-shell atoms or molecules, which do have such low-lying excited states.

It should be noted that the above remarks would not apply strictly if the coefficient matrix were used as a criterion of convergence, instead of the density matrix, although this might seem an equally valid procedure. The difficulty is that if there are one or more sets of degenerate molecular

10

orbitals, and the matrix C is a solution of equation (2.3), then the matrix C' = CU, where U is a unitary transformation among the degenerate molecular orbitals, will also be a solution. However, the density matrix and the wave function are invariant to any unitary transformation among the doubly occupied molecular orbitals,[27] so that such a transformation has no physical significance. This means that in a calculation in which the orbital coefficients are used as the criterion of convergence, the coefficients may keep changing on successive iterations after the population matrix and wave function have converged, so that orbital coefficients are not a suitable criterion of convergence.

The Roothaan equations have been used extensively in molecular-orbital computations on small molecules.[29,30,39] For an extended basis set, the wave function approaches the Hartree-Fock wave function as the size of the basis set increases,[1,2] since the permitted functional form of the molecular orbitals becomes more and more flexible as the basis approaches completeness. Many calculations, however, have been done with minimum basis sets, in the sense defined in Chapter 1. The expectation values of one-electron operators are well approximated by Hartree-Fock wave functions.[50] Physical properties involving two-electron operators are not so well estimated. In particular, molecular bonding energies, or dissociation energies, are seriously underestimated.[29,30]

The applicability of the Roothaan equations is limited by the extensive computer time and memory required to evaluate and store the electron-interaction integrals. The three- and four-centre integrals cannot be expressed in closed analytic form, but must be evaluated[51] either by numerical integration, or by summation of an infinite series to convergence, both of which are time-consuming procedures even with a computer. Furthermore there are approximately $N^4/8$ such integrals, where N is the number of orbitals in the basis set, so that the computer time and storage space required is proportional to the fourth power of the size of the basis.[30] A recent molecular-orbital calculation, including all electron-interaction integrals, on the molecule B_4H_4, with a minimum basis set of 24 Slater-type orbitals, required 20 hours of computation time on an IBM 7094 computer, mostly for the computation of four-centre integrals.[52]

The time required to evaluate a single integral is reduced for a basis set of Gaussian-type orbitals, for which the three- and four-centre integrals can be evaluated in closed form.[31] The disadvantage of this method is that it has been found necessary to use several Gaussian-type orbitals to approximate the behaviour of a single atomic orbital, so that the size of the basis set required to give a good approximation to the wave function is greatly increased.[30] The use of a Gaussian basis therefore results in only a moderate saving of computer time, and a great increase in computer storage requirements.

In order to reduce the computation involved in the Roothaan method so that it may be extended to larger molecules, it is therefore necessary to eliminate the computation of three- and four-centre electron-interaction integrals from the problem. One possibility is to estimate these integrals using simple approximation formulae,[53] and some authors[38,54] have developed approximate molecular orbital theories using the Mulliken approximation.[55] In this thesis, however, a theory is considered, in which the three- and four-centre integrals are eliminated entirely.

B. THE ZERO-DIFFERENTIAL OVERLAP(ZDO) APPROXIMATION

The electronic-interaction integrals given by equation (2.16) have as integrand a product of two one-electron orbitals and the electrostatic potential-energy operator $(1/r_{12})$. Each one-electron function has the form

$$\phi_k^* (1) \; \phi_1 \; (1) \tag{2.17}$$

called the differential overlap of orbitals k and 1, since its integral over all space is the overlap integral, defined by equation (2.5). Parr[40] proposed the zero-differential-overlap approximation (ZDO), in which the differential overlap is assumed to be zero except when k and 1 refer to the same orbital. It follows that all electron-interaction integrals vanish,[40] except for coulomb integrals of the form

$$g_{kr} = (kk/rr) = \iint \phi_k^* (1) \; \phi_k \; (1) \; \frac{1}{r_{12}} \; \phi_r^* (2) \; \phi_r \; (2) \; d \, V_1 \; d \, V_2 \tag{2.18}$$

representing the electrostatic repulsion between an electron in the k^th^ orbital and one in the r^th^ orbital, and that the overlap integrals are zero for $k \neq 1$. Pople[42] pointed out that it is consistent to neglect both the overlap integrals, representing the magnitude of overlap charge distributions, and the electron-interaction integrals representing their interaction with other charge distributions.

3

The ZDO approximation has been justified[56] by reference to a basis set consisting of symmetrically orthogonalized orbitals, or Lowdin orbitals. These orbitals are defined[47] by the matrix equation

$$\bar{\phi} = \phi\, S^{-1/2} \tag{2.19}$$

where $\bar{\phi}$ is a row vector containing the Lowdin orbitals, ϕ is a row vector containing the original basis orbitals, and $S^{-1/2}$ is a matrix satisfying the equation

$$S^{-1/2}\, S\, S^{-1/2} = I \tag{2.20}$$

where I is the unit matrix.

The basis set defined by equation (2.19) is that orthogonal basis set which most closely resembles the non-orthogonal basis set ϕ, in the sense that the sum of integrals,

$$\sum_i \int \left| \bar{\phi}_i - \phi_i \right|^2 d\,V \tag{2.21}$$

is a minimum.[57] In fact the Lowdin orbitals are similar to the original atomic orbitals, except that each is more localized around the atom on which it is centred.[58] If the Roothaan equations are considered to apply to a basis set of Lowdin orbitals, then the overlap integrals vanish since the new basis is orthogonal. The electron-interaction integrals, except for the coulomb integrals defined by equation (2.18), have been shown to be quite small.[56,58] For a basis set consisting of Lowdin orbitals, therefore, the ZDO approximation is a valid approximation. If this approximation is used with a basis set of ordinary atomic orbitals, it is implicitly assumed that the orbitals are similar enough to the Lowdin orbitals for the approximation to remain reasonable. Adams and Miller[59] have recently shown that, in the case of conjugated hydrocarbons, the Pariser-Parr-Pople theory is improved by transforming all matrix elements so that they refer explicitly to a basis set of Lowdin orbitals, but such a transformation is not usually carried out.[1]

The ZDO approximation has been used extensively in the study of the properties of conjugated organic molecules, together with the pi-electron approximation.[1] Pople[42] described the simplification of the Roothaan equations for the case of a basis consisting of one pi-orbital on each atom, and applied these simplified equations to the study of conjugated hydrocarbons. Pariser and Parr[41] treated the integrals in the simplified equations as empirical parameters, to be given the values leading to best agreement with observed electronic spectra, instead of being calculated directly, so that the method is semi-empirical in the sense of Chapter 1. The Pariser-Parr-Pople theory[41,42] has been used in molecular orbital calculations on a wide variety of conjugated hydrocarbons and heterocyclic molecules.[1] The parameters used in the Pariser-Parr-Pople theory are discussed further in Chapters 3 and 4 in relation to the parameters of the semi-empirical self-consistent field molecular orbital theory for all valence electrons.

Pople, Santry and Segal[43-46] have recently considered the extension of the ZDO approximation to molecular orbital calculations including all valence electrons, and considered its effect on the invariance properties of the wave function.[43] If the Roothaan equations are solved without further approximation, then the determinantal wave function is invariant to all orthogonal transformations of the basis set. Pople et al.[43] showed that this invariance depends on the transformation properties of the one- and two-electron integrals H_{kl} and (kr/ls), defined by equations (2.13) and (2.16) respectively, and that it is not preserved under the ZDO approximation. However, it is possible to make ZDO-type approximations which preserve the invariance of the wave function to orthogonal transformations among atomic orbitals centred on the same atom.[43] There are two types of these atomic transformations:

(i) Rotations of the molecular co-ordinates, or transformations among atomic orbitals of the same azimuthal quantum number (e.g., p_x, p_y, and p_z) on the same atom. Since there is in general no unique choice of axes for a molecule, it is important that any calculated wave function be invariant to such rotations.

(ii) Hybridizations of the atomic orbitals, or transformations among atomic orbitals of different azimuthal quantum number (e.g., s and p). Since it is often useful to discuss chemical bonding in terms of hybrid atomic orbitals, the calculated wave functions should also be invariant to hybridization of the basis set.

It is less important that the wave function be invariant to general transformations among atomic orbitals on different atoms, since non-atomic basis sets are not normally used in descriptions of chemical bonding. Pople, Santry and Segal[43] therefore proposed two methods of formulating the ZDO approximation so as to retain the invariance of the wave function with respect to orthogonal transformations among atomic orbitals on the same atom.

(i) The simplest is that of "complete neglect of differential overlap" (CNDO). In this approximation, all differential overlaps of the form given by equation (2.17) are assumed to be zero, even when the two overlapping orbitals are centred on the same atom. In order to preserve the invariance of the wave function, it is also necessary to make certain further approximations, described in Section C.

(ii) A less drastic approximation is that of "neglect of diatomic differential overlap" (NDDO), in which the differential overlap of two orbitals is assumed to be zero only when they are centred on different atoms. This means that the electron-interaction integrals (kl/rs) are included in the calculations whenever the k^{th} and l^{th} orbitals are centred on one atom, and the r^{th} and s^{th} orbitals are centred on a second atom.

Dahl[60] has shown that the CNDO approximation can be justified by reference to a basis of Lowdin orbitals, although this is not possible for the NDDO approximation.[60] Kaufman[61] also suggested a series of ZDO-type approximations for use in SCF-MO theories including all valence electrons, but did not consider their invariance properties. Ruttink[62] and Manne[38] have considered the invariance properties of SCF-MO theories in which differential overlap is retained, but the electron-interaction integrals are estimated by simple approximation formulae.

In addition to the two levels of approximation proposed by Pople,

17

Santry and Segal,[43] intermediate approximations have been suggested by Dixon,[63] and by Dewar and Klopman.[64] The salient difference between the theories proposed by these authors and the CNDO approximation is the inclusion of one-centre exchange integrals, of the form

$$(kr/kr) = \iint \phi_k^* (1)\, \phi_r (1)\, \frac{1}{r_{12}}\, \phi_k^* (2)\, \phi_r (2)\, d\,V_1\, d\,V_2 \tag{2.22}$$

where k and r are different orbitals of the same atom. These integrals were included by Dixon[63] in order to predict splittings of configurational degeneracies in open-shell molecules, and by Dewar and Klopman[64] to predict accurate heats of formation for hydrocarbons.

Pople and Segal[44,45] have used the CNDO approximation in molecular-orbital calculations on a number of small molecules, and compared the calculated charge distributions, dipole moments, equilibrium configurations and force constants with those obtained from the exact Roothaan equations, as well as with experiment. Santry and Segal[46] have extended this work to molecules containing atoms in the second row of the periodic table, and included the 3d orbitals of these atoms in the basis set. The CNDO approximation has also been used recently to study dipole moments of organic molecules,[65] hyperfine coupling constants in sigma-electron radicals,[66] and the electronic excited states of small molecules,[67] and of benzene and ethylene.[68]

The NDDO approximation has not yet been used in a molecular calculation, but the intermediate approximation with inclusion of one-centre exchange integrals has been used to study small molecules[63], simple

18

hydrocarbons[64] and highly strained hydrocarbons.[69]

In this thesis, molecular-orbital calculations are made using the CNDO approximation, as formulated by Pople and Segal.[45] However, the parameters in the Hamiltonian matrix elements are evaluated by different methods, so that the calculations are in effect made using a different theory. In the next section, the CNDO approximation is described in detail, and in Chapters 3 and 4, the parameters used are discussed.

C. THE COMPLETE NEGLECT OF DIFFERENTIAL OVERLAP (CNDO) APPROXIMATION

In the self-consistent field molecular orbital theory with complete neglect of differential overlap[43] (SCF-MO-CNDO), the following approximations are made to simplify the Roothaan equations:[20]

(i) All integrals containing differential overlaps of the form (2.17), where k and l are different atomic orbitals, are assumed to be zero. Specifically, overlap integrals (2.5) between different orbitals are neglected, and electron-interaction integrals given by equation (2.16) are neglected, except for coulomb integrals g_{kr}, as defined in equation (2.18).

If this approximation alone were made, the Hartree-Fock Hamiltonian matrix elements given by equation (2.12) would be simplified to

$$F_{kk} = H_{kk} + \sum_{r} P_{rr}\, g_{kr} - 1/2\, P_{kk}\, g_{kk} \qquad (2.23)$$

and

19

$$F_{kl} = H_{kl} - 1/2\, P_{kl}\, g_{kl} \qquad (2.24)$$

These equations, however, are not invariant to orthogonal transformations among atomic orbitals on the same atom, so that further modifications must be made.

In order to interpret the diagonal matrix elements given by equation (2.23), the expansion of the one-electron density matrix in terms of basis orbitals, equation (2.14), can be integrated over all space.

$$\int \rho \, d\, V = \sum_r \sum_s P_{rs} \int \phi_r^* \phi_s \, d\, V = \sum_r P_{rr} \qquad (2.25)$$

since the basis orbitals are orthogonal. Equation (2.25) corresponds to a partition of the total electronic charge among the atomic orbitals, so that P_{rr} is the population of the r^{th} orbital, in the sense used by Mulliken,[33] and the P-matrix is called the <u>population matrix</u>. The definition of orbital populations in molecular orbital theories which include overlap is discussed in Chapter 5.

The concept of orbital populations leads to a simple electrostatic interpretation[43] of equation (2.23). F_{kk} is the energy of an electron in the atomic orbital ϕ_k, which is equal to the sum of its energy H_{kk} in the field of its atomic cores, and the electrostatic repulsion due to the electron populations of all the valence-shell orbitals, less one-half the population of the k^{th} orbital itself. This last subtracted term is the contribution of the k^{th} orbital to the exchange charge density,[2] the contributions of other orbitals being omitted in the CNDO approximation.

(ii) The coulomb integrals g_{kr} for all orbitals ϕ_k and ϕ_r, on atoms A and B respectively, are all assigned a common value g_{AB}, characteristic of the atoms only and not of the orbitals themselves. This value g_{AB} represents "an average repulsion between an electron in a valence atomic orbital on A and another in a valence orbital on atom B."[43] It may be seen by considering the case where A and B are the same atom that this assumption is not strictly valid, since the coulomb repulsion energy between two electrons in the same atomic orbital would be expected on physical grounds to be greater than that between two electrons in different orbitals, since electrons in the same orbital have a greater probability of being close to one another. However, Pople, Santry and Segal[43] showed that this approximation is a consequence of the CNDO approximation and the requirement of invariance under orthogonal transformations of atomic orbitals on the same atom. The magnitude of the errors introduced by this approximation for the case when A and B are the same atom will be examined further in the next chapter.

(iii) The diagonal core matrix elements H_{kk}, defined by equation (2.13), are each partitioned into an atomic term U_{kk} and a sum of terms over the other atoms in the molecule.

$$H_{kk} = \int \phi_k^* \left(-\frac{1}{2}\nabla^2 + V_A\right) \phi_k \, dV + \sum_{B \neq A} \int \phi_k^* V_B \phi_k \, dV = U_{kk} + \sum_{B \neq A} V_{AB} \qquad (2.26)$$

U_{kk} is the diagonal matrix element of the k^{th} orbital on atom A with respect to the kinetic energy and to the potential energy of the core of atom A, and may have different values for different orbitals on the same

21

atom, denoted by U_{ss}, U_{pp}, etc. V_{AB} is the interaction of an orbital on atom A with the core of atom B, and must be given the same value for all orbitals on atom A in order to preserve the invariance of the Roothaan equations to atomic transformations.[43] The evaluation of U_{kk} and V_{AB} is considered in Chapters 3 and 4.

(iv) Off-diagonal core matrix elements between orbitals on the same atom are each partitioned into a sum of an atomic term and interatomic terms:

$$H_{kl} = U_{kl} + \sum_{B \neq A} \int \phi_k^* V_B \phi_l \, dV \quad (2.27)$$

where ϕ_k and ϕ_l are both orbitals on atom A. The interatomic terms represent the interaction of an overlap charge distribution with the potential of the core of other atoms, and therefore vanish according to the ZDO approximation. The atomic term U_{kl} is the matrix element of the kinetic energy and the spherically symmetric potential energy of the core of atom A, and is zero when ϕ_k and ϕ_l are eigenfunctions of angular momentum, i.e., pure s, p, d,. . .orbitals. For hybrid orbitals, however, this is not necessarily so.[43] For this reason, the most convenient basis set for computation is a basis set of pure s and p (and d) orbitals. Since the equations have been formulated so as to preserve invariance with respect to hybridization, however, the results may be interpreted in terms of a hybrid basis set.

(v) The off-diagonal core matrix elements between orbitals on different atoms contain the differential overlap of two orbitals as a

22

factor in their integrand. However they cannot be neglected since if they were, the theory would not predict bonding. Furthermore, it is not necessary to neglect them for consistency with the neglect of electron-interaction integrals, since they are not small if evaluated over the Lowdin orbitals, defined by equation (2.19).

These integrals are evaluated by the equation[44]

$$H_{kl} = -\frac{1}{2}(\beta_A^o + \beta_B^o) S_{kl} \tag{2.28}$$

where β_A^o and β_B^o are bonding parameters characteristic of atoms A and B respectively, and S_{kl} is the overlap integral, defined by equation (2.5). The invariance properties of the Roothaan equations in the CNDO approximation are ensured by setting the off-diagonal core matrix elements between all orbitals on a given pair of atoms proportional to the overlap integrals. Actually, the proportionality constant could be allowed to vary with the interatomic distance or the molecular environment.[43] However, in order to test the theory with as few different parameters as possible, Pople and Segal[44] proposed the formula (2.28), in which the proportionality constant between the core matrix elements and overlap integrals depends only on the nature of the two atoms on which the orbitals are centred.

If all the above approximations are made, the matrix elements, equations (2.23) and (2.24) are reduced to the simplified forms[44]

$$F_{kk} = U_{kk} + (P_{AA} - \frac{1}{2} P_{kk})\, g_{AA} + \sum_{B \neq A} (P_{BB}\, g_{AB} + V_{AB}) \tag{2.29}$$

and

$$F_{kl} = -\frac{1}{2}(\beta_A^o + \beta_B^o)\, S_{kl} - \frac{1}{2} P_{kl} \quad g_{AB}, \quad k \neq l \tag{2.30}$$

where the orbitals ϕ_k and ϕ_l are on atoms A and B respectively. P_{AA} is the total valence-shell electronic charge on atom A, defined by

$$P_{AA} = \sum_{k}^{A} P_{kk} \tag{2.31}$$

where the summation extends over all valence-shell orbitals on the atom. All other symbols in equations (2.29) and (2.30) have been defined previously.

For a basis set of pure s and p (and d) orbitals, equation (2.30) applies even when it refers to two orbitals on the same atom, when the first term vanishes, since the orbitals are orthogonal.

The matrix elements given by equations (2.29) and (2.30) have been used in the self-consistent field molecular orbital calculations described in this thesis. With neglect of differential overlap, the secular equations (2.2) reduce to

$$\sum_{l=1}^{n} F_{kl}\, C_{li} = \sum_{l=1}^{n} C_{li} \quad E_i \qquad (k = 1, \ldots, n) \tag{2.32}$$

which is just the eigenvalue problem,

$$F\, C = C\, E \tag{2.33}$$

The orthonormality condition, equation (2.7), is now

$$\sum_{k} \sum_{l} C_{ki}^{*}\, C_{lj}\, \delta_{kl} = \sum_{k} C_{ki}^{*}\, C_{kj} = \delta_{ij} \tag{2.34}$$

or in matrix form,

$$C^{+} C = I \qquad (2.35)$$

A minimum basis set of valence-shell s and p orbitals on atoms other than hydrogen, and 1 s orbitals on hydrogen atoms, has been used. The calculations do not include any d orbitals in the basis set, and have therefore been restricted to molecules in which d orbitals are not needed in simple valence-bond descriptions of the chemical bonding. That is, no calculations have been made on molecules with a transition-metal atom, or on molecules with an atom surrounded by a total of five or more bonds and lone pairs (e.g. PF_5, SF_4).

The next two chapters are devoted to the evaluation of the parameters appearing in the matrix elements defined by equations (2.29) and (2.30). Detailed consideration of these parameters is essential since their values determine quantitatively the calculated molecular orbitals, and therefore the values of physical properties derived from molecular orbital theory. In Chapter 3, the atomic parameters U_{ss}, U_{pp} and g_{AA}, which may be related to atomic spectra, are discussed. Chapter 4 concerns the interatomic parameters parameters g_{AB}, V_{AB}, β_A^o, and S_{kl} , which are defined only with reference to the molecule.

CHAPTER 3

EVALUATION OF ATOMIC PARAMETERS

A. EVALUATION OF PARAMETERS IN MOLECULAR ORBITAL THEORY

There are several different approaches for evaluating the parameters in molecular orbital theory. In accurate calculations,[29,30] in which all electron-interaction terms are included in the Roothaan equations, an explicit basis set is chosen, consisting of atomic orbitals of a specified functional form, such as Slater orbitals,[70] and all the integrals are evaluated explicitly. The simpler integrals can be evaluated analytically, and the more complex integrals computed numerically.[51] The assigned parameters are in the functions chosen as basis orbitals. In the CNDO approximation, however, many terms in the Roothaan equations are neglected, and in order to improve the SCF-MO-CNDO theory, the remaining terms can be modified so as to include the effect of the neglected terms, as well as to correct for errors due to approximating the wave function by a single Slater determinant. The details of these modifications are discussed in this chapter and the next.

Alternatively, all the parameters can be assigned empirically, as in simple molecular-orbital calculations, such as the Huckel theory of pi-electron systems, for which a set of coulomb and resonance "integrals" for different atoms is selected to give the best agreement between calculated and experimental physical and chemical properties for a variety of molecules.[15] Such an approach is not very satisfactory because it has been found that the best parameters depend on:

(i) The properties whose calculated values are compared with experiment. Thus in conjugated hydrocarbons, the estimates of the carbon-carbon resonance integral vary from -1.4 ev. to -3.14 ev., depending on whether the estimate is based on ionization potentials, electron affinities, electronic spectra, <u>or</u> resonance energies.[15]

(ii) The molecule for which the parameters are determined, as can be seen from the wide ranges of the heteroatom parameters surveyed by Streitwieser.[15]

These defects are inherent in the simple Huckel theory which has too few parameters for one set to correctly predict different properties of different molecules. On the other hand, it would not be satisfactory to assign <u>all</u> the parameters empirically in a less approximate theory, such as the SCF-MO-CNDO theory, since the parameters are formally defined as quantum-mechanical integrals. If the parameters were evaluated completely empirically, then the relation of the theory to quantum mechanics would be lost. It is therefore necessary to base the parameters on theoretical arguments, with systematic modifications to allow for correlation and achieve agreement with experiment.

In this thesis, the parameters which can be defined for isolated atoms are evaluated from atomic spectroscopic data, which is thereby used to predict molecular properties. This is the reason for the separate discussion of atomic and interatomic parameters.

Atomic spectroscopic data were first used in a molecular calculation by Moffitt,[71] to predict the electronic spectrum of the oxygen molecule by his method of "atoms in molecules". Pariser and Parr[72,41] used Moffitt's idea to determine parameters in molecular orbital calculations on pi-electron systems of conjugated molecules, and introduced atomic spectroscopic data in the form of valence-state energies.

B. VALENCE-STATE ENERGIES:

A valence state of an atom, as defined by van Vleck,[73] is a state in which the electronic interactions within the atom are the same as those in a molecule.[73-75] Such a valence state would be formed in a hypothetical process in which an atom was removed adiabatically from the molecule, without the central atom being affected. In methane, for example, if the neutral hydrogen atoms were removed, the carbon atom would be left in a valence state with four tetrahedrally hybridized orbitals, each occupied by one electron.[73,75] Ionic valence states are formed by dissociation into ionic products.[74] In the neutral valence state, each carbon orbital is occupied by an electron of opposite spin to the electron on the hydrogen atom, to which the orbital is bonded in the original molecule, but the relative orientation of the electrons in any two carbon orbitals is not fixed by the process of formation of the valence state, so that it is equally probable that two electrons in different orbitals have parallel or opposite spins.[73-75] This random relative orientation of spins is a general property of a valence state, in contrast to a spectroscopic state, which has a definite number of electrons of each spin. Thus a valence state is, in general, a linear combination of several spectroscopic states, and its energy can, in principle, be calculated directly from spectroscopic data.[76,77] Unfortunately, some of the spectroscopic components in the expansion of valence states are highly excited, and have either not been observed, or observed only with doubtful accuracy. Since the energy of a valence state depends on the energies of all its component spectroscopic states, the energies of many valence states either cannot be calculated in this way, or are seriously in error.[78,79]

In order to avoid this problem, Hinze and Jaffe[78,79] expressed both valence and spectroscopic state energies in terms of <u>Slater-Condon parameters</u>, using the multiplet theory of atomic spectra.[7, 24, 80] The Slater-Condon parameters were evaluated by a least-squares fit of calculated spectroscopic state energies with the observed energies. Valence-state energies were then calculated from the Slater-Condon parameters, thereby making use of all available atomic spectral data.[81] Pilcher and Skinner[82] used similar methods to determine valence-state energies for boron, carbon, nitrogen, and oxygen, and obtained almost identical results to those of Hinze and Jaffe.

Hinze and Jaffe[78,79] calculated <u>valence state promotion energies</u>, defined for neutral valence states as

$$P^{o} = E - E^{o} \tag{3.1}$$

where E is the valence-state energy and E^{o} the energy of the spectroscopic ground state of the neutral atom. Similarly for ionic valence states,

$$P^{+} = E - E^{+} \tag{3.2}$$

and $$P^{-} = E - E^{-} \tag{3.3}$$,

where E^{+} and E^{-} are ionic ground state energies.

Valence state ionization potentials, for example, are given by equations of the form

$$I_v = I_g + P^{+} - P^{o} \tag{3.4}$$

I_g is the ground-state ionization potential, and P^{+} and P^{o} the promotion energies of the appropriate valence states. Ground-state ionization potentials, usually obtained by extrapolation from spectral data, are listed by Moore,[81] and may be considered as accurately known. Ground state electron affinities are less accurately known. Hinze and Jaffe used either directly determined experimental values, or values determined by extrapolation of experimental data.

In this work valence state energies are taken from the work of Hinze and Jaffe,[78,79] and introduced into the SCF-MO-CNDO theory following the Pariser approximation, as described in Section C.

C. MOLECULAR ORBITAL PARAMETERS FROM ATOMIC VALENCE STATE ENERGIES

The use of atomic valence state energies to determine parameters in molecular orbital theory is based on a suggestion made by Pariser[72] concerning the pi-electron theory of conjugated hydrocarbons. Pariser considered the hypothetical electron-transfer process:

$$C + C \longrightarrow C^{+} + C^{-} \tag{3.5}$$

in which an electron is transferred between the pi-orbitals of two neutral carbon atoms at infinite distance apart in valence states suitable for pi-bonding. In the pi-electron approximation, the energy of a singly occupied orbital is equal to its ionization potential, while the energy of a doubly occupied orbital is equal to its ionization potential plus the repulsion energy of the two electrons. The energy increase in the process represented by equation (3.5) is then equal to the electrostatic repulsion of two pi electrons in the same orbital, or g_{pp} in the notation of equation (2.18). But the process consists of removing an electron from one carbon atom and transferring it to another, so that the energy increase is the difference of the ionization potential I_p, and the electron affinity A_p, of the p orbital. That is,

$$g_{pp} = I_p - A_p \qquad (3.6)$$

If I_p and A_p are evaluated from the valence-state energies of Hinze and Jaffe for trigonally hybridized carbon,[78,79] then g_{pp} equals 11.13 ev. However, the corresponding integral equals 16.93 ev., for a Slater orbital with an effective nuclear charge of 3.18.[83] This large difference was originally ascribed by Pariser[72] to changes in the energy of the sigma electrons, but other authors[84-88] have stressed the fact that the motion of the two electrons occupying the same orbital in the negative ion is correlated, so that each tends to avoid the other's instantaneous position. In general, the most important correlation effects in an atom or molecule are the pair correlations between electrons in the same orbital.[89] The average distance between the two electrons in the pi-orbital is greater than it would be if their motion were completely independent as assumed in the orbital approximation, so that their electrostatic repulsion energy is less. Dewar and Wulfman,[85] for example, have shown that the empirical value of g_{ii} for carbon can be rationalized by assuming that the electrons remain on opposite sides of the nodal plane of the p orbital. Although this is an over-simplified treatment, it does show the importance of correlation. More detailed treatments of the relative importance of different effects have been given by Orloff and Sinanoglu,[90] Hermann,[91] and Alexander.[92]

In semi-empirical pi-electron calculations, the combined magnitude of both effects is assumed to be the same in molecules and free atoms, and g_{pp} is evaluated from equation (3.6). This parametrization has been highly successful in the molecular orbital theory of pi-electron systems.[1]

In this thesis, a generalization of Pariser's formula is used to determine the atomic parameters of the SCF-MO-CNDO theory for all valence electrons. For a basis set of s and p orbitals, there are four distinct atomic electron-repulsion parameters: g_{ss}, g_{sp}, g_{pp}, and $g_{pp'}$ (where p and p' are two different valence p orbitals of the same atom.) In the CNDO approximation, these are all assigned a common value characteristic of the atom, g_{AA}, which measures the average repulsion of the two valence electrons in atom A.[43]

Oleari et al.[93] evaluated the g_{kl} from valence-state energies, but they did not evaluate the g_{AA} required in the CNDO approximation.

They generalized Pariser's formula and determined C, U_{ss}, U_{pp}, g_{ss}, g_{pp}, and $g_{pp'}$, so that the equation

$$E = C + \sum_k n_k U_{kk} + 1/2 \sum_k \sum_{l \neq k} n_k n_l g_{kl} + 1/2 \sum_k n_k (n_k - 1) g_{kk} \tag{3.7}$$

(where k and l are summed over all valence-shell orbitals on an atom) best fits certain atomic valence-state energies as a function of orbital occupation numbers n_k.

Equation (3.7) is similar in form to the theoretical expression for valence-state energies in the CNDO approximation,[44] except that

(i) It is not invariant to rotation or hybridization (see Section D), and

(ii) The parameters are determined from atomic spectra, and vary markedly with atomic charge.[93] For use in molecular calculations, it is important to evaluate the parameters from the energies of valence states, which are as close as possible to electroneutrality. The constant C is included in equation (3.7) so that the "core state", with all valence electrons removed, is not used in evaluating the parameters. If C were set equal to zero, the core state would be fixed as the zero of energy, and therefore used in determining the parameters.

In this work, the following changes have been made from the procedure of Oleari et al.:

(i) The valence-state energy data of Hinze and Jaffe[78,79] have been used, rather than those of Skinner and Pritchard,[94] since the former are the result of a more complete examination of atomic spectral data, and systematic calculation of Slater-Condon parameters and non-observable states. Also, the energies of all valence states needed are available.[79]

(ii) Parameters for each atom have been evaluated entirely from the valence-state energies of that atom. Oleari et al. adjusted their parameters to vary linearly with atomic number, since they found some valence-state energies by extrapolation.[95] This was unnecessary in the present work since more complete valence state energy data was used. Table (3.2) shows that the assumption of a linear variation with atomic number is not justified in all cases.

(iii) The electron-repulsion integrals, g_{ij}, have been averaged to find the atomic parameter g_{AA} (Section D).

(iv) The atomic core matrix element, U_{ss} and U_{pp}, have been adjusted after the averaging process (Section D).

Equation (3.7) contains seven atomic parameters: core integrals U_{ss} and U_{pp}; electron-repulsion integrals $g_{ss}, g_{sp}, g_{pp}, g_{pp'}$; and an additive constant C. For each atom, the core and electron-repulsion integrals were evaluated by substituting into equation (3.7) the energies of seven valence states, selected according to the following principles:

(i) Each electron-repulsion integral was calculated as the difference between an ionization potential and an electron affinity of the neutral atom, as in Pariser's formula. All valence states used to evaluate the parameters were either neutral, unipositive, or uninegative.

(ii) For each atom, the states chosen formed a set sufficient to evaluate the seven parameters in equation (3.7).

(iii) When conditions (i) and (ii) permitted a further choice of states, valence states with low promotion energies were preferred to highly excited states, as the less excited states resemble more closely the spectroscopic states used to derive the Slater-Condon parameters, and are therefore more accurate.[79]

(iv) Valence states were preferred which resemble the state of the atom in a large number of molecules.

(v) Unipositive valence states were preferred to uninegative states, since the ground-state ionization potentials of most atoms are more accurately known than the ground-state electron affinities.

In Table (3.1), the formulae for the evaluation of the core and electron-repulsion integrals are listed for hydrogen and the atoms in the first row of the periodic table. The formulae for heavier atoms are identical with those for the corresponding first-row atoms. The evaluation of the additive constant C is described below.

D. ATOMIC PARAMETERS IN THE CNDO APPROXIMATION:

As pointed out in Chapter 2, if the full SCF-LCAO-MO equations are simplified by the CNDO approximation, without the additional restrictions necessary for invariance, the diagonal element of the total electronic Hamiltonian for the k^{th} orbital on atom A is given by equation (2.23).

TABLE (3.1)

EVALUATION OF ATOMIC PARAMETERS FROM VALENCE STATE ENERGIES

For hydrogen,

$$g_{ss} = E\ (H^-,\ s^2) - 2\ E(H,\ s) + E\ (H^+)$$

$$U_{ss} = E\ (H,s) - E\ (H^+)$$

For lithium,

$$g_{ss} = E\ (Li^-,s^2) - 2\ E\ (Li,s) + E\ (Li^+)$$

$$g_{sp} = E\ (Li^-,sp) - E\ (Li,s) - E(Li,p) + E(Li^+)$$

$$g_{pp} = E\ (Li^-,\ p^2) - 2E\ (Li,p) + E\ (Li^+)$$

$$g_{pp'} = E\ (Li^-,\ pp) - 2E\ (Li,p) + E\ (Li^+)$$

$$U_{ss} = E\ (Li,s) - E\ (Li^+)$$

$$U_{pp} = E\ (Li,p) - E\ (Li^+)$$

For beryllium,

$$g_{ss} = E\ (Be^-,\ s^2p) - 2E\ (Be,sp) + E\ (Be^+,\ p)$$

$$g_{sp} = E\ (Be^-,\ s^2p) - E\ (Be,sp) - E\ (Be,s^2) + E\ (Be^+,\ s)$$

$$g_{pp} = E\ (Be^-,\ sp^2) - 2E\ (Be,sp) + E\ (Be^+,\ s)$$

$$g_{pp'} = E\ (Be^-,\ spp) - 2E\ (Be,sp) + E\ (Be^+,\ s)$$

$$U_{ss} = E\ (Be,\ sp) - E\ (Be^+,\ p) - g_{sp}$$

$$U_{pp} = E\ (Be,sp) - E\ (Be^+,\ s) - g_{sp}$$

For boron,

$$g_{ss} = E\ (B^-,\ s^2pp) - 2\ E\ (B,\ spp) + E\ (B^+, pp)$$

$$g_{sp} = E\ (B^-,\ s^2pp) - E\ (B, spp) - E\ (B, s^2p) + E(B^+,\ sp)$$

$$g_{pp} = E\ (B^-,\ sp^2p) - 2E\ (B, spp) + E\ (B^+,\ sp)$$

$$g_{pp'} = E\ (B^-,\ sppp) - 2\ E\ (B, spp) + E\ (B^+,\ sp)$$

$$U_{ss} = E\ (B, spp) - E\ (B^+,\ pp) - 2\ g_{sp}$$

$$U_{pp} = E\ (B,\ spp) - E\ (B^+,\ sp) - g_{sp} - g_{pp'}$$

For carbon,

$$g_{ss} = E\ (C^-,\ s^2ppp) - 2\ E\ (C, sppp) + E\ (C^+,\ ppp)$$

$$g_{sp} = E\ (C^-,\ s^2ppp) - E\ (C, sppp) - E\ (C, s^2pp) + E\ (C^+, spp)$$

$$g_{pp} = E\ (C^-,\ sp^2pp) - 2E\ (C, sppp) + E\ (C^+, spp)$$

$$g_{pp'} = E\ (C^-,\ sp^2pp) - E\ (C, sppp) - E\ (C, sp^2p) + E\ (C, spp)$$

$$U_{ss} = E\ (C, sppp) - E\ (C^+, ppp) - 3\ g_{sp}$$

$$U_{pp} = E\ (C, sppp) - E\ (C^+,\ spp) - g_{sp} - 2g_{pp'}$$

For nitrogen,

$$g_{ss} = E\ (N^-,\ s^2p^2pp) - 2E\ (N,\ sp^2pp) + E\ (N^+,\ p^2pp)$$

$$g_{sp} = E\ (N^-,\ s^2p^2pp) - E\ (N,\ s^2ppp) - E\ (N, sp^2pp) + E(N^+,\ sppp)$$

$$g_{pp} = E\ (N^-,\ s^2p^2pp) - 2E\ (N, s^2ppp) + E\ (N^+, s^2pp)$$

$$g_{pp'} = E\ (N^-,\ sp^2p^2p) - 2\ E\ (N,\ sp^2pp) + E\ (N^+,\ sppp)$$

$$U_{ss} = E\ (N, s^2ppp) - E\ (N^+,\ sppp) - g_{ss} - 3g_{sp}$$

$$U_{pp} = E\ (N,\ s^2ppp) - E\ (N^+,\ s^2pp) - 2\ g_{sp} - 2g_{pp'}$$

For oxygen,

$$g_{ss} = E\ (O^-,\ s^2p^2p^2p) - 2E(O, sp^2p^2p) + E\ (O^+, p^2p^2p)$$

$$g_{sp} = E\ (O^-,\ s^2p^2p^2p) - E\ (O, sp^2p^2p) - E\ (O, s^2p^2pp) + E(O^+, sp^2pp)$$

$$g_{pp} = E\ (O^-, s^2p^2p^2p) - 2E\ (O, s^2p^2pp) + E\ (O^+,\ s^2p^2p)$$

$$g_{pp'} = E\ (O^-, s^2p^2p^2p) - 2E\ (O, s^2p^2pp) + E\ (O^+,\ s^2ppp)$$

$$U_{ss} = E\ (O,\ s^2p^2pp) - E\ (O^+, sp^2pp) - g_{ss} - 4g_{sp}$$

$$U_{pp} = E\ (O,\ s^2p^2pp) - E\ (O^+,\ s^2ppp) - 2g_{sp} - g_{pp} - 2g_{pp'}$$

For fluorine,

$$g_{ss} = E\ (F^-,\ s^2p^2p^2p^2) - 2E\ (F,\ sp^2p^2p^2) + E\ (F^+,\ p^2p^2p^2)$$

$$g_{sp} = E(F^-, s^2p^2p^2p^2) - E\ (F, s^2p^2p^2p) - E(F, sp^2p^2p^2) - E(F^+, sp^2p^2$$

$$g_{pp} = E(F^-, s^2p^2p^2p^2) - 2E\ (F, s^2p^2p^2p) + E\ (F^+,\ s^2p^2p^2)$$

$$g_{pp'} = E(F^-,\ s^2p^2p^2p^2) - 2E\ (F, s^2p^2p^2p) + E(F^+,\ s^2p^2pp)$$

$$U_{ss} = E\ (F, s^2p^2p^2p) - E\ (F^+,\ sp^2p^2p) - g_{ss} - 5g_{sp}$$

$$U_{pp} = E\ (F, s^2p^2p^2p) - E\ (F^+,\ s^2p^2pp) - 2g_{sp} - g_{pp}\ 3g_{pp'}$$

If, in addition, the diagonal core matrix elements are partitioned into atomic and interatomic terms, as in equation (2.26), then the diagonal matrix element for the k^{th} orbital is

$$F_{kk} = U_{kk} + \sum_{1} P_{11}\, g_{k1} \left(1 - \frac{1}{2}\delta_{k1}\right) + \sum_{m} P_{mm}\, g_{km} + \sum_{B \neq A} V_{AB} \qquad (3.8)$$

P_{kk} is the electronic population of the k^{th} orbital in the molecule, 1 is summed over all valence orbitals on atom A, and m over all valence orbitals on other atoms, denoted by B. Because of the restrictions needed for invariance of the SCF equations in the CNDO approximation,[43] this must be modified to

$$F_{kk} = U_{kk} + g_{AA} \sum_{1} P_{11} \left(1 - \frac{1}{2}\delta_{k1}\right) + \sum_{m} P_{mm}\, g_{AB} + \sum_{B \neq A} V_{AB} \qquad (3.9)$$

These two equations are not equivalent in general, but the parameters may be chosen so that they are equivalent for a <u>specific charge distribution</u>. In this thesis, the parameters are evaluated by equating the diagonal matrix elements given by equations (3.8) and (3.9), when each atom in a molecule, except for hydrogen, has its valence-shell electron population equally distributed among one s and three p orbitals. In this case equations (3.8) and (3.9) become

$$F_{kk} = U_{kk} + \frac{P_{AA}}{4} \sum_{1} g_{k1} \left(1 - \frac{1}{2}\delta_{k1}\right) + 1/4 \sum_{m} P_{BB}\, g_{km} + \sum_{B \neq A} V_{AB} \qquad (3.10)$$

and

$$F_{kk} = U_{kk} + \frac{7}{8} g_{AA} P_{AA} + \sum_{B \neq A} (P_{BB}\, g_{AB} + V_{AB}) \tag{3.11}$$

respectively, where P_{AA} is the total valence-shell electron population on atom A. The atomic terms are equal for

$$g_{AA}^{k} = \frac{2}{7} \sum_{l} g_{kl} \left(1 - \frac{1}{2} \delta_{kl}\right) \tag{3.12}$$

where the superscript indicates that the matrix element for the k^{th} orbital is used to evaluate g_{AA}. The interatomic terms are dealt with in Chapter 4.

Equation (3.12) averages the intra-atomic valence-shell electron repulsion on an electron in the k^{th} atomic orbital for the given charge distribution, if the spin density in the orbital is zero, as in a closed-shell molecule. There is no reason to prefer the use of any one orbital for the evaluation of g_{AA}, so equation (3.12) is averaged over all orbitals on atom A:

$$g_{AA} = \frac{1}{4} \sum_{k} g_{AA}^{k} = \frac{1}{14} \sum_{k} \sum_{l} g_{kl} \left(1 - \frac{1}{2} \delta_{kl}\right) \tag{3.13}$$

For a basis set of s and p orbitals,

$$g_{AB} = \frac{1}{28} (g_{ss} + 12\, g_{sp} + 3\, g_{pp} + 12\, g_{pp'}) \tag{3.14}$$

The replacement of equation (3.12) by equation (3.13) destroys the equality of the atomic terms in equations (3.10) and (3.11). It is impossible to adjust the parameters, within the framework of the CNDO approximation, so as to restore this equality for all values of P_{AA}. It therefore seems best to restore the equality for the case of an exactly neutral atom, so that in molecules with homopolar bonding, the error is eliminated. In calculations involving all valence-shell electrons, the total valence-shell electron population, P_{AA}, of an exactly neutral atom equals the core charge, Z_A. Equality of the atomic terms will then be restored, in the case of a neutral atom, by adjusting the core matrix elements in equation (3.11), for any value of P_{AA}, to

$$\bar{U}_{kk} = U_{kk} + \frac{Z_A}{4} \left[\sum g_{kl} \left(1 - \frac{1}{2}\delta_{kl}\right) - \frac{7}{2} g_{AA} \right] \tag{3.15}$$

where the bar indicates an adjusted parameter. For s and p orbitals,

$$\bar{U}_{ss} = U_{ss} + \frac{Z_A}{4} \left[\frac{1}{2} g_{ss} + 3g_{sp} - \frac{7}{2} g_{AA} \right] \tag{3.16}$$

and

$$\bar{U}_{pp} = U_{pp} + \frac{Z_A}{4} \left[\frac{1}{2} g_{pp} + g_{sp} + 2g_{pp'} - \frac{7}{2} g_{AA} \right] \tag{3.17}$$

Table (3.2) lists the atomic parameters for hydrogen and the main group elements of the first four rows of the periodic table. The parameter g^*_{AA} is used to evaluate interatomic electron-repulsion integrals, as described in Chapter 4. The additive constant, C^o, is chosen so that valence-state energies are given by an equation similar to equation (3.7) but with the invariance properties required in the CNDO approximation.

$$E = C^o + \sum_k n_k \bar{U}_{kk} + \frac{1}{2} \left(\sum_k n_k \right) \left(\sum_k n_k - 1 \right) g_{AA} \tag{3.18}$$

TABLE 3.2

SEMI-EMPIRICAL ATOMIC PARAMETERS (in ev.)

Element	$\bar{U}_{ss}$	$\bar{U}_{pp}$	g_{AA}	g^*_{AA}	C
H	- 13.595	-	12.848	12.848	13.595
Li	- 4.999	- 3.673	3.469	3.458	4.999
Be	- 15.543	- 12.280	5.935	5.953	25.151
B	- 30.371	- 24.702	8.000	8.048	61.444
C	- 50.686	- 41.530	10.207	10.333	123.517
N	- 70.093	- 57.848	11.052	11.308	204.291
O	-101.306	- 84.284	13.625	13.907	335.908
F	-129.544	-108.933	15.054	15.233	487.697
Na	- 4.502	- 3.247	2.982	3.031	4.502
Mg	- 13.083	- 9.603	4.623	4.656	21.544
Al	- 22.828	- 18.592	5.682	5.680	47.203
Si	- 36.494	- 30.375	6.964	7.015	92.438
P	- 58.610	- 50.940	9.878	9.886	172.095
S	- 66.796	- 58.008	9.205	9.260	227.860
Cl	- 86.774	- 75.681	10.292	10.366	335.847
K	- 3.170	- 3.115	3.702	3.560	3.170
Ca	- 9.842	- 7.696	3.977	3.979	15.707
Ga	- 25.032	- 19.807	5.936	5.942	52.063
Ge	- 35.844	- 29.973	6.608	6.634	92.527
As	- 50.151	- 44.485	8.399	8.361	150.653
Se	- 66.005	- 57.927	9.121	9.156	227.686

TABLE 3.2 cont.

Element	$\bar{U}_{ss}$	$\bar{U}_{pp}$	g_{AA}	g^*_{AA}	C
Br	- 76.413	- 65.412	8.823	8.838	294.760
Rb	- 3.555	- 2.804	2.495	2.384	3.555
Sr	- 9.430	- 7.074	3.749	3.761	15.110
In	- 23.056	- 17.663	5.530	5.582	47.185
Sn	- 26.981	- 21.869	4.297	4.304	72.317
Sb	- 47.427	- 40.923	7.657	7.761	141.347
Te	- 64.464	- 57.144	8.985	9.039	223.174
I	- 76.905	- 69.091	9.448	9.382	301.030

relative to the ground state of the neutral atom. This is chosen as the zero of energy, rather than the core with all valence electrons removed, since the higher ionization potentials of some of the heavier atoms in Table (3.2) are uncertain or unknown. C^o was evaluated, for each atom, by equating the energy of the most stable neutral valence state to its promotion energy.

E. COMPARISON WITH ATOMIC PARAMETERS OF POPLE AND SEGAL

In contrast to the procedure described here, Pople and Segal[44,45] evaluated all electron-repulsion integrals theoretically using the formal definition, equation (2.18). For each atom, g_{AA} was found by evaluating the integral in equation (2.18) with ϕ_k and ϕ_r equal to the same valence-shell Slater s orbital, using integral formulae derived by Roothaan.[96]

In this procedure, no allowance is made for the correlation of electronic motions, or for energy changes associated with the electrons in one atomic orbital, such as the sigma electrons considered by Pariser,[72] due to changes in the population of other orbitals on the same atom.

After evaluating electron-repulsion integrals theoretically they assigned empirical values to the local core matrix elements U_{kk}. In their original theory,[44] they assigned U_{kk} by equating the valence-state ionization potential of the kth orbital to that found from atomic spectra. Later,[45] they revised their method so that the average of the ionization potential and electron affinity of a specified state was given correctly. This is an improvement, since the tendency of atoms to gain and lose electrons is equally well represented.[45]

In order to compare the atomic parameters of Pople and Segal with those in this thesis, atomic valence-state ionization potentials and electron affinities may be determined from equation (3.18) using both sets of parameters, and compared with those determined directly from atomic spectra. In Tables (3.3) and (3.4), these quantities are listed for several valence states of carbon and fluorine, as examples of elements usually participating in relatively homopolar and heteropolar bonds respectively. In some cases, one energy calculated from equation (3.18) corresponds to several valence states, since, in the CNDO approximation, the energies of all valence states with the same number of s and p electrons are the same.[44] The valence state data of Hinze and Jaffe[78,79] show this to be true within 2-3ev. The ionization potentials and electron affinities derived from the parameters in Table (3.2) are accurate within 1 ev, except for the ionization potential, $s^2p^2p^2p \longrightarrow s^2p^2p^2$, of the singly occupied p orbital in fluorine. Those derived from the final parameters of Pople and Segal[45] are in error by several ev., since they are not based on electron-repulsion integrals determined from atomic spectra.

There is another difference between the two sets of parameters. Pople and Segal[44,45] equated g_{AA} to the electron-repulsion integral between two electrons in the same s orbital, g_{ss}, rather than a weighted average of g_{ss}, g_{pp}, g_{sp} and $g_{pp'}$, as in equation (3.14). For theoretical electron-repulsion integrals, this difference is unimportant, since it can

TABLE 3.3

VALENCE-STATE IONIZATION POTENTIALS RECALCULATED FROM ATOMIC PARAMETERS

(in ev.)

Ionization Process	Valence State Ionization Potential		
	From atomic spectra	From parameters in this thesis	From parameters of POPLE and SEGAL[45]
C(sppp → ppp)	21.008	20.065	22.078
C(sppp → spp)	11.269	10.909	13.579
$F(s^2p^2p^2p \rightarrow sp^2p^2p)$	39.389	39.220	45.116
$F(s\,p^2p^2p^2 \rightarrow p^2p^2p^2)$	38.244		
$F(s^2p^2p^2p \rightarrow s^2p^2pp)$	18.109		
$F(sp^2p^2p^2 \rightarrow sp^2p^2p)$	18.514	18.609	23.924
$F(s^2p^2p^2p \rightarrow s^2p^2p^2)$	20.860		

TABLE 3.4

VALENCE-STATE ELECTRON AFFINITIES RECALCULATED FROM ATOMIC PARAMETERS

(in ev.)

Process	Valence State Electron Affinity		
	From atomic spectra	From parameters in this thesis	From parameters of POPLE and SEGAL.[45]
$C(sppp \rightarrow s^2ppp)$	8.917	9.858	6.023
$C(sppp \rightarrow sp^2pp)$	0.345	0.702	- 2.456
$F(sp^2p^2p^2 \rightarrow s^2p^2p^2p^2)$	24.372	24.166	19.428
$F(s^2p^2p^2p \rightarrow s^2p^2p^2p^2)$	3.497	3.555	- 1.764

be shown from the analytical integral formulae of Roothaan[96] that g_{AA}, as given by equation (3.14), equals 0.992 g_{ss}. For most atoms, however, g_{ss} is the highest of the four electron-repulsion parameters derived from atomic spectra, and is quite different from g_{AA}. This may be because an s orbital does not extend as far into space as a p orbital in the same valence shell, so that less correlation is possible between two electrons in an s orbital than in a p orbital, or in two different orbitals. When the g_{ij} are evaluated from atomic spectra, therefore, it is important to evaluate g_{AA} from equation (3.14) instead of equating g_{AA} to g_{ss}.

F. DISCUSSION

The atomic parameters in this thesis are chosen so that, for a specific charge distribution, the atomic terms of the diagonal Hamiltonian matrix elements, which are a measure of the atomic orbital electronegativities in the molecule, have the same values as if g_{ss}, g_{sp}, g_{pp} and $g_{pp'}$ were not given a common value. It is impossible, however, to assign parameters in the CNDO approximation, so that the matrix elements depend on orbital population in the same way as they would without this restriction.

The atomic parameters have been calculated by considering a charge distribution with the valence-shell electrons of each atom equally distributed among the valence orbitals. If only s and p orbitals are considered, this is a rough approximation to the charge distribution in many molecules, so that the parameters obtained are reasonable for molecular calculations. For main-group elements, whose d orbitals are only slightly occupied in many molecules, the inclusion of d orbitals on the same basis as s and p orbitals would be a much worse approximation. The treatment of such d orbitals in a semi-empirical theory is a subject for future research, although Santry and Segal[46] have included d orbitals in their calculations, using theoretical electron-repulsion integrals.

One possible criticism of the procedure described in this chapter is that equation (3.13) is not itself invariant to a change in basis set. It was found for several atoms, however, that g_{AA} varies by only a few tenths of an electron volt, if a hybrid basis set is used in its evaluation, so that the value derived from s-p valence state energies may be used in MO calculations with a basis set of hybrid orbitals. It is better to evaluate the parameters from s-p valence state energies, rather than hybrid orbital valence state energies, because:

(i) the s-p valence-state promotion energies from atomic spectral data are more accurate, and

(ii) as mentioned in Chapter 2, the atomic terms of the off-diagonal elements of the core Hamiltonian matrix between pure s, p, d,.... valence orbitals on the same atom are zero because of symmetry.[43] The off-diagonal matrix elements between hybrid orbitals are not zero, and cannot be evaluated by the procedure of Section D.

CHAPTER 4

EVALUATION OF INTERATOMIC PARAMETERS

Those parameters of the SCF-MO-CNDO theory which are defined only within molecules have no meaning for free atoms, so that they cannot be evaluated from atomic spectra. They can either be evaluated theoretically, or assigned empirical values derived from molecular properties. As discussed earlier (Chapter 3), it is best to combine theoretical and empirical ideas when assigning parameters.

In Sections A and B, the evaluation of the interatomic parameters of the diagonal matrix elements F_{kk} is described: Section A deals with the interatomic electron-electron repulsion integral, g_{AB}; and Section B with the interatomic electron-core attraction integral, V_{AB}. The overlap integrals, S_{kl}, and the bonding parameters, β_A^o, in the off-diagonal core matrix elements, H_{kl}, are dealt with in Sections C and D respectively.

A. INTERATOMIC ELECTRON-ELECTRON REPULSION INTEGRALS

The interatomic electron-electron repulsion integral, g_{AB}, is defined as the average electrostatic repulsion between two electrons in the valence-shell orbitals of two atoms.[43] The repulsion between an electron in the k^th^ orbital of atom A, and one in the r^th^ orbital of atom B is formally defined (Chapter 2) as the integral

$$g_{kr} = (kk/rr) = \int \phi_k^* (1)\ \phi_k (1)\ \frac{1}{r_{12}}\ \phi_r^* (2)\ \phi_r (2)\ d V_1\ d V_2 \qquad (2.18)$$

which may be evaluated for orbitals of a specified functional form. The g_{kr} may then be averaged in some way to evaluate g_{AB}. Pople and Segal[44,45] equated g_{AB}, for each pair of atoms, to the integral defined by equation (2.18) for valence-shell Slater s orbitals, which they evaluated using formulae listed by Roothaan.[96]

The CNDO approximation, however, is analogous to the ZDO approximation in pi-electron theory, which is in better agreement with experiment if the interatomic electron-repulsion integrals, as well as the atomic ones, are reduced below their theoretical values.[1,41] This is necessary because of the correlation between electrons on different atoms.[1,84-86,88,97] The interatomic electron-repulsion integrals in the SCF-MO-CNDO theory have therefore been evaluated by empirical formulae similar to those which have been proved successful in pi-electron theory, with the ZDO approximation.[41,98-100] This procedure is tested by comparing physical properties, calculated using both the empirical and the theoretical interatomic electron-repulsion integrals, with experiment.

In the semi-empirical pi-electron theory, the interatomic electron-repulsion integrals, g_{kr}, are functions of the internuclear distance, and of the atomic electron-repulsion integrals of the two atoms. These functions behave as follows:[41,98-100]

(i) As the internuclear distance approaches zero, the value of g_{kr} for two pi-orbitals of similar atoms approaches the atomic electron-repulsion integral, g_{kk}, for a pi-orbital of either atom, while for dissimilar atoms it approaches the arithmetic mean of the atomic electron-repulsion integrals for the pi-orbitals of the two atoms.

(ii) As the internuclear distance becomes infinite, the effect of correlation becomes small, and each electron-repulsion integral approaches its theoretical value, which is, at infinite distance, the electrostatic repulsion of two point charges.

These conditions may be expressed mathematically as

$$\lim_{R_{AB} \to 0} g_{kr} = 1/2\ (g_{kk} + g_{rr}) \tag{4.1}$$

and

$$\lim_{R_{AB} \to \infty} g_{kr} = \frac{1}{R_{AB}} \tag{4.2}$$

where the k^{th} and r^{th} orbital are on atoms A and B respectively. Pariser and Parr[41] used interatomic repulsion integrals given by

$$g_{kr} = 1/2\ (g_{kk} + g_{rr}) + a\ R_{AB} + b\ R_{AB}^2, \quad R_{AB} \leqslant 2.8\ A \tag{4.3}$$

where the constants a and b were chosen so that g_{kr} is equal to its theoretical value at two distances (2.8 A and 3.7 A), which were considered to be large enough for the correlation effects to be negligible. For internuclear distances larger than 2.8 A, they used theoretical electron-repulsion integrals, since g_{kr}, as defined in equation (4.3), becomes infinite at large internuclear distances. This formula is not satisfactory for all molecules, because the distances 2.8 A and 3.7 A were chosen simply because of their frequent occurrence in conjugated hydrocarbons, and consequently have no general significance. Also, the artificial assumption that correlation effects vanish at distances greater than 2.8 A is due to the inclusion of positive powers of R_{AB}, which prevent equation (4.3) being valid at large internuclear distances.

Several other formulae for the interatomic integrals have been suggested, which have the correct asymptotic behaviour, and can be used at all internuclear distances. Mataga[98] used the formula

$$g_{kr} = \frac{1}{R_{AB}+a} \quad , \quad a = \frac{2}{g_{kk}+g_{rr}} \qquad (4.4)$$

In conjugated molecules,[101] equation (4.4) leads to smaller g_{kr} than the Pariser-Parr formula, equation (4.3). Bloor and Brearley[102] have found that the use of equation (4.4) leads to more accurate predictions of the electronic spectra of alternant hydrocarbons.

Another formula is that of Ohno:[99]

$$g_{kr} = \frac{1}{\sqrt{R_{AB}^2 + a^2}} \quad , \quad a = \frac{2}{g_{kk} + g_{rr}} \qquad (4.5)$$

For conjugated hydrocarbons,[101] equation (4.5) leads to values of g_{kr} about equal to those found from the Pariser-Parr formula, equation (4.3), in the range of R_{AB} for which equation (4.3) is applied. These two formulae provide a representative sample of the values of g_{kr} used in semi-empirical molecular orbital calculations on pi-electron systems.[101]

Miller et al.[103] used theoretical interatomic electron-repulsion integrals, but modified the Slater exponent of the orbitals so that the atomic electron-repulsion integrals agreed with semi-empirical values, derived from atomic spectra. This implies that the effects of correlation, and reorganization of the sigma electrons, may be accounted for by using "effective atomic orbitals" more diffuse than actual atomic orbitals. However, interatomic electron-repulsion integrals evaluated by this method are almost identical[104] to those found from Ohno's formula, and will not be considered separately.

Three different ways of estimating electron-repulsion integrals are compared here:

(i) All the electron-repulsion integrals, both atomic and interatomic, are calculated by evaluating the theoretical integral, equation (2.18), for valence-shell s orbitals, as in the work of Pople and Segal.[44,45]

(ii) Atomic electron-repulsion integrals are evaluated from valence state energies as described in Chapter 3, and interatomic integrals by the Mataga formula,[98] which is here adapted to calculations including all valence electrons.

$$g_{AB} = \frac{1}{R_{AB} + a} \quad , \qquad a = \frac{2}{g^*_{AA} + g^*_{BB}} \tag{4.6}$$

where g^*_{AA} and g^*_{BB} are atomic limits, defined by equation (4.11).

(iii) Atomic integrals are evaluated as described in Chapter 3, and interatomic integrals by Ohno's formula,[99] modified to apply to all valence electrons.

$$g_{AB} = \frac{1}{\sqrt{R_{AB}^2 + a^2}} \quad , \qquad a = \frac{2}{g^*_{AA} + g^*_{BB}} \tag{4.7}$$

In Part B of this thesis, molecular properties are computed, using electron-repulsion integrals evaluated by all three methods. It is shown that methods (ii) and (iii) are significantly better than method (i). This justifies the use of electron-repulsion integrals derived from atomic spectra.

The atomic limits g^*_{AA} and g^*_{BB} of equations (4.6) and (4.7) are derived by slightly modifying the derivation of the atomic electron-repulsion integrals, g_{AA}, in Chapter 3. If the interatomic electron-repulsion terms of equations (3.10) and (3.11) are equated, for a basis of s and p orbitals, and the resulting expression averaged over all orbitals on atom A, it is found that

$$g_{AB} = \frac{1}{16} \sum_{k} \sum_{r} g_{kr} \tag{4.8}$$

where g_{kr} is the electron-repulsion integral between the k^{th} orbital on atom A, and the r^{th} orbital on atom B. At zero internuclear distance, by analogy with equation (4.1),

$$\lim_{R_{AB} \to 0} g_{kr} = \frac{1}{2} \left(g^{A}_{kr'} + g^{B}_{k'r} \right) \tag{4.9}$$

where $g^{A}_{kr'}$ is the electron-repulsion integral between the k^{th} orbital, and the valence-shell orbital r' on atom A, of the same type (s, $p\sigma$, $p\pi$ or $p\pi'$) as the r^{th} orbital on atom B. An analogous definition holds for $g^{B}_{k'r}$.

By substituting (4.9) into the limiting form of (4.8),

$$\lim_{R_{AB} \to 0} g_{AB} = \frac{1}{2} \left(g^{*}_{AA} + g^{*}_{BB} \right) \tag{4.10}$$

where

$$g^*_{AA} = \frac{1}{16} \sum_k^A \sum_l^A g_{kl} = \frac{1}{16} (g_{ss} + 6g_{sp} + 3g_{pp} + 6g_{pp'}) \qquad (4.11)$$

and similarly for g^*_{BB}.

The g^*_{AA} values for the main-group elements of the first four rows of the periodic table are listed in Table (3.2), with the corresponding atomic parameters. In fact, g^*_{AA} and g_{AA} differ by less than 0.2 ev. for all atoms listed, since they are both weighted averages of the orbital parameters g_{kl} , but with different weights. The distinction between the two parameters has been maintained, since there is no advantage in making the further approximation $g^*_{AA} = g_{AA}$.

For the electron-repulsion integral between two hydrogen atoms, equation (4.11) is replaced by

$$g^*_{HH} = g_{ss} \qquad (4.12)$$

For the electron-repulsion integral between a hydrogen atom and another atom, equation (4.11) should formally be replaced by

$$g^*_{AA} = \frac{1}{4} (g_{ss} + 3g_{sp}) \qquad (4.13)$$

for both hydrogen and the other atom. As g_{sp} is not defined for hydrogen, g^*_{AA} has been equated to g_{ss} for hydrogen, and evaluated from equation (4.11) for the other atom. This procedure is justified by the fact that the first approximation raises g_{AB}, and the second lowers it. Also, there is the further advantage that g^*_{AA} has a characteristic value for each element, independent of the other atom B in the electron-repulsion integral g_{AB}.

For theoretical electron-repulsion integrals, it can be shown that g^{*}_{AA}, as defined by equation (4.11), is equal to g_{ss}, so that Pople and Segal are correct in equating them. But for integrals determined from atomic spectra, this is not so, as discussed in Chapter 3 for g_{AA}, and equation (4.11), must be used, except for hydrogen.

B. INTERATOMIC ELECTRON-CORE ATTRACTION INTEGRALS

The interatomic electron-core attraction integral, V_{AB}, is defined as the electrostatic attraction between an electron in a valence-shell orbital of atom A, and the core of atom B.[43] For the k^{th} orbital, it follows from equation (2.26) that

$$V_{AB} = \int \phi^{*}_{k} \; V_B \; \phi_k \; d\,V \tag{4.14}$$

Pople and Segal[44] originally evaluated equation (4.14) for the valence-shell s orbital, using formulae listed by Roothaan.[96] This procedure implies a net electrostatic interaction between an electron on atom A, and the neutral atom B, given by

$$V^{o}_{AB} = V_{AB} + Z_B \, g_{AB} \tag{4.15}$$

The superscript denotes that V^{o}_{AB} refers to the potential of a neutral atom. If the two charge distributions of atoms A and B are spherically symmetric, then V^{o}_{AB} differs from zero entirely because of the mutual penetration of the two charge distributions, and is called a <u>penetration integral</u>.[1,41,45]

Later, Pople and Segal[45] showed that their theory is in better agreement with experiment when penetration integrals are neglected. They showed that for the hydrogen molecule-ion, H_2^+, the errors caused by the neglect of penetration integrals are approximately equal and opposite to those caused by the CNDO approximation. They therefore evaluated the interatomic core-attraction integrals so as to eliminate penetration integrals, i.e.,

$$V_{AB} = - Z_B \, g_{AB} \tag{4.16}$$

The interatomic electron-repulsion integrals described in Section A of this chapter are considerably smaller than the theoretical integrals used by Pople and Segal. Theoretical interatomic core-attraction integrals would imply large effective penetration integrals. Penetration integrals have therefore been eliminated by using equation (4.16) to evaluate all V_{AB}. The diagonal matrix elements given by equation (2.29) are then simplified to

$$F_{kk} = U_{kk} + (P_{AA} - \frac{1}{2} P_{kk}) \, g_{AA} + \sum_{B \neq A} (P_{BB} - Z_B) \, g_{AB} \tag{4.17}$$

and the diagonal core matrix elements in equation (2.26) to

$$H_{kk} = U_{kk} - \sum_{B \neq A} Z_B \, g_{AB} \tag{4.18}$$

C. OVERLAP INTEGRALS

The overlap integral between two orbitals, $\emptyset_k$ and $\emptyset_1$, was defined in Chapter 2 as

$$S_k = \int \emptyset_k^* \, \emptyset_1 \, d \, V \tag{2.5}$$

Overlap integrals are explicitly included in Roothaan's equations, but are eliminated in the CNDO approximation. They do appear, however, in the off-diagonal core-Hamiltonian matrix elements, H_{kl} (equation 2.28).

Overlap integrals can be evaluated for an explicit form of the atomic orbitals.[105] In a central field, every atomic orbital can be expressed as the product of a radial and an angular function

$$\phi^{nlm} = R_{nl}(r)\, Y_{lm}(\theta, \phi) \tag{4.19}$$

where n, l and m are principal, azimuthal and magnetic quantum numbers respectively. The angular function, Y_{lm}, is a spherical harmonic, and for hydrogen-like atoms, R_{nl} has the form

$$R_{nl}(r) = P(r)\, e^{-Zr/na_o} \tag{4.20}$$

where P(r) is an associated Laguere polynomial, Z is the atomic number, and a_o is the Bohr radius. For other atoms, radial functions have been calculated from the self-consistent field theory, using either the Hartree-Fock equations,[7,23] or Roothaan's equations for atoms.[26] Atomic orbitals calculated from the Hartree or Hartree-Fock equations are expressed as numerical tables, and those from Roothaan's equations are linear combinations of a number of basis functions.[26] Several authors[7,70,106-110] have proposed approximate analytical orbitals, which are more convenient for computation. The simplest of these are the Slater orbitals,[70] which have been widely used in molecular orbital calculations.

The radial part of a Slater orbital has the form[70]

$$R_{nl}(r) = N_n r^{n'-1} e^{-Z'r/n'a_o} \tag{4.21}$$

N_n is a normalization constant, and the parameters Z' and n' are chosen to fit more accurate atomic orbitals. From equations (4.20) and (4.21) it can be seen that Z' is an effective atomic number. Slater evaluated it as

$$Z' = Z - s \tag{4.22}$$

where s is a "shielding constant,"[70] which allows for the shielding, or screening, of the nucleus by the electrons in orbitals other than the one considered. Also, n' is an effective principal quantum number. Slater[70] found that s and p orbitals best fit accurate atomic orbitals when n' was given by:

$$\begin{aligned} n' &= n, & n &= 1 - 3 \\ n' &= 3.7, & n &= 4 \\ n' &= 4, & n &= 5 \end{aligned} \tag{4.23}$$

Since the radial functions of Slater orbitals have no nodes,[70] valence-shell orbitals are not orthogonal to inner-shell orbitals. However, as inner-shell orbitals are not treated explicitly in this thesis, this causes no non-orthogonality difficulty.

In this thesis, Slater orbitals are used, with the parameters Z' and n' given by Slater's rules,[70] except for hydrogen. In the hydrogen atom, there is no screening, so $Z'_H = Z_H = 1$, and the Slater orbital is identical to the exact wave function. In the hydrogen molecule, however, it has been found[111] that the lowest energy for an LCAO-MO wave function is obtained for $Z'_H = 1.2$. Also, in accurate molecular calculations for other molecules,[112] using the Roothaan equations, in which the hydrogen exponent has been varied, the value $Z'_H = 1.2$ leads to lower energies than $Z'_H = 1.0$. Physically, this is due to the fact that the contraction of the hydrogen orbital leads to more stable bonding.[113] Pople and Segal[44,45] used $Z'_H = 1.2$, but Hoffmann,[114] in the Extended Huckel theory described in Chapter 5, used $Z'_H = 1.0$. In this thesis both values are used, and a comparison is made on the basis of computed physical properties. It will be shown in Chapter 8 that $Z'_H = 1.2$ is preferred in the semi-empirical SCF-MO-CNDO theory, since it leads to more accurate bonding energies.

Overlap integrals for Slater orbitals, of principal quantum number 1, 2, 3 or 5, may be evaluated analytically by the methods of Mulliken et al.[105] The computation of these integrals is described in Appendix B.

For n = 4, the radial function, equation (4.21), becomes

$$R_4\,(r) = N_4\, r^{2.7}\, e^{-Z'r/3.7a_o} \tag{4.24}$$

Overlap integrals for such an orbital cannot be evaluated analytically, because of the non-integral power of r, which is present as a factor. This difficulty can be avoided by using an approximate orbital, which is a linear combination of orbitals for which overlap integrals can be evaluated. The approximate combination is obtained by assuming that R_4 can be interpolated between R_3 and R_5 in the same way that the corresponding n' is interpolated. Two forms for the approximate orbital were tried:

$$R_4'(r) = N_4^* (0.3\ R_3 + 0.7\ R_5) = N_4'(0.3\ r^2\ e^{-Z'r/3a_o} + 0.7\ r^3\ e^{-Z'r/4a_o}) \tag{4.25}$$

and

$$R_4''\ (r) = N_4''\ (0.3\ r^2 + 0.7\ r^3)\ e^{-Z'r/3.7a_o} \tag{4.26}$$

where the N's are normalization constants. The accuracy of these approximations to equation (4.24) may be examined by computing their overlap with the Slater orbital. The required overlap integrals are one-centre integrals, and can be computed using gamma functions. The overlap integrals of R_4 with R_4' and R_4'' are 0.99651 and 0.99979, respectively, showing that these simple interpolations are quite justified. In computations for orbitals with n = 4, $R_4(r)$ has been replaced by $R_4''(r)$, the more accurate of the two approximations. The value of N_4'' is 1.01384531.

Leifer, Cotton and Leto[115] used series expansions of 8-10 terms each to approximate overlap integrals involving R_4, but the simpler method proposed here should be as good, since R_4'' is such a close approximation to R_4.

D. BONDING PARAMETERS

The bonding parameters, β_A^o, are used to evaluate the off-diagonal core Hamiltonian matrix elements,

$$H_{kl} = \frac{1}{2}\ (\beta_A^o + \beta_B^o)\ S_{kl} \tag{2.28}$$

which are analogous to the core resonance integrals in the Pariser-Parr-Pople theory of pi-electron systems.[1,41] In this section, a theoretical basis for equation (2.28) is given, and the evaluation of the bonding parameters is described.

Equation (2.28) may be approximately derived, using arguments of a type suggested by Mulliken[55] for the evaluation of difficult integrals in molecular orbital theory. H_{kl} is formally defined as

$$H_{kl} = \int \phi_k^* \overset{o}{H}_{core} \phi_l \, dV \tag{2.13}$$

As Ruedenberg[116] pointed out, the orbital ϕ_l can be expanded in the complete set of orbitals, ϕ_k, of atom A:

$$\phi_l = \sum_{k'}^{A} \phi_{k'} S_{k'l} \tag{4.27}$$

The overlap charge distribution is then

$$\phi_k^* \phi_l = \sum_{k'}^{A} \phi_k^* \phi_{k'} S_{k'l} \tag{4.28}$$

Similarly, on expanding ϕ_k in terms of the orbitals of atom B,

$$\phi_k^* \phi_l = \sum_{l'}^{B} \phi_l \phi_{l'}^* S_{kl'} \tag{4.29}$$

Averaging equations (4.28) and (4.29) leads to the identity

$$\phi_k^* \phi_l = \frac{1}{2} \left(\sum_{k'}^{A} \phi_k^* \phi_{k'} S_{k'l} + \sum_{l'}^{B} \phi_l^* \phi_{l'} S_{kl'} \right) \tag{4.30}$$

In the <u>Mulliken approximation</u>,[55,116] the dominant terms of equation (4.30) are assumed to be the ones which are not themselves overlap distributions, so that

$$\phi_k^* \phi_1 = \frac{1}{2} (\phi_k^* \phi_k + \phi_1^* \phi_1) S_{k1} \tag{4.31}$$

Equation (4.31) seems a drastic approximation, but on integration over all space, the errors cancel, and the definition of the overlap integral is obtained. It has been shown that three- and four-centre electron-interaction integrals are fairly well approximated using equation (4.31), or modifications of it.[53]

Substitution of equation (4.31) into the definition of H_{k1}, equation (2.13), gives

$$H_{k1} = \frac{1}{2} (H_{kk} + H_{11}) S_{k1} \tag{4.32}$$

Equation (4.32) is similar to Pople and Segal's form for H_{k1}, equation (2.28), in that the overlap integral S_{k1} is included as a factor.

It differs from equation (2.28), however, in that H_{kk} depends on the orbital for which it is evaluated, as well as on the molecular environment, whereas β_A^o, in the theory of Pople and Segal,[43] is characteristic of the atom A only. In order to transform equation (4.32) to an equation with the same properties as equation (2.28), two further approximations are made.

(i) The interatomic parts of H_{kk} and H_{11} are omitted, so that equation (4.32) becomes

$$H_{k1} = \frac{1}{2} (U_{kk} + U_{11}) S_{k1} \tag{4.33}$$

where U_{kk} and U_{11} are defined by equation (2.26).

(ii) U_{kk} and U_{11} must be averaged over the orbitals on each atom, so that

$$H_{kl} = \frac{1}{2}(U_{AA} + U_{BB})\, S_{kl} \tag{4.34}$$

where the atomic parameter, U_{AA}, is defined as

$$U_{AA} = \frac{1}{4} U_{ss} + \frac{3}{4} U_{pp} \tag{4.35}$$

for a basis set of s and p orbitals. Equation (4.34) has the same form as equation (2.28), with the bonding parameter

$$\beta_A^o = U_{AA} \tag{4.36}$$

Equation (4.34) can be improved, while retaining the transformation properties of equation (2.28), by introducing a multiplicative parameter K to allow for the effect of the terms omitted in deriving equation (4.34), so that

$$H_{kl} = \frac{K}{2}(U_{AA} + U_{BB})\, S_{kl} \tag{4.37}$$

and the bonding parameters are given by

$$\beta_A^o = K\, U_{AA} \tag{4.38}$$

Equation (4.37) is similar to the Wolfsberg-Helmholz approximation,[17] used in the independent-electron theories described in Chapter 5. In these theories, for which overlap is included, K is evaluated empirically, and generally has values between 1 and 2. In the semi-empirical SCF-LCAO-MO theory of Yonezawa et al,[54] which also includes overlap, K is empirically evaluated as 1.1.

It was shown in Chapter 2, however, that in the CNDO approximation, all matrix elements should refer to the basis of Lowdin orthogonalized orbitals, defined by equation (2.19). Lowdin[47] showed that in this basis, H is transformed to the matrix

$$H^{ortho} = S^{-1/2} \cdot H \ S^{-1/2} \qquad (4.39)$$

Since the magnitudes of the overlap integrals, S_{k1}, are less than one, $S^{-1/2}$ may be expanded by the binomial theorem,

$$S^{-1/2} = (I + s)^{-1/2} = I - \frac{1}{2} s + \frac{3}{8} s^2 \ldots\ldots \qquad (4.40)$$

where I is the unit matrix. Substitution of equation (4.40) into equation (4.39) yields

$$H^{ortho}_{k1} = H_{k1} - \frac{1}{2} \Big(\sum_{r \neq k} S_{kr} H_{r1} + \sum_{r \neq 1} H_{kr} S_{r1} \Big) \qquad (4.41)$$

to first order in s. Since the diagonal elements of the core-Hamiltonian matrix are largest in magnitude, then, very approximately,

$$H^{ortho}_{k1} \approx H_{k1} - \frac{1}{2} (H_{kk} + H_{11}) S_{k1} \qquad (4.42)$$

From equations (4.42) and (4.32), H^{ortho}_{k1} is close to zero. If H_{k1} has the form suggested by Pople and Segal, the bonding parameters β^o_A and β^o_B must be much smaller than U_{AA} and U_{BB}. If equation (4.37) is true, K must be much smaller than one.

The above analysis gives the basis for the simple formula (2.28), and indicates that the bonding parameters might obey equation (4.38), for some K less than one. Preliminary calculations, showed, however, that computed physical properties were quite sensitive to variations in K, and that satisfactory results could not be obtained with a single value of K.

This shows that the approximations made in deriving equation (4.38), and equation (4.42), are too drastic for equation (4.38) to be accurate for any K. Also, no provision has yet been made for empirical evaluation of any of the parameters of the theory, using molecular properties. It was therefore decided to evaluate empirical bonding parameters for each element, and then to see how closely equation (4.38) is obeyed.

There are several molecular properties which could be used to evaluate the bonding parameters. In the Pariser-Parr theory of pi-electron systems,[41] the core resonance integral was evaluated using electronic spectra, while Pople[42] was concerned with ground state ionization potentials, electron affinities, resonance energies, and charge distributions. Dewar and Gleicher[117] have pointed out that, in a semi-empirical theory, ground-state properties should be calculated with parameters evaluated from ground-state properties, since the use of parameters evaluated from electronic spectra may include a correction for effects present only in excited electronic states.

In this thesis, ionization potentials, molecular bonding energies, dipole moments, and nuclear quadrupole coupling constants have been computed from the SCF-MO-CNDO theory, as described in Part B. Preliminary calculations showed that the bonding energies are most sensitive to variations in the bonding parameters (Table 4.1). The following procedure was therefore used to evaluate the bonding parameters:

(i) The bonding parameter for hydrogen, β_H^o, was chosen to give the correct dissociation energy for the hydrogen molecule. For hydrogen, the bonding molecular orbital is determined by symmetry to be

$$\psi = \frac{\phi_1 + \phi_2}{\sqrt{2}} \tag{4.43}$$

The dissociation energy, as shown in Chapter 8, is

$$D_e = 2\,\beta_H^o\, S_{12} + \frac{1}{2}\,(g_{12} - g_{11}) \tag{4.44}$$

which may be equated to the experimental value, 4.751 ev. (see Chapter 8) to find β_H^o, for a given choice of the interatomic electron-repulsion integrals, and of the hydrogen exponent (which determines the overlap integral S_{12}).

(ii) The bonding parameters for other elements were chosen to give the correct bonding energies of binary hydrides, AH_n. The binary hydrides were chosen as the reference molecules because they form a series including a molecule for each element of interest. The bonding energy of each hydride, AH_n, was computed for a range of values of the bonding parameter, β_A^o. The details of this calculation, and the variation of the atomization energies with β_A^o, are shown in Chapter 8. In this chapter, the best values of the bonding parameters are of prime interest. Table (4.2) lists these values for each choice of electron-repulsion integrals and hydrogen exponent.

TABLE 4.1

VARIATION OF MOLECULAR PROPERTIES OF HF AND HCl WITH HALOGEN BONDING PARAMETER β_A^o

	HF				HCl			
Physical Property	$\beta_A^o = 20$	19	18	17	10	9	8	ev
Bonding Energy	7.30	6.87	6.44	6.03	5.22	4.66	4.11	ev
First Ionization Potential (π)	16.27	16.24	16.21	16.18	13.19	13.18	13.17	ev
Second Ionization Potential (σ)	16.78	16.64	16.49	16.35	14.27	14.09	13.89	ev
Third Ionization Potential (σ)	37.90	37.79	37.69	37.58	24.98	24.88	24.79	ev
Dipole Moment	1.897	1.897	1.898	1.898	2.058	2.025	1.991	D
Cl^{35} Quadrupole Coupling Constant					85.72	86.02	86.29	Mc/s

Note: SCF-MO Calculations with CNDO Approximation.

Parameters: g_{AA} from Atomic Spectra, g_{AB} from Mataga formula, $Z_H' = 1.2$, $\beta_H^o = 5.4$ ev.

Calculation of Physical Properties Described in Part B.

TABLE 4.2

BONDING PARAMETERS β_A^o (in ev.)

	Code (a)	M1	M2	01	02	R1	R2	PS (b)
Parameter Set	Atomic Parameters	Empirical (c)	Empirical	Empirical	Theoretical (d)	Theoretical	Theoretical	Theoretical
	Interatomic g_{AB}	Mataga (e)	Mataga	Ohno (f)	Ohno	Theoretical (d)	Theoretical	Theoretical
	Hydrogen Exponent Z'_H	1.0	1.2	1.0	1.2	1.0	1.2	1.2
	Evaluation of B_A^o	Empirical(g)	Empirical	Empirical	Empirical	Empirical	Empirical	Pople & Segal(h)
Values of β_A^o	H	4.9	5.4	3.9	4.3	5.4	5.2	9
	Li	0.4	0.7	-0.9	-0.8	2.5	3.8	9
	Be	3.8	4.0	3.2	3.4	4.3	5.2	13
	B	5.8	5.6	5.2	5.0	6.2	6.5	17
	C	8.7	8.2	7.8	7.3	9.1	9.0	21
	N	9.6	8.8	8.0	7.3	11.2	10.6	25
	O	14.2	12.8	11.7	10.5	16.1	14.7	31
	F	19.2	17.2	15.7	14.1	22.6	20.4	39
	Si	5.0	5.2	4.6	4.7			
	P	6.0	6.0	5.3	5.3			
	S	6.7	6.5	5.8	5.6			
	Cl	9.3	8.9	8.1	7.8			

TABLE 4.2 (continued)

Values of β^o_A	Ge	4.3	4.4	3.8	4.0
	As	4.6	4.7	4.0	4.1
	Se	5.7	5.7	5.0	4.9
	Br	7.3	7.2	6.4	6.3
	Sn	3.4	3.6	1.9	2.1
	Sb	4.5	4.7	3.9	4.2
	Te	5.7	6.1	5.1	5.4
	I	6.5	6.7	5.8	6.0

NOTES

(a) Arbitrary code for parameter set.

(b) CNDO/2 Method of Pople and Segal.[45]

(c) From atomic spectra as described in Chapter 3.

(d) From theoretical integral formulae of Roothaan--first row only.

(e) From equation (4.6).

(f) From equation (4.7).

(g) From hydride bonding energies as described in text.

(h) By comparison with minimal-basis set calculations by Roothaan method.

Since the bonding parameter for each element is evaluated with reference to its hydrides, it depends on the value of the hydrogen exponent, so that the results of calculations on molecules, which do not contain hydrogen, depend indirectly on the choice of the hydrogen exponent in the calibration. It will be shown in Chapter 8, however, that the value $Z'_H = 1.2$, and the corresponding bonding parameters, lead to more accurate molecular energies.

The negative bonding parameter for lithium, for interatomic electron-repulsion integrals given by the Ohno approximation, indicates that the arithmetic mean of bonding parameters, used in equation (2.28) for H_{kl}, breaks down in this case. The use of a geometric mean would resolve this particular difficulty, but it would require extensive computation to show that a geometric mean is better for all molecules. Also, the geometric mean does not have a theoretical basis. In this thesis, the arithmetic mean has been used, and the bonding parameter for lithium has been treated like the others, even though it has the wrong sign.

Table (4.2) also lists the Pople-Segal[44] bonding parameters for hydrogen and the first-row elements. The values of Santry and Segal[46] for second-row elements are not included, since they were published after the completion of the work described here. These parameters were chosen by comparing the coefficients of computed molecular orbitals, and the differences between orbital energy eigenvalues, with those obtained by accurate solution of the Roothaan equations for small molecules.[44] They are much larger than the empirical bonding parameters. A detailed comparison of the two sets of bonding parameters for first-row atoms is made in Part B. It is noted here, however, that the empirical values are more consistent with the values of core resonance integrals in pi-electron theories. For carbon, for example, Pople[42] showed that the resonance energy of benzene is correctly given for a carbon-carbon core resonance integral of 2.13 ev. Since the overlap integral between two carbon pi-orbitals at the nearest-neighbour distance in benzene is 0.248,[105] this corresponds to a carbon bonding parameter of 8.6 ev.

Clark and Ragle[118] have recently assigned the value 11.15 ev. for the bonding parameter of carbon in order to fit the electronic spectrum, but they have not proposed a general empirical scheme for the evaluation of bonding parameters, as is done here, nor tested their value in calculations on a wide variety of molecules.

From Table (4.2) the bonding parameters increase with atomic electronegativity, in agreement with equation (4.38), since $\bar{U}_{ss}$ and $\bar{U}_{pp}$ increase similarly, as shown in Table (3.2). A more complete check of equation (4.38) is made in Table (4.3), which contains the values of K_A, defined as

$$K_A = \beta_A^o/U_{AA} \tag{4.45}$$

for each bonding parameter. If equation (4.38) were true, then for a given parameter set, all K_A would be equal. Table (4.3) shows, however, that the K_A vary too widely for equation (4.38) to be useful in evaluating bonding parameters.

The theoretical arguments leading to equation (4.38), however,

TABLE 4.3

VALUES OF K_A

Parameter Set	M1	M2	01	02	R1	R2	PS
H	0.36	0.40	0.29	0.32	0.40	0.38	0.66
Li	0.10	0.17	-0.22	-0.20	0.62	0.95	2.25
Be	0.29	0.31	0.24	0.26	0.33	0.40	0.99
B	0.22	0.21	0.20	0.19	0.24	0.25	0.65
C	0.20	0.19	0.18	0.17	0.21	0.21	0.48
N	0.16	0.14	0.13	0.12	0.18	0.17	0.41
O	0.16	0.14	0.13	0.12	0.18	0.17	0.35
F	0.17	0.15	0.14	0.12	0.20	0.18	0.34
Si	0.16	0.16	0.14	0.15			
P	0.11	0.11	0.10	0.10			
S	0.11	0.11	0.10	0.09			
Cl	0.12	0.11	0.10	0.10			
Ge	0.14	0.14	0.12	0.13			
As	0.10	0.10	0.09	0.09			
Se	0.10	0.10	0.08	0.08			
Br	0.11	0.11	0.09	0.09			
Sn	0.15	0.16	0.08	0.09			
Sb	0.11	0.11	0.09	0.10			
Te	0.10	0.10	0.09	0.09			
I	0.09	0.09	0.08	0.08			

are partially verified by Table (4.3), since for each row of the periodic table, K_A is approximately constant for the more electronegative elements. For the less electronegative elements, it appears that KU_{AA} is small enough so that the terms omitted in deriving equation (4.38) become important. The variations between rows of the periodic table cannot be explained in this way, but must be due to another systematic failure of equation (4.38).

Finally, the fact that all the K_A values, except for lithium and beryllium, are much less than one, confirms the conclusion drawn from equation (4.42) that K should be small if overlap is neglected, since the matrix elements refer to Lowdin orbitals.

CHAPTER 5

EXTENDED HUCKEL THEORY

A. INTRODUCTION

Two different versions of molecular orbital theory, which include all valence electrons, are the SCF-MO-CNDO theory, for which a semi-empirical parametrization has been described in Chapters 3 and 4, and the Extended Huckel Theory (EHT) of Hoffmann,[114] an example of an independent-electron molecular orbital theory. Many of the other approximate all-valence electron theories in the recent literature are modifications of one of these two theories.[63,64,119-124]

In an independent-electron molecular orbital theory, the Hartree-Fock Hamiltonian $\overset{o}{F}$ of Roothaan's equations is replaced by a sum of effective one-electron Hamiltonian operators,[1,15,16]

$$\overset{o}{h}^{\mathrm{eff}} = \sum_{i} \overset{o}{h}{}_{i}^{\mathrm{eff}} \qquad (5.1)$$

The molecular orbitals and their energies are found by solving the secular equations:

$$h\,C = S\,C\,E \qquad (5.2)$$

where h is the matrix corresponding to the one-electron operator $\overset{o}{h}{}_{i}^{\mathrm{eff}}$. The matrix elements, h_{kl} , do not depend on the electronic charge distribution, and it is not necessary to iterate the equations to obtain a self-consistent solution. The advantage of such a theory is that the computation involved is simpler. This was especially important before the availability of digital computers, but even at the present time, the shorter computation times and smaller storage requirements make it possible to apply non-iterative theories to larger molecules than iterative theories. The disadvantage, of course, is that no allowance is made for variation of the matrix elements with molecular charge distribution.

Prior to the introduction of the Extended Huckel Theory,[114] independent-electron theories had been developed to treat some of the electrons in organic molecules and transition-metal complexes. The first was the Huckel theory of pi-electron systems, which was originally applied to ethylene, benzene, and cyclic polyenes,[12] in which the molecular orbitals are determined by symmetry. A general Huckel theory for pi-electron systems was developed by Coulson and Longuet-Higgins,[14] and has recently been reviewed by Streitwieser,[15] and by Salem.[16] In this theory, the diagonal Hamiltonian matrix elements, or Coulomb integrals, are characteristic of each element. The off-diagonal elements, or resonance integrals, between bonded atoms are characteristic of the bonded pair of atoms, and those between non-bonded atoms are neglected. Overlap integrals are also neglected.

Later, independent-electron molecular orbital theories were developed for alkanes and their derivatives. Hall[48] and Brown[125] constructed molecular orbitals from linear combinations of bond orbitals, while Sandorfy[126] developed a Huckel-like theory, in which the basis orbitals are tetrahedral carbon orbitals and hydrogen 1 s orbitals. The overlap and resonance interactions between non-bonded atoms were omitted, as in the pi-electron theory. Alkyl derivatives have been treated similarly to pi-electron systems with heteroatoms.[127,128] Dewar and Pettit,[129] and later Pople and Santry,[130] developed perturbation theories for alkanes, and obtained qualitative results which do not depend on the exact values ofthe Hamiltonian matrix elements.

Molecular orbital theory was first applied to transition-metal complexes by Wolfsberg and Helmholz,[17] who considered the electronic spectra of the chromate, permanganate and perchlorate ions. The extensive literature on this subject is primarily concerned with electronic spectra.[18,19] The high symmetry of many complex ions is used to simplify the secular equations, and to classify the calculated electronic states.

The parameters of Wolfsberg and Helmholz[17] are of interest because they are similar to those of the EHT. The diagonal matrix element, h_{kk}, is defined as

$$h_{kk} = \int \phi_k^* \, h_k^{eff} \, \phi_k \, dV \tag{5.3}$$

where the operator h_k^{eff} acts on an electron in the k^{th} orbital. It represents the energy of an electron in the k^{th} orbital, on atom A, in the field of the nuclei and the other electrons, and it is equated to the valence-state ionization potential of the k^{th} orbital.[17]

Some authors have modified h_{kk} to take into account the charge on atom A, by choosing matrix elements corresponding to an assumed charge,[123,13 or by using an iterative procedure to evaluate the h_{kk}.[19,119,132-135] In the iterative theories, which are not strictly independent-electron theories, h_{kk} is assumed to depend only on the charge of atom A, and not on the charges of other atoms. Only Basch and Gray[124] have included the effects of the charges on other atoms, as in the SCF theory.

The off-diagonal Hamiltonian matrix elements in the Wolfsberg-Helmholz approximation are given by

$$h_{kl} = \frac{K}{2}(h_{kk} + h_{11})\; S_{k1} \qquad (5.4)$$

with K an empirical constant. This equation is analogous to equation (4.32) for the off-diagonal core-Hamiltonian matrix element in the SCF theory, and may be derived similarly. All overlap integrals were included by Wolfsberg and Helmholz. The problem of three- and four-centre electron-interaction integrals does not arise in independent-electron theories, since matrix elements do not depend on the molecular charge distribution.

B. HOFFMANN'S EXTENDED HUCKEL THEORY (EHT)

Hoffmann[114] proposed an independent-electron molecular orbital theory, including all valence electrons of a molecule, and using a basis set consisting of a 1 s orbital for each hydrogen atom, and valence-shell s and p orbitals for each other atom. This is the same basis that is used in the SCF-MO-CNDO theory described in Chapters 2 to 4. Other authors have introduced d orbitals in calculations on such molecules as IF_7,[136] the xenon halides,[137] and metal porphyrins.[132]

Hoffmann[114] used the parametrization of Wolfsberg and Helmholz.[17] He evaluated the diagonal matrix element of the k^th orbital, h_{kk}, as the valence-state ionization potential of the k^th orbital in the neutral atom, using the valence-state energies of Skinner and Pritchard.[94] Off-diagonal matrix elements were given by the Wolfsberg-Helmholz formula, equation (5.4), with K chosen as 1.75, as a "compromise between the desire to match the experimental barrier (to internal rotation) in ethane, and the necessity to work in a region where populations are stable."[114]

The invariance properties of equation (5.4) under atomic transformations of the basis set may be considered using the methods of Pople, Santry and Segal.[43] Since the h_{kk} for all p orbitals of the same atom are equal, equation (5.4) is invariant under rotation, but not under hybridization. Hoffmann himself considered only a non-hybrid basis set of s and p orbitals.[114]

All overlap integrals are included explicitly in the EHT, and are calculated for Slater orbitals as described in Appendix B. The Slater exponent for hydrogen was taken as 1.0 by Hoffmann. The solution of the secular equations with overlap included is described in Section C.

Hoffmann[114] used his Extended Huckel Theory to compute molecular energies, as described in Chapter 8, and molecular charge distributions, using a Mulliken population analysis[33] to assign charges to the various atoms in a molecule. The population analysis is obtained by integrating the expansion of the one-electron density matrix in terms of the basis orbitals, equation (2.14), over all space,

$$\int \rho \, d\,V = \sum_k \sum_l P_{kl} \int \phi_k^* \, \phi_l \, d\,V = \sum_k \sum_l P_{kl} \, S_{kl} \qquad (5.5)$$

The population matrix, Q, is now defined as the matrix product

$$Q = P \, . \, S \qquad (5.6)$$

For real basis orbitals, the matrices P and S are symmetric, so that the elements of Q are given by

$$Q_{kl} = \sum_m P_{km} \, S_{lm} \qquad (5.7)$$

and equation (5.5) may be written as a partition of the electronic charge among the atomic orbitals.

$$\int \rho \, d\,V = \sum_k Q_{kk} \qquad (5.8)$$

where the diagonal elements Q_{kk} are (gross) orbital populations. The (gross) atomic population of an atom, Q_{AA}, is defined as the sum of the Q_{kk} for the orbitals of that atom, and the atomic charge, q_A, is

$$q_A = Z_A - Q_{AA} = Z_A - \sum_k^A q_{kk} \qquad (5.9)$$

where Z_A is the core charge of atom A.

If overlap is neglected, the population matrix Q is identical with the P-matrix, so that in the CNDO approximation, P is referred to as the population matrix, as in Chapter 2.

Mulliken[33] referred to each Q_{kk} as a gross orbital population, which he further partitioned into a net orbital population, and a sum of orbital overlap populations.

$$Q_{kk} = P_{kk} + \sum_{l \neq k} P_{kl} S_{kl} \qquad (5.10)$$

The gross overlap population between two bonded atoms, given by

$$Q_{AB} = \sum_{k}^{A} \sum_{l}^{B} P_{kl} S_{kl} \qquad (A \neq B) \qquad (5.11)$$

is regarded as a measure of the strength of the bond.[33] Hoffmann[114] calculated the gross atomic charge of each atom, and the gross overlap population between each pair of bonded atoms. In the present work, however, the emphasis is on the calculation of observable properties, so that a complete Mulliken population analysis is not made.

A more general type of population analysis, applicable to wave functions calculated from an arbitrary basis set, has recently been proposed by Davidson,[35] but the Mulliken population analysis is satisfactory for the interpretation of wave functions calculated with a minimum basis set of atomic orbitals.

C. SOLUTION OF THE SECULAR EQUATIONS INCLUDING OVERLAP

When overlap integrals are included in a molecular orbital theory, the secular equations are, in matrix form,

$$h\,C = S\,C\,E \qquad (5.2)$$

Equation (5.2) is not an eigenvalue equation because of the presence of the overlap matrix S. Lowdin[47] showed, however, that it can be transformed to to eigenvalue problem in the orthogonalized basis set $\overline{\phi}$, defined by

$$\bar{\phi} = \phi\, S^{-1/2} \tag{2.19}$$

where ϕ is the original basis. In this basis, the transformed Hamiltonian matrix is

$$\bar{h} = S^{-1/2}\, h\, S^{-1/2} \tag{5.12}$$

and the transformed matrix of molecular orbital coefficients is

$$\bar{C} = S^{1/2}\, C \tag{5.13}$$

The overlap matrix for an orthogonalized basis is, of course, the unit matrix. From equations (5.2), (5.12) and (5.13),

$$\bar{h}\,\bar{C} = S^{-1/2}\, h\, C = S^{-1/2}\, S\, C\, E = \bar{C}\, E \tag{5.14}$$

an eigenvalue equation in the new basis.[47] The diagonal matrix, E, of energy eigenvalues is the same as in the original basis.

Equation (5.2) may be solved, therefore, by the following procedure:

(i) the matrix $S^{-1/2}$ is evaluated, as described below.

(ii) the Hamiltonian matrix in the new basis is computed from equation (5.12).

(iii) the eigenvalue equation in the new basis, equation (5.14), is solved.

(iv) the coefficients of the molecular orbitals in the original basis are found from equation (5.13).

Lowdin[47] approximated the matrix $S^{-1/2}$ by the binomial expansion

$$S^{-1/2} = (I + s)^{-1/2} = I - \frac{1}{2}\, s + \frac{3}{8}\, s^2 + \ldots . \tag{5.15}$$

where I is the unit matrix, but it is possible to compute $S^{-1/2}$ exactly.[57] The overlap matrix is Hermitian, so that it may be diagonalized by a unitary transformation.

$$U^{+} S U = D \tag{5.16}$$

where the eigenvalues D_{kk} are positive, since S is positive definite.[138] The diagonal matrix $D^{-1/2}$ can be defined as the matrix with the real elements,

$$(D^{-1/2})_{kk} = (D_{kk})^{-1/2} \tag{5.17}$$

since it satisfies the identity

$$D^{-1/2} D D^{-1/2} = I \tag{5.18}$$

Actually, there is an ambiguity in sign in equation (5.17), so that there are 2^n possible matrices $D^{-1/2}$, but they are all equivalent in the present problem, so all $(D^{-1/2})_{kk}$ are assumed to be positive. Then the matrix $S^{-1/2}$ is given by

$$S^{-1/2} = U D^{-1/2} U^{+} \tag{5.19}$$

which satisfies the definition, equation (2.20).

D. APPLICATIONS

The Extended Huckel Theory, either in its original form, or in one of the modifications described in Section E, has been applied to a wide variety of chemical problems.

Hoffmann calculated the equilibrium geometry of small organic molecules,[114] and the energies of hydrocarbons,[114,139] boron-nitrogen analogues of hydrocarbons,[140] carbonium ions,[141] and chains and rings of carbon atoms,[139] as well as ground and excited states of diazirine and diazomethane.[142] He emphasized stereochemical aspects,[114] such as isomerization energies, barriers to internal rotation, and chair-boat energy differences. He also considered ionization efficiency curves for alkanes,[143] and qualitative interpretations of the population analyses for some molecules.[144,114,140,141]

The topics dealt with by other authors may be roughly classified into molecular energies, chemical reactivity, and physical properties dependent on charge distribution. Calculations of molecular energy have concentrated on stereochemical aspects, as in the work of Hoffmann. Allen and Russell[145] have recently examined the theoretical basis of conformational predictions using the EHT, by comparing the wave functions and orbital energies of small molecules with those calculated using Roothaan's equations, without approximation.

Hoffmann and Lipscomb[138,146] have studied the conformations of boron hydrides, carboranes, and related compounds. Several other inorganic molecules have been studied, including boron and aluminum halides and alkyls,[147,148] IF_7,[136] xenon halides,[137] phosphorus (V) chlorofluorides,[135] and cis- and trans-diimide[149] (N_2H_2). Organic molecules studied using the EHT include α-substituted carboxylic acids,[150] peracids and peresters,[151] and sydnones,[152] as well as a number of molecular complexes, such as the charge transfer complex of tetracyanoethylene and benzene,[153] excimers of hydrocarbons,[154] and hydrogen-bonded species.[155] Also, the electronic spectra of metal porphyrins have been considered by an iterative EHT.[132]

Kato et al.[156,157] have correlated the reactivities of the nitro cation, radical and anion, with the form of the highest occupied molecular orbital. The transition state for nucleophilic substitution in methyl chloride has been calculated using the EHT. Adam and Grimison have predicted the site of nucleophilic substitution in pyridine, quinoline and isoquinoline from the ground-state charge distribution.

Physical properties have also been calculated from the molecular charge distributions of the Extended Huckel Theory. Adam and Grimison[159] have computed the dipole moments of heterocyclic molecules. Correlations of chemical shift with charge distribution have been made by Sichel and Whitehead[160] for alkanes, halogenated alkanes, and molecules containing methyl and vinyl groups; and by Adam and Grimison[158,159] for heterocyclic molecules. Spin-spin coupling constants,[161,162] nuclear quadrupole coupling constants,[163] and hyperfine splittings in electron spin resonance[164] have also been considered. Finally, the vibrational force constants of acetonitrile adducts have been related to gross overlap populations by Purcell and Drago.[165]

E. MODIFICATIONS OF THE EXTENDED HUCKEL THEORY

A number of authors have proposed modifications to the EHT. Although the original theory of Hoffmann[114] is used in this thesis, the modifications which have been proposed are reviewed here, and reasons given for not using them.

Several authors[19,119, 132-135] have varied the diagonal matrix elements, h_{kk}, with the net charge of atom A, on which the k th orbital is centred. This is done to allow for variation of the valence-state ionization potential with charge, and to prevent the accumulation of excess charge density on electronegative atoms.[119] Usually, h_{kk} is assumed to vary linearly with the net charge of atom A, as suggested by Cusachs and Reynolds.[166] In the notation of this thesis,

$$h_{kk} = h^{o}_{kk} + q_A \Delta h_{kk} \tag{5.20}$$

where h^{o}_{kk} is the value of h_{kk} for a neutral atom, q_A is the net atomic charge, and Δh_{kk} can be evaluated empirically, from atomic spectra or otherwise. Veillard and Berthier[167] separated the contributions of different orbitals to the variation in h_{kk}, with

$$h_{kk} = h^{o}_{kk} + \sum_{1}^{A} q_1 (J_{k1} - \frac{1}{2} K_{k1}) \tag{5.21}$$

where the q_1 are orbital charges, and the J_{k1} and K_{k1} are Coulomb and exchange integrals respectively, derived from atomic spectra.

If the h_{kk} are dependent on charge distribution, the secular equations must be solved iteratively, so that the theory has been referred to as the Iterative Extended Huckel Theory[119] (IEHT); equations (5.20) and (5.21) may be compared with equation (2.29), in which the variation of F_{kk} with charge distribution was derived by systematic simplification of the complete Roothaan equations. The most important difference is that in equations (5.20) and (5.21), the matrix elements for the orbitals of one atom are independent of the charges of other atoms. In this respect, the IEHT is similar to the "omega technique"[15,168-170] in pi-electron theory, in which the Coulomb integral for each atom is given by equation (5.20), and is independent of the charges of other atoms.

Streitwieser[15,170] has claimed that the omega technique is an improvement over the Huckel method, since the effect of charge distribution on the Coulomb integrals is included. Baird and Whitehead,[171] however, considered the Coulomb integrals of both the Huckel theory and the omega technique as approximations to the diagonal matrix elements, F_{kk}, of the Pople SCF-MO pi-electron theory,[42] which includes all electron-repulsion integrals. They showed that the variations in Coulomb integrals with charge distribution in the omega technique bear little resemblance in sign, magnitude, or relative order to variations of F_{kk} in the PPP theory, since the interatomic electron-repulsion integrals, g_{kr}, which are neglected in the omega technique are of comparable magnitude to the atomic integrals, g_{kk}. The situation is not improved if the effects of charges on neighbouring atoms only are included.[42] All atoms in the molecule must be included, as in the PPP theory. As Dewar[87] has said,

"If one is going to make allowance for the terms in F_{ii} involving the charge densities q_i, one might as well do the thing properly and use the full Pople expression."

Similar objections can be made against the IEHT. Newton, Boer and

Lipscomb[172] have shown that the diagonal matrix elements in complete minimum-basis SCF-MO calculations are not related in any simple way to atomic charges. If an iterative method is used at all, then it is better to use the full SCF-MO-CNDO equations, as described in Chapters 2 to 4. The non-iterative EHT, however, involves substantially less computation, and therefore may be worthwhile, if it leads to results of comparable accuracy to the approximate SCF theory.

Other authors[137,173-175] have attempted to improve the off-diagonal matrix elements by replacing the arithmetic mean of diagonal matrix elements in equation (5.4) by a geometric mean, so that

$$h_{kl} = K' \sqrt{h_{kk}\, h_{ll}} \quad S_{kl} \tag{5.22}$$

Equation (5.22) does not have the theoretical basis of the Mulliken approximation, but Ballhausen and Gray[173] pointed out that it has the property that the interaction between two orbitals, h_{kl}, decreases when the difference $\left| h_{kk} - h_{ll} \right|$ increases, if the sum $(h_{kk} + h_{ll})$ is constant. This is in accordance with the concept of orbital matching,[176] in which orbitals are best suited for bonding if their energies are not too different. The SCF-MO-CNDO theory automatically includes this feature, since the off-diagonal matrix element, F_{kl}, is given by

$$F_{kl} = \frac{1}{2} (\beta_A^o + \beta_B^o) \quad S_{kl} - \frac{1}{2} P_{kl}\, g_{AB} \tag{2.30}$$

Both terms of equation (2.30) are negative, and if two orbitals are not well matched, the bond order P_{kl} is small, and does not contribute significantly to the interaction F_{kl}. In the EHT, however, h_{kl} is fixed during the calculation, so that the geometric mean might improve the theory, for molecules with polar bonds. It is not used in this thesis, however, since the EHT is only used as a comparison standard for the approximate SCF theory, and the use of an arithmetic mean in both theories provides a more direct comparison.

Cusachs[177] assumed a quadratic dependence on overlap for the kinetic energy part of h_{kl}, so that equation (5.4) should be replaced by

$$h_{kl} = \frac{1}{2}(h_{kk} + h_{ll}) \quad S_{kl}\,(2 - |S_{kl}|) \tag{5.23}$$

Newton[178] showed, however, that kinetic energy integrals for many pairs of orbitals were poorly approximated by Cusachs' formula, and also that Cusachs' original formula was not invariant to rotation. A modified form of Cusachs' formula, which is invariant to rotation, has been used in EHT calculations by some authors.[119,120] Since Newton's first objection still holds however, Cusachs' formula is not used in this thesis.

Newton, Boer and Lipscomb[172] have made a more systematic attempt to improve the matrix elements of the non-iterative Extended Huckel Theory. They evaluated the potential energy integrals by comparison with non-empirical SCF calculations on small molecules, and evaluated kinetic energy integrals exactly. Their method is essentially an attempt to reproduce the results of an SCF calculation by a non-iterative procedure. It is similar to the pi-electron theory of Orloff and Fitts,[179] who evaluated Huckel matrix elements by comparison with Pariser-Parr-Pople calculations. For Newton et al. however, the standard of comparison is the exact non-empirical SCF theory.[172]

In this thesis, physical properties are computed using Hoffmann's original EHT[114] as an example of a non-iterative, independent electron theory for comparison with the SCF-LCAO-MO theory in the CNDO approximation. The Iterative Extended Huckel Theory, as well as Cusachs' formula, were not considered because of the theoretical objections outlined above. The theory of Newton, Boer and Lipscomb is on a sounder theoretical basis, but is not considered here, since Hoffmann's semi-empirical theory provides a better comparison with the semi-empirical SCF theory described in Chapters 2 to 4.

A few minor modifications to Hoffmann's EHT have been made, however, in order to provide a more direct comparison with the SCF theory. Valence state ionization potentials have been taken from the work of Hinze and Jaffe,[78,79] rather than that of Skinner and Pritchard,[94] since the former are more complete and reliable, as explained in Chapter 3. For each element, valence-state ionization potentials were assigned for a valence state typical of the atom in a molecule, as done by Hoffmann.[114,140] The actual values used, and the valence states for which they were evaluated, are listed in Table (5.1). Values of both 1.0 and 1.2 for the Slater exponent of hydrogen were tried, as for the SCF-MO-CNDO theory. Finally, 4s and 4p orbitals, which were not considered by Hoffmann, were approximated by equation (4.26) in order to compute overlap integrals.

TABLE 5.1

ATOMIC VALENCE-STATE IONIZATION POTENTIALS FOR EHT

Element	Valence State (s)	h_{ss}	h_{pp}
H	s	13.595 ev.	--
Li	s,p	5.390	3.543 ev.
Be	sp	9.916	5.958
B	spp	14.916	8.425
C	sppp	21.012	11.273
N	s^2ppp	25.588	13.946
O	$s^2p^2p\underline{p}$	32.297	17.274
F	$s^2p^2p^2\underline{p}$	39.391	20.862
Si	sppp	17.307	9.190
P	s^2ppp	18.612	10.733
S	$s^2p^2p\underline{p}$	21.135	12.396
Cl	$s^2p^2p^2\underline{p}$	25.227	15.037
Ge	sppp	18.578	9.432
As	s^2ppp	17.403	9.359
Se	$s^2p^2p\underline{p}$	20.811	11.675
Br	$s^2p^2p^2\underline{p}$	23.735	13.101
Sn	sppp	16.158	8.326
Sb	s^2ppp	16.255	8.751
Te	$s^2p^2p\underline{p}$	19.733	11.038
I	$s^2p^2p^2\underline{p}$	20.833	12.670

PART B

CALCULATION OF PHYSICAL PROPERTIES

CHAPTER 6

INTRODUCTION

The molecular orbital theories described in part A can be tested by using them to calculate the physical properties of molecules. There are, however, different views in the literature of quantum chemistry on the question of how much the choice of parameters in an approximate theory should be guided by agreement with experiment, and how much by theoretical considerations.

A purely empirical approach is taken, for example, in the Huckel theory of pi-electron systems in unsaturated organic molecules, as outlined by Streitwieser,[15] who recommends values of Coulomb integrals for each element, and of resonance integrals for each type of bond, chosen to provide a good overall fit with experiment. In such a theory, the different parameters are determined independently and have little theoretical basis. They vary with the class of molecules for which they are evaluated, and with the molecular properties used to evaluate them.[15]

The parameters of the Extended Huckel Theory, on the other hand, have some theoretical basis, as described in Chapter 5. The diagonal Hamiltonian matrix elements are found from atomic valence state energies, and the off-diagonal elements from a theoretical equation, equation (5.4), with one empirical constant.[114] Hoffmann, however, has not compared the results of the EHT, in detail, with experiment. Although he has calculated the energies of a large number of molecules, only a limited number of energy differences between isomers and conformations are compared with experiment.[114,139] Hoffmann did not consider the bonding energies of single molecules, as is done in Chapter 8. His many population analyses are not used to determine physical properties, although qualitative correlations with chemical reactivity are made.[114,141] It is very difficult, however, to quantitatively relate chemical reactivity directly to the ground state wave function of a molecule.[180] Other authors have used the EHT wave function to compute molecular properties,[158-165] but often the computed properties are only approximately related to the ground-state wave function, and therefore do not provide a good test of the theory. No systematic comparison of the EHT with experiment has been made using properties which depend directly on the ground state wave function, as is done in this thesis.

In some approximate molecular orbital theories, the primary emphasis is upon agreement with a less approximate theory, rather than with experiment. Orloff and Fitts,[179] for example, derived parameters for the Huckel theory by comparing their molecular orbitals with those calculated using the Pariser-Parr-Pople theory.[41,42] In the non-empirical modification of the Extended Huckel Theory by Newton et al.[172], described in Chapter 5, the basis of comparison is the exact SCF-MO theory, based on Roothaan's equations for a minimum basis set.[20]

Similarly, Pople and Segal[44] determined bonding parameters by comparison of molecular orbitals and orbital energies for small molecules with those of the exact SCF theory, since:

> "The CNDO method should be regarded as an approximation to a full LCAO-SCF calculation using a minimal basis set..... As a number of such calculations have already been carried out for very small molecules without approximation, a reasonable procedure which we follow is to find out how well the simplified method will reproduce the accurate work (with empirical adjustment of a limited number of parameters if necessary) and then, if such 'calibration' is successful, to extend the theory to systems beyond the present range of the full calculations."[44]

In the author's view, however, the test of a theory is agreement with experiment, rather than agreement with other approximate theories. Pople and Segal acknowledge that "the CNDO method.... attempts to reproduce the results of full minimal basis LCAO-SCF calculations which may not themselves give satisfactory agreement with experimental data."[44] In particular, as discussed in Chapter 2, they are quite accurate for one-electron properties,[50] but they are much less so for dissociation or bonding energies.[29,30] Pople and Segal have not, however, modified their bonding parameters to achieve better agreement of computed molecular energies with experiment, as is done in this thesis.

Also, neither Newton et al., nor Pople and Segal, have obtained complete agreement between the results of their approximate theories and the exact solution of Roothaan's equations, so that the approximate theories are not a complete substitute for the exact solution of Roothaan's equations. Since the approximate theory is in complete agreement with neither experiment nor the exact SCF theory, it is better that the parameters be chosen to give partial agreement with experiment than with exact SCF theory.

In this thesis, an intermediate position is taken between the empirical approach of Streitwieser,[15] and the complete dependence on more exact theories, as in the work of Newton et al.,[172] and of Pople and Segal.[44,45] As described in Chapters 3 and 4, the molecular orbital parameters are based on theoretical considerations, and on atomic spectra. When a choice between alternate sets of parameters remains, it is based on an overall comparison of computed molecular properties with experiment, as described in Chapters 7 -10. <u>The greatest reliance is placed on those experimental quantities, which can be calculated from the ground state wave function of a molecule with the fewest subsidiary assumptions</u>. Also, as molecular orbital computations refer to isolated molecules, computed properties are compared with gas-phase experimental data whenever possible, to eliminate the effects of intermolecular, solid-state and solvent interactions.

All calculations were made for molecules in their most stable conformation. Experimental bond lengths and angles were taken from the Tables of Interatomic Distances of the Chemical Society,[181] except for certain molecules for which the required data are not available, and had to be estimated from data for similar molecules. The bond lengths and angles used are listed in Appendix A. No attempt has been made to calculate the most stable conformation of molecules by computing the molecular energy as a function of geometry.

In Chapter 7, calculated molecular orbital energies are compared with experimental ionization potentials, using Koopmans' theorem.[182] In Chapter 8, the atomization energies of molecules are considered, which are given less accurately than ionization potentials by approximate theories, since they represent small differences between two large quantities. They are, however, quite sensitive to variations in the bonding parameters, β^{o}_{A}, and are therefore used to evaluate them, as described in Chapter 4. Dipole moments are considered in Chapter 9. They are directly related to molecular charge distribution, but are less accurate criteria of a theory than energy quantities, since energies are, in general, more accurately calculated in approximate quantum chemical theories than charge distributions. Chapter 10 deals with nuclear quadrupole coupling constants, which also depend upon charge distribution, although less directly than dipole moments. They are, however, of special interest to the author's research colleagues.

The sets of parameters used in the calculations are shown in Table (6.1). For the SCF-MO theory in the CNDO approximation, the empirical bonding parameters, β^{o}_{A} , evaluated from hydride energies, as described in Chapter 4, were compared with those of Pople and Segal. Values of 1.0 and 1.2 for the Slater exponent of hydrogen, Z'_{H}, were compared using empirical β^{o}_{A}'s. Since $Z'_{H} = 1.2$ was found to give more accurate molecular energies for empirical β^{o}_{A}'s, only this value was

TABLE (6.1) PARAMETER SETS FOR COMPUTATION OF MOLECULAR PROPERTIES

SCF-MO Theory in CNDO Approximation	Interatomic g_{AB}	Mataga (Eq. 4.6)	Ohno (Eq. 4.7)	Theoretical (Roothaan integral formulae)
	Atomic g_{AA}	From Atomic spectra (Chap. 3)	From Atomic spectra (Chap. 3)	
Bonding Parameters β_A^o	Z'_H			
Empirical - from hydride energies (Chap. 4)	1.0	M1	01	R1
Empirical - from hydride energies (Chap. 4)	1.2	M2	02	R2
Pople - Segal	1.2	MP	OP	RP*

Extended Huckel Theory: $Z'_H = 1.0$ H 1

$Z'_H = 1.2$ H 2

* Parameters of Pople and Segal.

used with the β_A^o's of Pople and Segal. The electron-interaction integrals were evaluated by the three methods described in Chapter 4. Each set of parameters is denoted for convenience by a code given in Table (6.1) The parameter sets MP, OP, R1, R2, and RP were only used in calculations of molecules containing hydrogen and first-row atoms. It is shown, however, that these parameter sets are inferior to the empirical sets M1, M2, O1, and O2, so that there is no reason to extend them to heavier atoms.

For the Extended Huckel Theory, values of 1.0 and 1.2 for Z_H' are also compared, as shown in Table (6.1).

CHAPTER 7

IONIZATION POTENTIALS

A. KOOPMANS' THEOREM

The ionization potential of a molecule, M, is defined as the energy required to remove one electron from the molecule,[183]

$$I = E(M^+) - E(M) \qquad (7.1)$$

where $E(M)$ and $E(M^+)$ are the energies of the molecule and ion respectively. If equation (7.1) is used to calculate ionization potentials, the SCF-MO equations for the molecule and the ion must be solved separately. This procedure has several disadvantages:

(i) More computation is required, because the SCF-MO equations must be solved twice, and because the equations in Part A apply to closed-shell molecules, and must be modified to apply to open shells.[21,45]

(ii) The parameters evaluated for neutral molecules may not be suitable for calculations on ions, especially in excited states. For example, the parameters of the Pariser-Parr-Pople theory[41,42] which are suitable for the prediction of spectra in neutral pi-electron systems must be modified to give accurate ionization potentials.[184,185]

(iii) Ionization potentials are given by equation (7.1) as a small difference of two large energies, so that small errors in $E(M)$ and $E(M^+)$ may lead to large errors in I, even when both $E(M)$ and $E(M^+)$ are Hartree-Fock energies.[186]

These difficulties can be avoided by evaluating the ionization potentials directly from the molecular wave function, using Koopmans' theorem, according to which the energy required to remove an electron from the ith orbital of a molecule, leaving the nuclei fixed and the orbitals unaltered, is given by

$$I_i = -E_i \tag{7.2}$$

if both the molecular and ionic wave functions satisfy the Hartree-Fock, or the Roothaan, equations.[2,20,182] E_i is the energy eigenvalue of the ith orbital, found by solving the secular equations. Peters[187] has shown that the E_i correspond more closely to experimental ionization potentials than do energies of localized orbitals.

Equation (7.2) indicates that a molecule has a distinct ionization potential for each orbital energy eigenvalue. The first ionization potential corresponds to the removal of an electron from the highest occupied molecular orbital, or set of degenerate orbitals, and the formation of an ion in its ground state. Higher (or inner) ionization potentials correspond to the formation of electronically excited ions by the removal of an electron from a more tightly bound orbital.[188]

The proof of Koopmans' theorem assumes that the removal of an electron from one orbital leaves the orbitals unaltered.[2,182] In fact, the removal of an electron alters the potential acting on the remaining electrons, so that the ion may attain a lower energy if the orbitals are reorganized, leading to ionization potentials lower than those given by equation (7.2).[186,189] Devaquet and Salem[189] have shown that the effect of reorganization is of the order of 0.1 ev. for the first ionization potential of pi-electron systems, by considering the loss of an electron as a perturbation acting on the orbitals. Ruendenberg[190] suggested that the effect of re-organization should be small if the electron removed is only one of many.

The empirical validity of Koopmans' theorem has been examined by Birss and Laidlaw,[186] who used accurate SCF wave functions calculated separately for atoms and ions to show that the amount of re-organization decreases with increasing total number of electrons in the series He, Li, Be. The agreement of Koopmans' theorem with experiment is best for Li, since "No orbital pair correlations are greatly disturbed in the ionization of lithium whereas in helium and beryllium the 1s and 2s electron pair correlations are removed upon ionization." Changes in correlation energy on ionization are of course not accounted for in orbital calculations. On comparing the two closed-shell atoms, however, Koopmans' theorem is more accurate for Be, since there are more electrons in the atom. For all these atoms, Koopmans' theorem leads to more accurate ionization potentials than equation (7.1), when accurate SCF energies are used. Birss and Laidlaw[186] also showed that the validity of Koopmans' theorem is retained if overlap is neglected, both in atoms and in the Pariser-Parr-Pople theory for pyridine.

Koopmans' theorem refers to the vertical ionization process, in which the nuclei remain fixed. This may or may not be identical with the adiabatic ionization process, in which the ion is formed in its ground vibrational state.[183] The two processes are shown in Figures (7.1) and (7.2), for the case of a diatomic molecule. If an electron is removed from a strongly bonding molecular orbital (Figure 7.1), the ion will have a lower bonding energy, and a greater equilibrium internuclear distance, than the molecule. According to the Franck-Condon principle,[183] the ion is more likely to be formed in a vibrational state whose wave function overlaps appreciably with the molecular ground state, with the same nuclear configuration as the molecule (vertical ionization). The calculated orbital energies are compared with vertical ionization potentials, when these are known. If an electron is removed from a weakly bonding or nonbonding orbital, however, the ion and the molecule will have approximately equal equilibrium internuclear distances, so that the vertical and adiabatic processes are the same.[183] (Figure 7.2) Antibonding orbitals are similar to bonding orbitals in this regard, since the loss of an electron is expected to cause a change in bond distance.

The different ionization potentials of a molecule are identified by the irreducible representation of the molecular symmetry group of the ionic state formed, and of the orbital from which an electron is removed. The ground state of a closed-shell molecule belongs to the totally symmetric representation, so that the orbital and the ionic state have the same symmetry.[20] Cotton's notation[191] has been used for symmetry groups and their irreducible representations. For the C_{2v} and D_{2h} groups, the assignment of axes is arbitrary, and standard notation[192] has been used for planar molecules. The only nonplanar molecules of these two symmetry groups

FIGURE 7·1 VERTICAL AND ADIABATIC IONIZATION FROM A BONDING ORBITAL

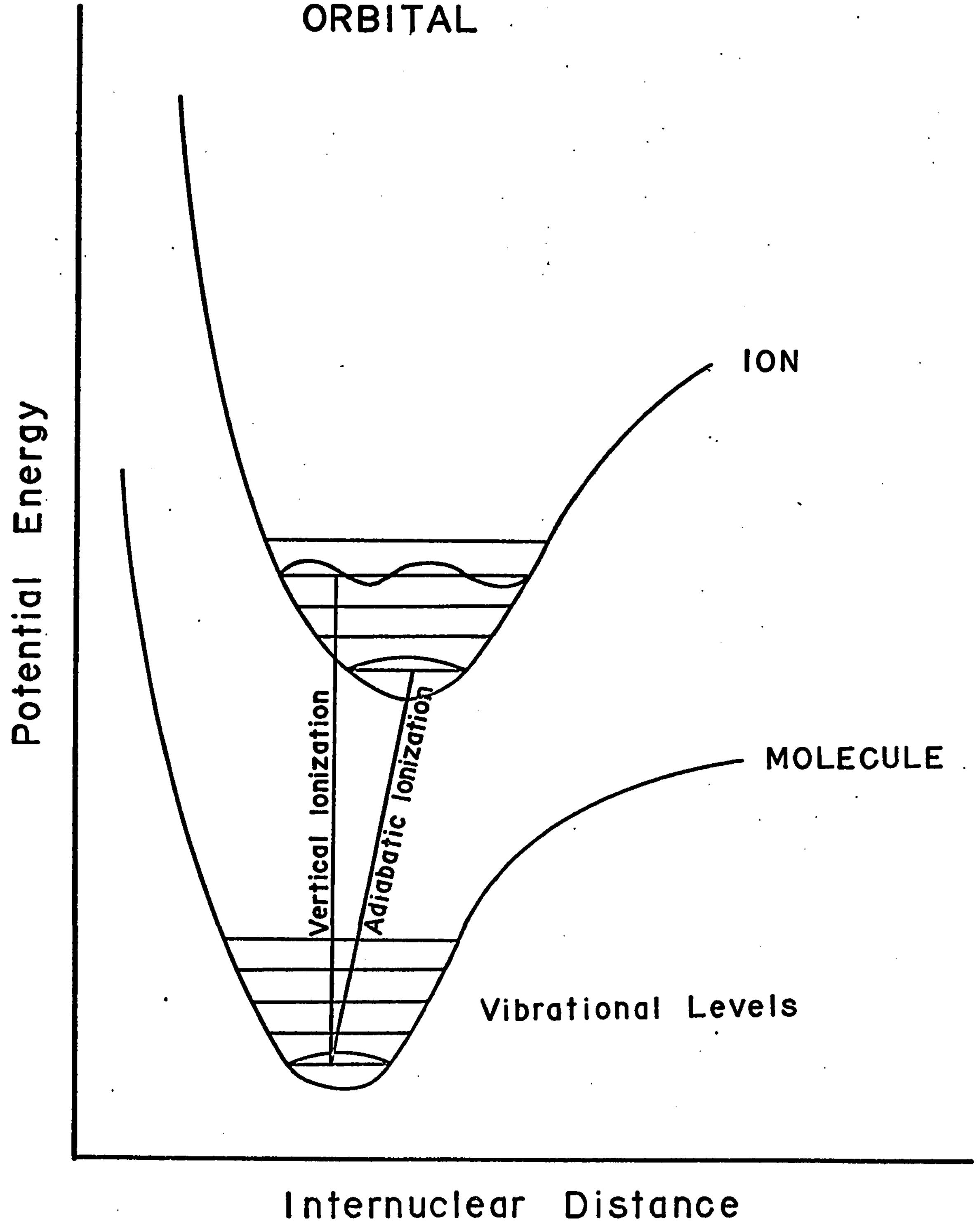
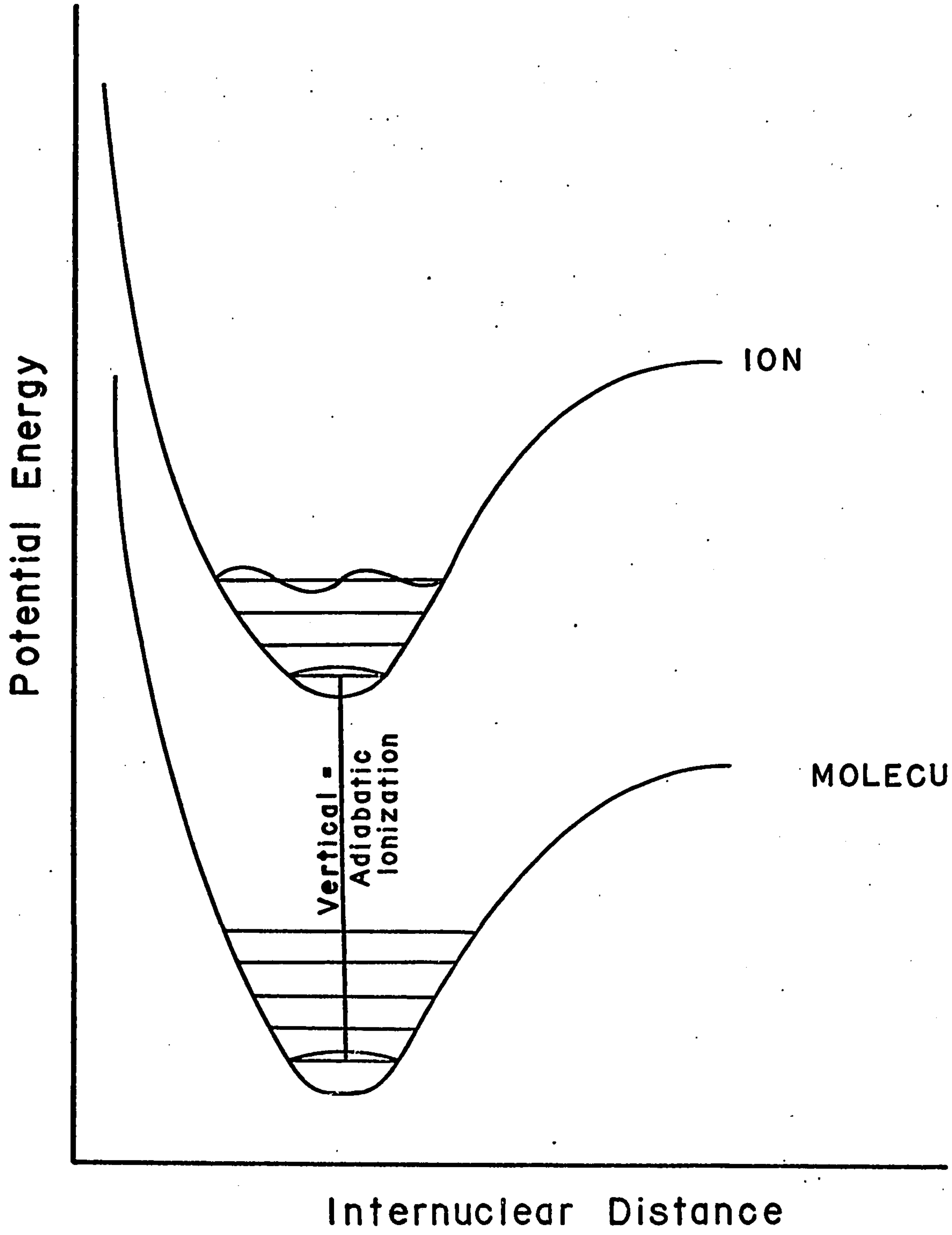


FIGURE 7·2 IONIZATION FROM A NON-BONDING ORBITAL



considered are C_3H_8 and B_2H_6, for which the choice of axes is stated later.

B. EXPERIMENTAL IONIZATION POTENTIALS

There are a number of methods for determining ionization potentials of which the most reliable is photoelectron spectroscopy.[188,193-205] Until recently, ionization potentials were determined by threshold methods, in which the energy of incident electrons or photons is increased until ionization occurs.[188] In electron impact methods such as mass spectrometry,[18 and in the photoionization method of Watanabe,[206] ionization is detected by measuring the positive ion currents. In spectroscopic methods, ionization corresponds to the convergence limit of a Rydberg series of absorption lines. In each case, the ionization threshold is identified as the first ionization potential.

Ionization potentials corresponding to the formation of excited ions have also been detected by threshold methods.[183,207-212] In electron impact, the probability of ionization from a given orbital is proportional to the excess energy of the incident electrons (in the approximate range of 0-50 ev.), so that higher ionization potentials correspond to breaks in the plot of ionization current against incident energy.[183,208-212] In spectroscopic methods, higher ionization potentials correspond to the convergence limits of Rydberg series, other than the one which converges to the first ionization potential.[207]

Some apparent higher ionization potentials determined by threshold methods, however, may correspond to processes such as dissociative ionization, in which the molecule dissociates into fragment ions, and auto-ionization (or pre-ionization), in which excitation to a neutral state of higher energy than the ionic ground state is followed by spontaneous ionization.[183,194] Both of these processes result in the production of positive ions, so that some of the observed "orbital energies" may be spurious.[194]

These difficulties are avoided by the use of photoelectron spectroscopy,[188,193-205] in which molecules are ionized by a monochromatic beam of photons whose energy, 21.21 ev., is greater than the first few ionization potentials of most molecules. The excess energy is carried away by the ejected electrons, whose kinetic energy distribution is observed, as in studies of the photo-electric effect. Dissociative ionization is not observed since only electrons reach the detector, while if auto-ionization occurs, the kinetic energy of the emitted electrons is the same as for the corresponding direct ionization process. The first derivative of the kinetic energy distribution is the photoelectron spectrum, with peaks corresponding to the ionization potentials of the different orbitals. Frost, McDowell and Vroom[202,203] have improved the accuracy of this technique to about 0.01 ev. by using a spherical-grid analyzer to determine the photoelectron-energy distribution.

In this thesis, calculated orbital energies are compared with ionization potentials determined by photoelectron spectroscopy when they are available, and by threshold methods for other molecules.

As discussed earlier (Section A), orbital energy levels should be compared with vertical ionization potentials. If no vibrational structure is resolved, as in electron impact, the observed ionization threshold does not necessarily correspond to either the vertical or the adiabatic ionization process.[183] If vibrational structure is resolved, as in photoelectron spectroscopy, the peak corresponding to the lowest ionization energy gives the adiabatic ionization potential, and the most intense peak corresponds to the vertical ionization potential. Only in the recent work of Turner and May[200] were the intensities obtained accurately enough so that vertical ionization potentials could be determined. For the bonding molecular orbitals of the molecules considered in this paper (CO_2, OCS, CS_2, NNO) the vertical and adiabatic ionization potentials differ by a few tenths of an electron volt.[200] For all other molecules, the ionization potentials determined by photoelectron spectroscopy are adiabatic.

When only the values of the experimental ionization potentials of a molecule are known, the computed energy of the highest occupied molecular orbital is compared with the lowest ionization potential, etc. It is often possible, however, to obtain experimental information about the orbital corresponding to each ionization potential, so that the <u>order</u> of the calculated orbital energies may be confirmed. For example, the electronic state of an ion may be determined by observing its vibrational and rotational spectra.[207,213] In photoelectron spectroscopy the Franck-Condon principle[183] can be used, since significant excitation to higher vibrational levels will be observed only for the ionization of the electron from a strongly bonding or anti-bonding orbital.[194] The corresponding peaks display vibrational structure, therefore, in contrast to the single sharp peak observed for a non-bonding molecular orbital. For small molecules, with not too many distinct levels, this information is often enough to identify the observed ionization potentials with specific orbitals.[193-198] Frost et al.[203] have recently shown that it is possible, in favourable cases, to distinguish bonding from antibonding orbitals, since the peaks corresponding to bonding orbitals have more vibrational structure, due to the asymmetry of the potential well.

In electron impact methods, no information is obtained to facilitate the identification of ionization potentials with orbitals for molecules containing only light atoms. For molecules containing heavy atoms, however, the splitting of degenerate ionic states, due to spin-orbit coupling, can often be resolved since for atoms this splitting is proportional to the fourth power of the atomic number.[80,207] The spin-orbit coupling energy has the form

$$E = a\,\vec{L}\cdot\vec{S} \tag{7.3}$$

where L is the orbital angular momentum, S is the spin angular momentum, and a is an interaction constant. In linear molecules, for example, $^2\pi$ levels are split into $^2\pi_{1/2}$ and $^2\pi_{3/2}$ components.[210] The mean spin-orbit coupling energy is zero, so that the computed orbital energy is compared with the mean of the two observed ionization potentials. The fact that the doublet is resolved, however, indicates that it corresponds to a degenerate pair of orbitals. Frost and McDowell identified the levels of methyl halides[208] and halogens[210] in this way, and have recently confirmed the halogen assignments by photoelectron spectroscopy.[204]

For molecules with many distinct orbital energies in the range observed by photoelectron spectroscopy, molecular orbital theory often predicts groups of orbitals closely spaced in energy, which correspond to a single observed ionization potential. In such cases it is assumed, as has been done by other authors,[64,172] that the observed ionization potential corresponds to several ionic states which have not been resolved.

C. COMPARISON OF CALCULATED ORBITAL ENERGIES WITH IONIZATION POTENTIALS

The energies of occupied molecular orbitals, as calculated by the molecular orbital theories described in Part A, are listed in Tables (7.1) to (7.3) for a number of molecules, and compared with experimental ionization potentials, when these are known. Results calculated using different sets of parameters are listed in different columns, which are identified by the symbols listed in Table (6.1).

Table (7.1) lists orbital energies for molecules containing only hydrogen and first row-atoms, calculated from the SCF-MO-CNDO theory with empirical bonding parameters calibrated using the energies of binary hydrides (Chapter 4). The six columns correspond to the three ways of evaluating electron-repulsion integrals (Chapter 4), and the two choices of the Slater exponent for hydrogen, (1.0 and 1.2). For a few molecules, no results are listed in certain columns, since the iterative calculation did not converge to self-consistency.

TABLE 7.1

SCF-MO ORBITAL ENERGIES (in ev.) OF FIRST-ROW MOLECULES USING CNDO APPROXIMATION AND EMPIRICAL BONDING PARAMETERS

Parameter Set		M1	M2	01	02	R1	R2	Exptl. IP.	Reference
$H_2(D_{\infty h})$	σ_g	-14.69	-14.69	-15.44	-15.44	-18.07	-18.62	15.45	199
$LiH(C_{\infty v})$	σ	- 8.10	- 8.09	- 7.89	- 7.90	- 9.95	- 9.94	(7.81-7.91)	214
$BeH_2(D_{\infty h})$	σ_u	-11.11	-11.41	-11.51	-11.77	-13.01	-13.43		
	σ_g	-13.07	-12.74	-13.10	-12.83	-15.12	-14.79		
$BH_3(D_{3h})$	e'	-11.79	-12.11	-12.59	-12.85	-14.38	-14.89	11.4	215
	a_1'	-18.39	-17.73	-18.40	-17.78	-21.26	-20.54		
$CH_4(T_d)$	t_2	-12.32	-12.70	-13.21	-13.50	-15.03	-15.64	12.99	198,212
	a_1	-24.37	-23.51	-24.19	-23.40	-27.14	-26.16	(24)	
$NH_3(C_{3v})$	a_1	-12.29	-12.45	-13.18	-13.30	-15.09	-15.47	10.35	205
	e	-13.27	-13.56	-13.95	-14.20	-16.12	-16.58	14.95	
	a_1	-27.55	-27.07	-27.07	-26.71	-31.10	-30.50		

TABLE 7.1 (continued)

Parameter Set		M1	M2	O1	O2	R1	R2	Exptl. I.P.	Reference
$H_2O(C_{2v})$	b_1	-13.96	-14.11	-14.21	-14.33	-17.68	-17.90	b_1 12.61	198
	a_1	-13.79	-14.03	-14.70	-14.88	-16.81	-17.25	14.23	
	b_2	-14.41	-14.68	-15.13	-15.36	-17.43	-17.85	18.02	
	a_1	-32.93	-32.69	-32.69	-32.51	-36.14	-35.84		
HF $(C_{\infty v})$	π	-16.04	-16.19	-16.57	-16.67	-20.59	-20.85	π 16.06	204
	σ	-16.16	-16.38	-17.12	-17.30	-19.71	-20.14	σ 16.48	
	σ	-37.66	-37.60	-37.93	-37.88	-42.89	-42.91		
$N_2(D_{\infty h})$	σ_g	-13.75	-13.57	-14.38	-14.25	-16.62	-16.49	σ_g 15.58	203
	π_u	-13.84	-13.62	-14.64	-14.44	-16.51	-16.34	π_u 16.70	
	σ_u	-23.01	-23.15	-23.31	-23.46	-25.86	-25.94	σ_u 18.80	
	σ_g	-30.68	-30.23	-30.06	-29.65	-34.33	-34.00		

TABLE 7.1 (continued)

Parameter Set		M1	M2	01	02	R1	R2	Exptl. IP.	Reference
CO($C_{\infty v}$)	σ	-13.43	-13.20	-13.97	-13.81	-16.16	-15.94	σ 14.00	199
	π	-14.03	-13.76	-14.68	-14.40	-17.07	-16.88	π 16.54	
	σ	-20.78	-20.83	-20.53	-20.53	-23.00	-22.97	σ 19.65	
	σ	-33.91	-33.40	-33.62	-33.15	-36.90	-36.50		
CO_2($D_{\infty h}$)	π_g	-13.66	-13.78	-14.47	-14.55	-17.15	-17.34	π_g 13.79	200,196
	π_u	-16.51	-16.26	-17.07	-16.83	-20.68	-20.51	π_u 17.59	
	σ_u	-13.91	-13.58	-14.85	-14.55	-16.66	-16.38	σ_u 18.07	
	σ_g	-20.63	-20.69	-21.02	-21.01	-23.30	-23.26	σ_g 19.36	
	σ_u	-34.04	-33.73	-34.08	-33.81	-37.64	-37.43		
	σ_g	-35.07	-34.67	-34.81	-34.46	-38.46	-38.18		
NNO($C_{\infty v}$)	π	---	---	-13.52	-13.58	-15.70	-15.81	π 12.90	200,196
	σ			-15.59	-15.35	-18.03	-17.88	σ 16.40	
	π			-16.89	-16.63	-20.38	-20.18	π 18.14	
	σ			-23.66	-23.83	-26.09	-26.22	σ 20.08	
	σ			-29.85	-29.54	-34.17	-33.93		
	σ			-34.73	-34.33	-39.21	-38.82		

TABLE 7.1 (continued)

Parameter Set		M1	M2	O1	O2	R1	R2	Exptl. IP.	Reference
$O_3(C_{2v})$	a_2	-13.98	-14.35	-14.31	-14.59	--	--	12.3	197
	a_1	-14.59	-14.72	-15.11	-15.20			12.52	
	b_2	-14.65	-14.75	-15.12	-15.20			13.52	
	b_1	-16.39	-16.18	-17.13	-16.85			16.4-17.4	
	b_2	-18.27	-18.11	-18.45	-18.19			$\left.\right\}$ 19.24	
	a_1	-18.81	-18.67	-18.54	-18.34				
	a_1	-29.84	-30.10	-30.46	-30.70				
	b_2	-33.40	-33.24	-33.43	-33.32				
	a_1	-39.34	-38.78	-38.41	-37.88				
$C_2H_2(D_{\infty h})$	π_u	-10.64	-10.49	-11.54	-11.38	-13.07	-13.09	π_u 11.40	201
	σ_g	-12.15	-12.33	-12.82	-12.94	-14.52	-14.88	σ_g 16.44	
	σ_u	-18.19	-18.20	-18.66	-18.63	-20.52	-20.59	σ_u 18.42	
	σ_g	-24.80	-24.20	-24.78	-24.19	-26.96	-26.57		

TABLE 7.1 (continued)

Parameter Set		M1	M2	O1	O2	R1	R2	Exptl. I.P.	Reference
$C_2H_4(D_{2h})$	b_{3u}	-10.41	-10.30	-11.23	-11.11	-12.69	-12.72	$b_{3u}(\pi)$ 10.48	194
	b_{3g}	-10.47	-11.10	-11.43	-11.95	-12.79	-13.61	12.50	
	a_g	-11.65	-11.63	-12.39	-12.36	-14.04	-14.21	14.39	
	b_{2u}	-14.64	-14.73	-15.21	-15.25	-17.51	-17.77	15.63	
	b_{1u}	-19.13	-19.14	-19.54	-19.48	-21.58	-21.61	(19.13)	
	a_g	-26.40	-25.43	-26.01	-25.12	-28.78	-27.90		
$C_2H_6(D_{3d})$	e_g	-10.73	-11.32	-11.76	-12.26	-13.24	-14.06	11.49	194,198
	a_{1g}	-11.36	-11.32	-12.12	-12.07	-13.55	-13.76		
	e_u	-14.05	-14.18	-14.72	-14.81	-16.91	-17.26	14.74	
	a_{2u}	-20.25	-20.22	-20.61	-20.52	-22.77	-22.80	(20.13)	
	a_{1g}	-27.36	-26.04	-26.76	-25.60	-29.96	-28.60		

TABLE 7.1 (continued)

Parameter Set		M1	M2	O1	O2	R1	R2	Exptl. IP.	Reference
$C_3H_8(C_{2v})$	b_1	-10.31	-10.93	-11.38	-11.93	-12.75	-13.63	11.07	194,198
	b_2	-10.48	-10.64	-11.36	-11.47	-12.63	-13.00		
	a_1	-10.66	-10.96	-11.56	-11.83	-12.92	-13.44		
	a_2	-11.78	-12.29	-12.74	-13.17	-14.49	-15.25	13.17	
	b_2	-12.43	-12.72	-13.26	-13.52	-15.06	-15.67		
	a_1	-14.09	-14.17	-14.76	-14.81	-16.84	-17.19	15.17	
	b_1	-15.07	-15.06	-15.62	-15.60	-18.03	-18.24		
	a_1	-19.34	-19.38	-19.76	-19.76	-21.85	-21.98	(19.8)	
	b_2	-23.20	-22.76	-23.19	-22.76	-25.74	-25.36		
	a_1	-29.18	-27.62	-28.35	-26.99	-31.75	-30.21		

TABLE 7.1 (continued)

Parameter Set		M1	M2	O1	O2	R1	R2	Exptl. IP.	Reference
$B_2H_6(D_{2h})$	b_{3g}	- 8.49	- 8.82	- 9.71	-10.02	-10.60	-11.22	12.0	215
	b_{2u}	-10.54	-10.65	-11.44	-11.54	-12.97	-13.39		
	b_{3u}	-12.42	-12.72	-13.38	-13.63	-14.79	-15.50		
	a_g	-13.58	-14.07	-14.10	-14.47	-16.09	-16.75		
	b_{1u}	-17.44	-17.20	-17.63	-17.36	-20.30	-19.96		
	a_g	-22.58	-21.28	-22.28	-21.16	-25.67	-24.38		
$LiF(C_{\infty v})$	π	-10.34	-10.10	-11.03	-10.88	-11.18	-11.02		
	σ	-10.39	-10.14	-11.04	-10.88	-11.37	-11.20		
	σ	-31.55	-31.22	-31.96	-31.75	-33.40	-33.20		
$F_2(D_{\infty h})$	π_g	-17.70	-17.80	-17.87	-17.94	-22.87	-22.97	π_g 15.63	204
	σ_g	-17.33	-17.02	-17.91	-17.66	-20.06	-19.68	σ_g 17.35	
	π_u	-19.51	-19.42	-19.35	-19.27	-25.00	-24.89	π_u 18.46	
	σ_u	-37.40	-37.56	-37.68	-37.82	-43.03	-43.20		
	σ_g	-41.52	-41.26	-41.11	-40.91	-47.69	-47.43		

TABLE 7.1 (continued)

Parameter Set		M1	M2	O1	O2	R1	R2	Exptl. IP.	Reference
$CH_3F(C_{3v})$	e	-12.23	-12.65	-13.33	-13.68	-15.34	-16.02	e 12.85	208
	a_1	-14.33	-14.11	-15.24	-15.06	-16.94	-16.84	a_1 14.10	
	e	-16.02	-15.87	-16.48	-16.34	-20.39	-20.38	(a_1) 16.89	
	a_1	-23.56	-23.15	-23.80	-23.33	-26.60	-26.16		
	a_1	-37.31	-36.87	-37.50	-37.16	-42.30	-42.04		
$HCN(C_{\infty v})$	π	-12.48	-12.44	-13.37	-13.33	-15.20	-15.31	13.91	216
	σ	-12.67	-12.81	-13.60	-13.72	-15.07	-15.31		
	σ	-20.24	-20.33	-20.67	-20.69	-22.67	-22.74		
	σ	-28.17	-27.86	-27.89	-27.60	-31.41	-31.31		
$CH_3CN(C_{3v})$	e	--	--	-12.31	-12.49	--	--	12.22	217
	a_1			-12.40	-12.32				
	e			-14.91	-14.90				
	a_1			-18.49	-18.68				
	a_1			-25.31	-24.75				
	a_1			-28.02	-27.62				

TABLE 7.1 (continued)

Parameter Set		M1	M2	01	02	R1	R2	Exptl. IP.	Reference
FCN($C_{\infty v}$)	π	-13.01	-13.01	-13.96	-13.97	-16.10	-16.18		
	σ	-14.99	-14.85	-15.97	-15.90	-17.60	-17.45		
	π	-17.30	-16.94	-17.85	-17.54	-21.71	-21.40		
	σ	-20.61	-20.63	-21.07	-21.04	-23.62	-23.50		
	σ	-28.94	-28.67	-28.65	-28.41	-32.61	-32.53		
	σ	-39.13	-38.59	-39.30	-38.86	-44.07	-43.60		

The molecular symmetry groups, and the irreducible representation of each calculated orbital, are listed in the first column on the left, using Cotton's notation.[191] Experimental information concerning the symmetry of the orbitals is given next to the experimental ionization potentials. When no such information is available, the experimental ionization potentials are listed in numerical order, and do not necessarily correspond to the calculated orbitals in the same rows. Experimental ionization potentials in parentheses refer to uncertain values.

The main feature of Table (7.1) is that the orbital energies calculated using electron repulsion integrals evaluated from atomic spectra (columns M1, M2, O1 and O2) are in all cases higher, and in most cases in better agreement with experiment, than those calculated using theoretical electron-repulsion integrals (columns R1 and R2). The use of theoretical electron-repulsion integrals leads to the prediction of ionization potentials which are too large in molecules, just as it does in atoms. If the electron-repulsion integrals are adjusted to give the correct atomic ionization potentials and electron affinities, they also give more accurate molecular ionization potentials.

The difference between the two empirical formulae for the inter-atomic electron-repulsion integrals, g_{AB}, is less significant since the choice affects the orbital energies by less than 1 ev. in most cases. The Ohno formula leads to closer agreement with experiment in a slightly greater number of cases than the Mataga formula, but this is not conclusive evidence in favour of the Ohno formula. The results are relatively insensitive to the exact values of the g_{AB}'s, so that the use of these approximate electron-repulsion integrals does not lead to serious error.

The value of the Slater exponent for hydrogen has even less effect upon the computed orbital energies, so that no clear choice of Z'_H can be based on them. It will be shown in Chapter 8, however, that the value 1.2 leads to more accurate bonding energies. The colums M2 and O2, therefore, list the orbital energies computed using the best sets of parameters.

In Table (7.2) the energies in columns M2 and O2 are compared with orbital energies using the Pople-Segal bonding parameters, and with those calculated from the Extended Huckel Theory. A comparison of columns MP and OP with columns M2 and O2 shows that the Pople-Segal bonding parameters lead to ionization potentials which are much higher than those obtained with empirical bonding parameters, and are in almost all cases in worse agreement with experiment. For many bonding and anti-bonding molecular orbitals, the effect of using the Pople-Segal bonding parameters is greater than that of using theoretical electron-repulsion integrals, since the ionization potentials of these orbitals in columns MP and OP are higher than the corresponding ones in columns R1 and R2. The energies of lone-pair or non-bonding orbitals, such as the a_1 and b_1 orbitals of ammonia and water respectively, are relatively insensitive to changes in the bonding parameters. The reason for this difference is clear if the orbital energy is expressed in terms of the orbital coefficients.

$$E_i = \sum_{k,l} C^*_{ki} C_{li} F_{kl} \qquad (2.11)$$

TABLE 7.2

COMPARISON OF ORBITAL ENERGIES OF FIRST-ROW MOLECULES (in ev.) IN DIFFERENT MO THEORIES

Parameter Set		M2	02	MP	OP	RP	H1	H2	Exptl.I.P.[a]
$H_2(D_{\infty h})$	σ_g	-14.69	-15.44	-17.11	-18.60	-20.09	-31.51	-29.65	15.45
$LiH(C_{\infty v})$	σ	- 8.09	- 7.90	-12.34	-13.21	-13.15	-13.84	-13.78	(7.81-7.91)
$BeH_2(D_{\infty h})$	σ_u	-11.41	-11.77	-16.27	-17.26	-17.89	-13.68	-13.94	
	σ_g	-12.74	-12.83	-17.15	-18.07	-18.85	-16.21	-15.79	
$BH_3(D_{3h})$	e'	-12.11	-12.85	-16.80	-17.94	-19.16	-13.85	-14.28	11.4
	a_1'	-17.73	-17.78	-24.56	-25.63	-26.91	-20.02	-19.60	
$CH_4(T_d)$	t_2	-12.70	-13.50	-17.05	-18.34	-19.78	-14.88	-15.31	12.99
	a_1	-23.51	-23.40	-32.32	-33.56	-34.68	-24.61	-24.40	(24)
$NH_3(C_{3v})$	a_1	-12.45	-13.30	-13.26	-14.00	-16.30	-14.21	-14.28	10.35
	e	-13.56	-14.20	-17.75	-19.22	-20.21	-16.35	-16.73	14.95
	a_1	-27.07	-26.71	-34.59	-35.89	-37.08	-27.80	-27.69	

(a) References as in Table 7.1.

TABLE 7.2 (continued)

Parameter Set		M2	O2	MP	OP	RP	H1	H2	Exptl. I.P.
$H_2O(C_{2v})$	b_1	-14.11	-14.33	-14.11	-14.72	-17.83	-17.27	-17.27	b_1 12.61
	a_1	-14.03	-14.88	-16.10	-17.11	-19.38	-17.67	-17.78	14.23
	b_2	-14.68	-15.36	-18.64	-20.22	-21.44	-18.75	-19.02	18.02
	a_1	-32.69	-32.51	-37.87	-39.03	-40.46	-33.34	-33.28	
$HF(C_{\infty v})$	π	-16.19	-16.67	-16.70	-17.33	-21.28	-20.86	-20.86	π 16.06
	σ	-16.38	-17.30	-19.48	-20.75	-23.14	-21.31	-21.43	σ 16.48
	σ	-37.60	-37.88	-40.87	-41.84	-45.55	-39.77	-39.74	
$N_2(D_{\infty h})$	σ_g	-13.57	-14.25	-15.34	-15.66	-18.30	-14.05		σ_g 15.58
	π_u	-13.62	-14.44	-18.16	-19.40	-20.38	-16.24		π_u 16.70
	σ_u	-23.15	-23.46	-22.03	-22.03	-25.16	-19.99		σ_u 18.80
	σ_g	-30.23	-29.65	-40.95	-41.87	-43.27	-31.59		

TABLE 7.2 (continued)

Parameter Set		M2	O2	MP	OP	RP	H1	H2	Exptl. I.P.
CO($C_{\infty v}$)	σ	-13.20	-13.81	-14.56	-14.78	-17.26	-14.39		σ 14.00
	π	-13.76	-14.40	-18.25	-19.52	-21.09	-17.80		π 16.54
	σ	-20.83	-20.53	-21.62	-22.00	-24.67	-20.09		σ 19.65
	σ	-33.40	-33.15	-43.03	-44.09	-45.33	-34.44		
CO_2($D_{\infty h}$)	π_g	-13.78	-14.55	-12.87	-13.88	-15.70	-17.20		π_g 13.79
	π_u	-16.26	-16.83	-21.18	-22.29	-24.81	-18.14		π_u 17.59
	σ_u	-13.58	-14.55	-17.24	-18.23	-20.43	-17.51		σ_u 18.07
	σ_g	-20.69	-21.01	-21.03	-21.81	-24.42	-19.56		σ_g 19.36
	σ_u	-33.73	-33.81	-41.31	-42.34	-43.99	-32.59		
	σ_g	-34.67	-34.46	-43.09	-44.06	-45.40	-35.50		

TABLE 7.2 (continued)

Parameter Set		M2	O2	MP	OP	RP	H1	H2	Exptl. I.P.
NNO($C_{\infty v}$)		--	-13.58	-11.83	-13.14	-14.44	-15.27		12.90
			-15.35	-17.28	-18.21	-20.72	-16.16		16.40
			-16.63	-21.82	-22.96	-25.44	-18.16		18.14
			-23.83	-21.62	-22.67	-24.98	-19.85		20.08
			-29.54	-38.01	-39.16	-41.03	-29.17		
			-34.33	-45.14	-46.22	-48.00	-35.71		
$O_3(C_{2v})$	a_2	-14.35	-14.59	-12.05	-13.13	-14.68	-17.16		12.3
	a_1	-14.72	-15.20	-13.32	-13.83	-17.35	-15.94		12.52
	b_2	-14.75	-15.20	-13.73	-14.29	-17.71	-16.86		13.52
	b_1	-16.18	-16.85	-20.31	-21.40	-23.54	-19.22		16.4-17.4
	b_2	-18.11	-18.19	-21.17	-22.14	-24.49	-19.40		19.24
	a_1	-18.67	-18.34	-21.73	-22.36	-25.73	-19.06		
	a_1	-30.10	-30.70	-28.14	-28.40	-32.10	-25.22		
	b_2	-33.24	-33.32	-36.72	-37.57	-39.90	-32.54		
	a_1	-38.78	-37.88	-47.55	-48.35	-50.49	-38.71		

TABLE 7.2 (continued)

Parameter Set		M2	O2	MP	OP	RP	H1	H2	Exptl. I.P.
C_2H_2 ($D_{\infty h}$)	π_u	-10.49	-11.38	-15.14	-16.40	-17.46	-13.39	-13.39	π_u 11.40
	σ_g	-12.33	-12.94	-18.12	-19.35	-20.62	-15.05	-15.30	σ_g 16.44
	σ_u	-18.20	-18.63	-24.03	-25.27	-26.55	-19.52	-19.47	σ_u 18.42
	σ_g	-24.20	-24.19	-34.98	-36.17	-36.84	-26.70	-26.64	
C_2H_4(D_{2h})	b_{3u}	-10.30	-11.11	-13.86	-15.01	-16.06	-13.07	-13.07	b_{3u}(π) 10.48
	b_{3g}	-11.10	-11.95	-13.40	-14.54	-15.82	-13.65	-14.49	12.50
	a_g	-11.63	-12.36	-16.66	-17.84	-19.15	-14.37	-14.48	14.39
	b_{2u}	-14.73	-15.25	-22.33	-23.68	-25.11	-16.05	-16.24	15.63
	b_{1u}	-19.14	-19.48	-24.97	-26.19	-27.49	-20.47	-20.38	(19.13)
	a_g	-25.43	-25.12	-37.16	-38.30	-39.06	-26.57	-26.47	
C_2H_6(D_{3d})	e_g	-11.32	-12.26	-13.74	-14.93	-16.32	-13.69	-14.46	} 11.49
	a_{1g}	-11.32	-12.07	-15.94	-17.02	-18.21	-13.98	-14.04	
	e_u	-14.18	-14.81	-20.63	-21.93	-23.41	-15.75	-15.96	14.74
	a_{2u}	-20.22	-20.52	-26.57	-27.79	-29.07	-21.62	-21.48	(20.13)
	a_{1g}	-26.04	-25.60	-38.13	-39.27	-40.08	-26.28	-26.14	

TABLE 7.2 (continued)

Parameter Set		M2	O2	MP	OP	RP	H1	H2	Exptl. I.P.
$C_3H_8(C_{2v})$	b_1	-10.93	-11.93	-12.72	-13.88	-15.28	-13.21	-14.11	11.07
	b_2	-10.64	-11.47	-13.78	-14.89	-16.12	-13.41	-13.62	
	a_1	-10.96	-11.83	-13.42	-14.55	-15.86	-13.54	-13.90	
	a_2	-12.29	-13.17	-16.16	-17.42	-18.91	-14.44	-15.00	13.17
	b_2	-12.72	-13.52	-18.10	-19.28	-20.67	-14.69	-15.14	
	a_1	-14.17	-14.81	-20.76	-22.00	-23.40	-15.57	-15.77	15.17
	b_1	-15.06	-15.60	-22.67	-23.98	-25.51	-16.13	-16.24	
	a_1	-19.38	-19.76	-25.94	-27.18	-28.55	-20.39	-20.34	(19.8)
	b_2	-22.76	-22.76	-31.80	-32.98	-34.05	-23.75	-23.58	
	a_1	-27.62	-26.99	-41.86	-42.97	-43.68	-27.12	-27.04	

TABLE 7.2 (continued)

Parameter Set		M2	O2	MP	OP	RP	H1	H2	Exptl. I.P.
$B_2H_6(D_{2h})$	b_{3g}	- 8.82	-10.02	- 9.14	-10.25	-10.94	- 9.87	-10.70	12.0
	b_{2u}	-10.65	-11.54	-14.56	-15.96	-16.70	-11.43	-11.78	
	b_{3u}	-12.72	-13.63	-19.39	-20.72	-21.20	-14.12	-14.46	
	a_g	-14.07	-14.47	-21.66	-23.04	-23.64	-15.16	-15.55	
	b_{1u}	-17.20	-17.36	-25.45	-26.87	-27.55	-18.85	-18.54	
	a_g	-21.28	-21.16	-35.01	-36.40	-36.84	-21.35	-20.98	
$LiF(C_{\infty v})$	π	-10.10	-10.88	-14.11	-15.05	-14.99	-20.86		
	σ	-10.14	-10.88	-14.17	-15.01	-15.37	-20.86		
	σ	-31.22	-31.75	-37.40	-38.38	-38.61	-39.41		
$F_2(D_{\infty h})$	π_g	-17.80	-17.94	-16.77	-16.77	-22.09	-20.09		π_g 15.63
	σ_g	-17.02	-17.66	-20.22	-21.19	-22.72	-22.46		σ_g 17.35
	π_u	-19.42	-19.27	-20.45	-20.45	-25.77	-21.57		π_u 18.46
	σ_u	-37.56	-37.82	-36.12	-36.12	-41.99	-36.06		
	σ_g	-41.26	-40.91	-44.31	-44.52	-49.73	-42.47		

TABLE 7.2 (continued)

Parameter Set		M2	O2	MP	OP	RP	H1	H2	Exptl. I.P.
$CH_3F(C_{3v})$	e	-12.65	-13.68	-13.96	-14.77	-17.57	-14.61	-15.08	e 12.85
	a_1	-14.11	-15.06	-18.61	-19.70	-21.27	-20.15	-20.08	a_1 14.10
	e	-15.87	-16.34	-20.42	-21.39	-24.12	-20.96	-20.95	(a_1) 16.89
	a_1	-23.15	-23.33	-28.82	-29.83	-32.05	-23.64	-23.57	
	a_1	-36.87	-37.16	-43.47	-44.40	-47.10	-40.00	-40.00	
$HCN(C_{\infty v})$	π	-12.44	-13.33	-16.40	-17.71	-18.58	-15.09	-15.09	13.91
	σ	-12.81	-13.72	-15.32	-15.94	-18.15	-14.64	-14.69	
	σ	-20.33	-20.69	-23.81	-24.90	-26.43	-19.68	-19.64	
	σ	-27.86	-27.60	-37.55	-38.64	-39.62	-29.31	-29.30	

TABLE 7.2 (continued)

Parameter Set		M2	02	MP	OP	RP	H1	H2	Exptl. I.P.
$CH_3CN(C_{3v})$	e	--	-12.49	-13.81	-15.09	-15.89	-14.48	-14.72	12.22
	a_1		-12.32	-14.61	-15.29	-17.28	-14.08	-14.11	
	e		-14.90	-20.54	-21.97	-23.21	-15.53	-15.69	
	a_1		-18.68	-20.43	-21.53	-22.88	-17.38	-17.41	
	a_1		-24.75	-34.24	-35.45	-36.46	-24.46	-24.34	
	a_1		-27.62	-39.07	-40.19	-40.83	-29.56	-29.56	
$FCN(C_{\infty v})$	π	-13.01	-13.97	-14.25	-15.20	-17.14	-14.94		
	σ	-14.85	-15.90	-15.92	-16.51	-19.15	-15.72		
	π	-16.94	-17.54	-21.55	-22.49	-25.51	-20.99		
	σ	-20.63	-21.04	-22.87	-23.87	-26.26	-21.67		
	σ	-28.67	-28.41	-37.37	-38.31	-39.92	-28.74		
	σ	-38.59	-38.86	-46.08	-47.14	-49.85	-40.26		

The only terms in the summation which depend on the bonding parameters are those involving matrix elements F_{kl} between orbitals on different atoms, and these terms are only significant if the coefficients of atomic orbitals in at least 2 atoms in the molecular orbital are large, i.e., if the orbital is a bonding (or anti-bonding) orbital.

Pople and Segal[44,45] evaluated neither the electron-repulsion integrals, nor the bonding parameters, empirically. Orbital energies calculated with all the parameters used by Pople and Segal are listed in column RP, and are generally in worse agreement with experiment than those calculated using either empirical bonding parameters, or empirical electron-repulsion integrals. The only empirical parameters used by Pople and Segal are the local terms of the diagonal core Hamiltonian matrix elements, U_{ss} and U_{pp}, which are evaluated from atomic spectra.[45] Table (7.2) shows that this degree of empiricism is not adequate for the calculation of accurate orbital energies.

The columns H1 and H2 list orbital energies calculated using the Extended Huckel Theory. For molecules that do not contain hydrogen, the results of the EHT do not depend on the Slater exponent for hydrogen, so that only one set of orbital energies is listed. On the whole, the EHT orbital energies are less accurate than the SCF-MO-CNDO energies in columns M2 and O2 although they are quite accurate for a few molecules, such as N_2 and CO. The results for the hydrides, and especially hydrogen, however, show that the EHT is unreliable. The effect of changing the Slater exponent for hydrogen is negligible.

Table (7.3) lists the orbital energies for molecules which contain atoms heavier than neon. SCF-MO-CNDO calculations for these molecules have only been made with empirical bonding parameters and electron-repulsion integrals, since empirical parameters have been shown to be better for molecules containing only light atoms in Tables (7.1) and (7.2). The accuracy of the computed orbital energies is about the same for both sets of molecules, for both the SCF-MO-CNDO theory and the EHT.

In summary, therefore, the best of the semi-empirical theories considered is the SCF-MO-CNDO theory, with empirical electron-repulsion integrals and bonding parameters, and a Slater exponent for hydrogen of 1.2.

The semi-empirical orbital energies of some small molecules are compared in Table (7.4) with approximate Hartree-Fock orbital energies from exact SCF-MO calculations with extended basis sets.[39,223-227] If Koopmans' theorem is assumed to be valid, the overall accuracy of the semi-empirical orbital energies is comparable with that of the Hartree-Fock orbital energies. Of course, the latter are far closer to exact solutions of the Hartree-Fock equations, but they are not always in good agreement with measured ionization potentials, since Koopmans' theorem does not hold exactly. In cases where the semi-empirical orbital energies are in better agreement with ionization potentials, the errors due to the approximate solution of Roothaan's equations partially cancel those due to Koopmans' theorem.

Some additional features of the orbital energies and ionization potentials are discussed below for specific molecules.

TABLE 7.3

COMPARISON OF ORBITAL ENERGIES (in ev.) IN DIFFERENT MO THEORIES FOR MOLECULES WITH NOT ALL FIRST-ROW ATOMS

Parameter Set		M1	M2	O1	O2	H1	H2	Exptl. I.P.	Reference
$SiH_4(T_d)$	t_2	-11.84	-12.08	-12.50	-12.67	-14.59	-14.79	12.2	218
	a_1	-18.62	-18.09	-18.67	-18.15	-21.63	-21.18		
$GeH_4(T_d)$	t_2	-11.95	-12.12	-12.59	-12.75	-14.82	-14.97	12.3	218
	a_1	-18.28	-17.78	-18.52	-18.14	-22.51	-22.07		
$SnH_4(T_d)$	t_2	-11.73	-11.85	-15.41	-15.42	-14.42	-14.54		
	a_1	-16.67	-16.22	-20.63	-20.43	-20.53	-20.02		
$PH_3(C_{3v})$	a_1	-12.08	-12.18	-12.68	-12.75	-11.68	-11.85	10.2	219
	e	-12.11	-12.31	-12.83	-13.02	-14.78	-15.04		
	a_1	-21.22	-20.88	-21.05	-20.76	-22.18	-21.78		
$AsH_3(C_{3v})$	a_1	-11.64	-11.72	-12.12	-12.17	-10.51	-10.70	10.6	220
	e	-11.70	-11.89	-12.35	-12.52	-14.14	-14.43		
	a_1	-18.53	-18.20	-18.38	-18.10	-21.23	-20.78		

TABLE 7.3 (continued)

Parameter Set		M1	M2	O1	O2	H1	H2	Exptl. I.P.	Reference
$SbH_3(C_{3v})$	a_1	-11.41	-11.42	-11.85	-11.86	-10.06	-10.27		
	e	-11.49	-11.62	-12.04	-12.18	-14.06	-14.29		
	a_1	-18.54	-18.28	-18.33	-18.13	-20.17	-19.67		
$H_2S(C_{2v})$	b_1	-11.57	-11.64	-11.76	-11.79	-12.40	-12.40	10.42	194
	b_2	-12.47	-12.66	-13.19	-13.35	-15.61	-15.87	12.62	
	a_1	-12.50	-12.61	-13.18	-13.25	-13.55	-13.75	14.82	
	a_1	-21.82	-21.61	-21.79	-21.58	-23.59	-23.29	20.12	
$H_2Se(C_{2v})$	b_1	-11.75	-11.81	-11.94	-11.97	-11.68	-11.68	9.88	221
	b_2	-12.45	-12.59	-13.13	-13.25	-15.34	-15.55		
	a_1	-12.51	-12.59	-13.15	-13.19	-13.05	-13.27		
	a_1	-20.99	-20.83	-21.02	-20.85	-23.24	-22.91		

TABLE 7.3 (continued)

Parameter Set		M1	M2	01	02	H1	H2	Exptl. I.P.	Reference
H_2Te	b_1	-11.69	-11.74	-11.82	-11.85	-11.04	-11.04	9.14	217
	b_2	-12.20	-12.33	-12.81	-12.92	-15.07	-15.19		
	a_1	-12.29	-12.37	-12.82	-12.87	-12.68	-12.90		
	a_1	-19.93	-19.83	-19.95	-19.85	-22.07	-21.69		
HCl($C_{\infty v}$)	π	-13.13	-13.18	-13.44	-13.46	-15.04	-15.04	π 12.80	204
	σ	-13.94	-14.07	-14.68	-14.79	-16.39	-16.59	σ 16.28	
	σ	-24.96	-24.87	-25.16	-25.07	-26.36	-26.19		
HBr($C_{\infty v}$)	π	-12.06	-12.09	-12.27	-12.28	-13.10	-13.10	π 11.87	204
	σ	-13.11	-13.22	-13.77	-13.86	-14.88	-15.11	σ 15.31	
	σ	-23.65	-23.58	-23.77	-23.69	-24.98	-24.76		
HI($C_{\infty v}$)	π	-12.06	-12.08	-12.17	-12.19	-12.67	-12.67	π 10.75	204
	σ	-12.63	-12.68	-13.18	-13.25	-14.62	-14.82	σ 14.03	
	σ	-20.38	-20.32	-20.44	-20.38	-22.26	-22.00		

TABLE 7.3 (continued)

Parameter Set		M1	M2	01	02	H1	H2	Exptl. I.P.	Reference
OCS($C_{\infty v}$)	π	--	-11.71	-12.20	-12.26	-13.14		π 11.27	200,196
	π		-14.76	-15.60	-15.36	-17.76		π 15.60	
	σ		-12.97	-14.04	-13.81	-14.67		σ 16.04	
	σ		-18.77	-19.28	-19.32	-18.40		σ 18.00	
	σ		-24.05	-24.03	-23.89	-24.25			
	σ		-33.71	-33.99	-33.58	-34.37			
CS_2($D_{\infty h}$)	π_g	-10.88	-10.93	-11.30	-11.33	-12.24		π_g 10.11	200,196
	π_u	-12.83	-12.73	-13.39	-13.28	-14.18		π_u 12.92	
	σ_u	-12.10	-12.01	-12.70	-12.59	-13.48		σ_u 14.49	
	σ_g	-17.62	-17.70	-18.14	-18.23	-15.72		σ_g 16.19	
	σ_u	-21.44	-21.35	-21.61	-21.52	-21.64		(17.05)	
	σ_g	-25.64	-25.42	-25.31	-25.08	-26.97			

TABLE 7.3 (continued)

Parameter Set		M1	M2	O1	O2	H1	H2	Exptl. I.P.	Reference
CS	π	-11.36	-11.31	-11.90	-11.82	-13.65			
	σ	-11.55	-11.49	-12.01	-11.94	-12.13			
	σ	-18.41	-18.46	-18.60	-18.66	-16.96			
	σ	-23.93	-23.77	-23.70	-23.52	-25.71			
$SO_2(C_{2v})$	a_1	-12.23	-12.30	-12.65	-12.69	-13.03		12.32	194
	b_2	-12.68	-12.71	-13.09	-13.09	-17.07			
	a_2	-12.94	-13.31	-13.11	-13.33	-17.23		13.17	
	b_1	-15.11	-15.06	-15.40	-15.30	-18.00			
	b_2	-15.40	-15.32	-15.55	-15.42	-17.86		16.42	
	a_1	-16.09	-15.99	-15.78	-15.66	-17.89			
	a_1	-21.58	-21.59	-21.56	-21.58	-19.72		(20.07)	
	b_2	-32.72	-32.63	-32.41	-32.34	-32.64			
	a_1	-33.95	-33.72	-33.34	-33.15	-34.82			

TABLE 7.3 (continued)

Parameter Set		M1	M2	01	02	H1	H2	Exptl. I.P.	Reference
$Cl_2(D_{\infty h})$	π_g	-13.01	-13.05	-13.13	-13.16	-13.80		π_g 11.50	204,210
	π_u	-14.85	-14.81	-14.73	-14.70	-16.05		π_u 14.11	
	σ_g	-13.57	-13.46	-14.02	-13.94	-16.42		σ_g 15.94	
	σ_u	-23.56	-23.61	-23.70	-23.74	-22.04		σ_u 20.61	
	σ_g	-27.08	-26.98	-26.86	-26.79	-28.62			
$Br_2(D_{\infty h})$	π_g	-11.73	-11.74	-11.82	-11.83	-11.98		π_g 10.71	204
	π_u	-13.22	-13.21	-13.13	-13.12	-14.01		π_u 12.52	
	σ_g	-12.14	-12.11	-12.56	-12.53	-14.36		σ_g 14.44	
	σ_u	-22.24	-22.25	-22.36	-22.37	-20.47			
	σ_g	-25.15	-25.12	-24.97	-24.94	-26.96			
$I_2(D_{\infty h})$	π_g	-11.81	-11.79	-11.88	-11.86	-11.72		π_g 9.65	204
	π_u	-12.99	-13.01	-12.93	-12.95	-13.46		π_u 11.28	
	σ_g	-11.42	-11.47	-11.79	-11.85	-13.94		σ_g 12.79	
	σ_u	-19.25	-19.23	-19.33	-19.31	-18.40			
	σ_g	-21.50	-21.55	-21.40	-21.45	-23.53			

TABLE 7.3 (continued)

Parameter Set		M1	M2	O1	O2	H1	H2	Exptl. I.P.	Reference
ClF($C_{\infty v}$)	π	-14.36	-14.44	-14.28	-14.34	-14.78		≤ 12.7	222
	π	-17.35	-17.24	-17.21	-17.11	-20.97			
	σ	-15.37	-15.14	-15.83	-15.64	-20.09			
	σ	-25.78	-25.82	-25.63	-25.65	-24.80			
	σ	-38.34	-38.16	-38.14	-37.98	-40.10			
BrF($C_{\infty v}$).	π	-13.13	-13.20	-12.90	-12.94	-12.91		≤ 11.9	222
	π	-16.40	-16.29	-16.25	-16.14	-20.92			
	σ	-14.34	-14.14	-14.76	-14.59	-19.52			
	σ	-24.33	-24.37	-24.05	-24.07	-23.62			
	σ	-37.43	-37.25	-37.20	-37.04	-39.95			

TABLE 7.3 (continued)

Parameter Set		M1	M2	01	02	H1	H2	Exptl. I.P.	Reference
IF($C_{\infty v}$)	π	-13.60	-13.65	-13.41	-13.45	-12.58		$\leq$ 10.5	222
	π	-15.81	-15.72	-15.65	-15.57	-20.88			
	σ	-13.40	-13.25	-13.79	-13.67	-18.88			
	σ	-21.60	-21.63	-21.37	-21.39	-21.99			
	σ	-36.61	-36.49	-36.42	-36.31	-39.63			
BrCl($C_{\infty v}$)	π	-12.27	-12.29	-12.33	-12.35	-12.53		$\leq$ 11.1	222
	π	-14.03	-14.00	-13.94	-13.92	-15.40			
	σ	-12.77	-12.70	-13.21	-13.15	-15.46			
	σ	-22.81	-22.84	-22.91	-22.94	-21.23			
	σ	-26.08	-26.02	-25.89	-25.84	-27.83			

TABLE 7.3 (continued)

Parameter Set		M1	M2	01	02	H1	H2	Exptl. I.P.	Reference
$ICl(C_{\infty v})$	π	-12.39	-12.40	-12.46	-12.46	-12.24		π 10.55	210
	π	-13.85	-13.84	-13.77	-13.76	-15.29		π 12.16	
	σ	-12.37	-12.35	-12.78	-12.77	-15.26			
	σ	-20.52	-20.52	-20.53	-20.54	-19.67			
	σ	-25.06	-25.04	-24.98	-24.97	-26.70			
$IBr(C_{\infty v})$.	π	-11.77	-11.76	-11.85	-11.85	-11.84		π 10.23	210
	π	-13.13	-13.14	-13.06	-13.06	-13.75		π 11.64	
	σ	-11.76	-11.77	-12.16	-12.17	-14.15			
	σ	-20.13	-20.12	-20.18	-20.18	-19.14			
	σ	-23.96	-23.97	-23.88	-23.88	-25.55			

TABLE 7.3 (continued)

Parameter Set		M1	M2	01	02	H1	H2	Exptl. I.P.	Reference
$CH_3Cl(C_{3v})$	e	-11.53	-11.81	-12.23	-12.41	-13.72	-14.11	e 11.42	208
	a_1	-12.24	-12.21	-13.00	-12.97	-15.63	-15.63	a_1 12.07	
	e	-14.06	-14.18	-14.67	-14.79	-15.96	-16.06	e 13.02	
	a_1	-21.67	-21.64	-22.11	-22.02	-21.54	-21.56	a_1 18.71	
	a_1	-26.64	-26.03	-26.51	-25.98	-27.60	-27.52		
$CH_3Br(C_{3v})$	e	-10.99	-11.19	-11.47	-11.61	-12.48	-12.68	e 10.69	208
	a_1	-11.44	-11.46	-12.17	-12.16	-14.20	-14.22	a_1 11.62	
	e	-13.57	-13.76	-14.26	-14.43	-15.29	-15.58	e 12.94	
	a_1	-21.17	-21.16	-21.55	-21.51	-20.84	-20.90	a_1 19.13	
	a_1	-25.83	-25.22	-25.65	-25.09	-26.66	-26.54		

TABLE 7.3 (continued)

Parameter Set		M1	M2	01	02	H1	H2	Exptl. I.P.	Reference
$CH_3I(C_{3v})$	e	-11.10	-11.30	-11.50	-11.64	-12.20	-12.35	e 9.80	208
	a_1	-10.93	-10.99	-11.60	-11.64	-13.85	-13.89	a_1 11.22	
	e	-13.36	-13.57	-14.06	-14.24	-15.19	-15.51	e 13.14	
	a_1	-16.86	-18.98	-19.17	-19.26	-19.45	-19.55	a_1 19.76	
	a_1	-24.70	-24.02	-24.55	-23.91	-25.29	-25.13		
$ClCN(C_{\infty v})$	π	--	-12.30	-13.09	-13.08	-14.47			
	σ		-12.87	-13.78	-13.69	-14.88			
	π		-14.40	-15.07	-14.93	-15.77			
	σ		-19.48	-19.87	-20.00	-17.70			
	σ		-25.83	-26.23	-26.08	-25.79			
	σ		-28.68	-28.64	-28.38	-29.99			

TABLE 7.3 (continued)

Parameter Set		M1	M2	O1	O2	H1	H2	Exptl. I.P.	Reference
BrCN($C_{\infty v}$)	π	-11.87	--	-12.41	-12.40	-13.19			
	σ	-12.17		-12.90	-12.81	-14.29			
	π	-13.68		-14.26	-14.16	-15.21			
	σ	-18.98		-19.48	-19.63	-16.87			
	σ	-24.71		-24.85	-24.75	-24.67			
	σ	-28.58		-28.25	-28.00	-29.71			
ICN($C_{\infty v}$)	σ	-11.76	-11.68	-12.44	-12.36	-14.14			
	π	-11.97	-11.92	-12.46	-12.42	-12.78			
	π	-13.47	-13.35	-13.98	-13.90	-15.15			
	σ	-18.31	-18.41	-18.74	-18.83	-16.64			
	σ	-22.03	-22.00	-22.13	-22.12	-22.41			
	σ	-28.30	-28.03	-27.97	-27.73	-29.42			

TABLE 7.4

COMPARISON OF SEMI-EMPIRICAL AND HARTREE-FOCK ORBITAL ENERGIES

Orbital Energy		M2	O2	Hartree-Fock	Reference	Exptl. I.P.
$CH_4(T_d)$	t_2	-12.70	-13.50	-14.72	223	12.99
	a_1	-23.51	-23.40	-25.63		(24)
$NH_3(C_{3v})$	a_1	-12.45	-13.30	-10.60	224	10.35
	e	-13.56	-14.20	-16.40		14.95
	a_1	-27.07	-26.71	-30.06		
$H_2O(C_{2v})$	b_1	-14.11	-14.33	-13.48	224	b_1 12.61
	a_1	-14.03	-14.88	-15.13		14.23
	b_2	-14.68	-15.36	-18.54		18.02
	a_1	-32.69	-32.51	-36.08		
$HF(C_{\infty v})$	π	-16.19	-16.67	-17.70	39	π 16.06
	σ	-16.38	-17.30	-20.91		σ 16.48
	σ	-37.60	-37.88	-43.57		
$HCl(C_{\infty v})$	π	-13.18	-13.46	-12.96	39	π 12.80
	σ	-14.07	-14.79	-17.02		σ 16.28
	σ	-24.87	-25.07	-30.38		

TABLE 7.4 (continued)

Orbital Energy		M2	02	Hartree-Fock	Reference	Exptl. I.P.
$N_2(D_{\infty h})$	σ_g	-13.57	-14.25	-17.36	225	σ_g 15.58
	π_u	-13.62	-14.44	-17.10		π_u 16.70
	σ_u	-23.15	-23.46	-20.92		σ_u 18.80
	σ_g	-30.23	-29.65			
$CO(C_{\infty v})$	σ	-13.20	-13.81	-15.08	39	σ 14.00
	π	-13.76	-14.40	-17.40		π 16.54
	σ	-20.83	-20.53	-21.87		σ 19.65
	σ	-33.40	-33.15	-41.39		
CO_2 $(D_{\infty h})$	π_g	-13.78	-14.55	-14.81	39	π_g 13.79
	π_u	-16.26	-16.83	-19.45		π_u 17.59
	σ_u	-13.58	-14.55	-20.23		σ_u 18.07
	σ_g	-20.69	-21.01	-21.77		σ_g 19.36
	σ_u	-33.73	-33.81	-40.19		
	σ_g	-34.67	-34.46	-41.63		
$NNO(C_{\infty v})$	π	--	-13.58	-13.37	39	π 12.90
	σ		-15.35	-19.01		σ 16.40
	π		-16.63	-20.73		π 18.14
	σ		-23.83	-22.63		σ 20.08
	σ		-29.54	-38.75		
	σ		-34.33	-43.82		

TABLE 7.4 (continued)

Orbital Energy		M2	02	Hartree-Fock	Reference	Exptl. I.P.
$C_2H_2(D_{\infty h})$	π_u	-10.49	-11.38	-11.17	39	π_u 11.40
	σ_g	-12.33	-12.94	-18.58		σ_g 16.44
	σ_u	-18.20	-18.63	-20.95		σ_u 18.42
	σ_g	-24.20	-24.19	-28.02		
$C_2H_4(D_{\infty h})$	b_{3u}	-10.30	-11.11	-10.38	226	$b_{3u}(\pi)$ 10.48
	b_{3g}	-11.10	-11.95	-14.08		12.50
	a_g	-11.63	-12.36	-15.86		14.39
	b_{2u}	-14.73	-15.25	-17.97		15.63
	b_{1u}	-19.14	-19.48	-21.95		(19.13)
	a_g	-25.43	-25.12	-28.80		
$F_2(D_{\infty h})$	π_g	-17.80	-17.94	-18.04	227	π_g 15.63
	σ_g	-17.02	-17.66	-20.30		σ_g 17.35
	π_u	-19.42	-19.27	-21.91		π_u 18.46
	σ_u	-37.56	-37.82	-40.68		
	σ_g	-41.26	-40.91	-47.80		

Hydrogen: In Table (7.1) the computed ionization potential is most accurate if g_{AB} is given by the Ohno formula, and it is independent of the Slater exponent of the atomic orbitals. In this case, these conclusions can be derived analytically, since the occupied orbital must by symmetry have the form

$$\psi = \frac{1}{\sqrt{2}} (\phi_1 + \phi_2) \tag{7.4}$$

The energy eigenvalue of an orbital is given by

$$E_i = \sum_{k,l} C_{ki}^* C_{li} F_{kl} \tag{2.11}$$

or, in this case,

$$E_1 = \frac{1}{2} (F_{11} + F_{12} + F_{21} + F_{22}) = F_{11} + F_{12} \tag{7.5}$$

The population matrix for H_2 is

$$P = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \tag{7.6}$$

so that the Hamiltonian matrix elements are

$$F_{11} = U_{11} + \frac{1}{2} g_{11} \tag{7.7}$$

and

$$F_{12} = - \beta_H^o S_{12} - \frac{1}{2} g_{12} \tag{7.8}$$

where all symbols have been defined in Chapter 2. For all the sets of parameters considered, including that of Pople and Segal, F_{11} is equal to the negative of the electronegativity of the 1s orbital of a neutral hydrogen atom (7.171 ev.).[79] The ionization potential of H_2 is, therefore,

$$I = 7.171 + \beta_H^o S_{12} + \frac{1}{2} g_{12} \tag{7.9}$$

Also, as shown in Chapter 8, the dissociation energy of H_2 is

$$E_B = 2\beta_H^o S_{12} + \frac{1}{2}(g_{12} - g_{11}) \tag{7.10}$$

From equations (7.9) and (7.10), the ionization potential and dissociation energy are both predicted correctly if g_{11} is evaluated using Pariser's formula,[72] g_{12} = 10.766 ev., and $\beta_H^o S_{12}$ = 2.896 ev. Empirical parameters have not been assigned in this way, however, since for other molecules the population matrix is not determined by symmetry, so that the ionization potentials and atomization energies cannot be expressed simply and solely in terms of the parameters. Instead, the interatomic electron-repulsion integrals were calculated using the Mataga and Ohno formulae, and the bonding parameters were chosen to fit atomization energies alone. For H_2, the values for g_{12} given by the Mataga and Ohno formulae are 7.731 ev. and 10.713 ev. respectively. Since the latter value is closest to the value required to fit the ionization potential exactly, it leads to a more accurate ionization potential.

It is also clear from equations (7.9) and (7.10) that if the electron-repulsion integrals, g_{11} and g_{12}, are kept constant and the overlap integral S_{12} is altered by varying the value of the Slater exponent, Z_H', then the change in the bonding parameter β_H^o, which is required to maintain the value of the dissociation energy, also keeps the predicted ionization potential constant. (Table (7.1))

If g_{11} is evaluated from the theoretical integral, equation (2.18), the value of g_{12} required to fit both the ionization potential and the dissociation energy is 3.206 ev., compared to the theoretical integral values 13.688 ev. and 15.896 ev., for $Z'_H = 1.0$ and 1.2 respectively, so that the use of theoretical electron-repulsion integrals leads to an inaccurate ionization potential.

Lithium hydride: No experimental value for the ionization potential of LiH is known. A rigorous upper bound, and a probable lower bound, for the energy of LiH^+ have been calculated exactly by Browne,[214] using a generalized valence-bond wave function. Such a calculation was possible for this ion because it contains only three electrons. These bounds have been combined with the experimental energy of LiH to give the ionization potential within the limits given in the table. The ionization potentials calculated using the SCF-MO theory with empirical bonding parameters and electron-repulsion integrals are in good agreement with the value from the ab initio calculation.

Methane: The approximate value 24 ev. for the second ionization potential was determined by Collin and Delwiche,[212] using mass spectrometry, and is considered uncertain by the authors. An earlier value of 19.42 ev., based on the electron impact spectrum,[208] has been shown to correspond to an autoionization level.[212] This conclusion has been confirmed by photoelectron spectroscopy, since no second ionization potential is observed for CH_4 below 21.21 ev.[198] It is probable, therefore, that the true second ionization potential is within 1 ev. of the value (23.4 to 23.5 ev.) predicted by the semi-empirical SCF-MO-CNDO theory. In the absence of the extension of photoelectron spectroscopy to higher incident photon energies, this conclusion would be supported if the predicted second ionization potentials for SiH_4, GeH_4 and SnH_4, which are in the range observable at present by photoelectron spectroscopy, were shown to be accurate.

Ammonia and Related Molecules: The highest occupied molecular orbital is the lone pair on nitrogen, so that its computed energy is insensitive to changes in the bonding parameters. For PH_3, AsH_3 and SbH_3, the two highest molecular orbital energies are predicted to be so close together that the photoelectron spectra should be examined to see how many distinct ionization potentials can be resolved. The two peaks may be further apart than predicted, however, since their spacing is seriously underestimated in ammonia.

Water and Related Molecules: The order of the computed orbital energies depends on the choice of parameters. The b_1 orbital, a lone pair on the oxygen atom, is, in fact, the highest since the first ionization potential is much sharper than the next two in the photoelectron spectrum.[198] For H_2S, H_2Se and H_2Te, on the other hand, the b_1 orbital is predicted to be the highest for all parameters tried. This is consistent with experiment for H_2S, for which Al-Joboury and Turner[194] assigned the first ionization potential to a non-bonding orbital.

Carbon Dioxide and Related Molecules: All the calculations predict that the highest σ_u orbital energy of CO_2 is higher than one or both π orbital energies, in disagreement with the experimental order of ionization potentials, which is based on the emission spectrum of the CO_2^+ ion.[213] Complete SCF-MO calculations give the correct order of orbital energies with an extended basis set,[39] but not with a minimum basis set,[228] so that the decrease of energy associated with improved flexibility of the wave function is greater for the σ_u orbital than for the π orbitals. The incorrect order of orbital energies in the semi-empirical theory, consequently, may also be due to the use of a minimum basis set.

For OCS and CS_2, the predicted order of orbital energies is again in disagreement with the experimental order, which is based on the similarity of the photoelectron spectra to that of CO_2, and the absence, as in CO_2, of a Rydberg series converging to the second ionization potential.[196] No complete SCF-MO calculations have been made for these molecules, but it can be assumed that the source of error is the same.

For NNO, which is isoelectronic to CO_2, the second ionization potential has been found to correspond to a σ orbital by photoelectron spectroscopy, so that both the semi-empirical and the complete SCF-MO theory are in agreement with experiment. The actual inversion of orbital energies on going from CO_2 to NNO may be due to the fact that the removal of the centre of symmetry allows mixing between g and u orbitals, which causes a greater separation of the energetically closer σ-orbital energies than the π-orbital energies. This mixing effect is absent in the symmetric

CO_2 and CS_2, and small in OCS, but is evidently important in NNO.

Sulphur dioxide and Ozone: No experimental information is available concerning the assignment of ionization potentials to specific orbitals, so that the predicted order cannot be verified. For SO_2, a good fit is obtained if the first two observed ionization potentials are assumed to be three incompletely resolved peaks, and the third observed peak to correspond to three unresolved energy levels. The fourth observed ionization potential at 20.07 ev. is considered uncertain by Turner,[194] but its existence is supported by the theoretical prediction of an orbital at -21.6 ev.

Ethylene: The b_{3u} orbital, which has its nodal plane in the plane of the nuclei, is the π-orbital of chemistry,[15,16] and has been shown experimentally to be the highest occupied orbital.[194] It is correctly predicted to be the highest with empirical bonding parameters, but not with the Pople-Segal bonding parameters.

The fifth ionization potential is considered uncertain by Turner,[194] but agrees well with the energy of the b_{1u} orbital, computed using empirical parameters.

Ethane: There are four calculated orbital energies (in columns M2 and 02) higher than -21.21 ev., and three observed ionization potentials[198] in this range. Good agreement of the computed energies with experiment is obtained only if it is assumed that the observed first ionization potential corresponds to the two highest orbital energies, which are not resolved.

It is clear from the observed photoelectron spectrum[198] of C_2H_6 that two peaks as close as the predicted orbital energies either would not be resolved, or would be interpreted as the vibrational structure of a single peak. Dewar and Klopman[64] have made the same assumption in order to fit calculated orbital energies to the observed ionization potentials.

Propane: The irreducible representations are labelled assuming that the z-axis is the twofold symmetry axis, and the x-axis is normal to the plane of the three carbon atoms. The first three observed ionization potentials are assumed to correspond to seven calculated orbital energies. Dewar and Klopman[64] also calculated seven orbital energies above -16 ev.

Diborane: The irreducible representations are labelled assuming that the z-axis lies along the boron-boron line, and the x-axis connects the two bridge hydrogens. The atomic orbitals on the bridge hydrogens participate in the a_g and b_{3u} orbitals, which provide the bridge bonding corresponding to the "three centre bonds" in the localized-orbital description[6] of B_2H_6.

Halogens: The σ_g orbital is predicted to be the highest occupied orbital in F_2 and I_2, according to the semi-empirical SCF-MO-CNDO theory, and the second highest in Cl_2 and Br_2, whereas the photoelectron spectra[204] show that it is below one π orbital in F_2, and both in the other halogens. Complete SCF-MO calculations for F_2, using either an extended[227] or a minimum[229] basis, predict the correct order of orbital energies, so that the error in the semi-empirical theory must be due to either the CNDO approximation or the choice of parameters. The orbital energies calculated with Pople-Segal bonding parameters are in the correct order, but are in error by several ev. as for other molecules.

Interhalogens: For the interhalogen molecules, the highest σ orbital energy in the SCF-MO-CNDO theory is also higher than one or both π-orbital energies, in disagreement with the experimental observation of spin-orbit splitting of the first two ionization potentials of ICl and IBr.[210]

For ClF, BrF, IF and BrCl, experimental ionization potentials have not been determined, but upper bounds to the first ionization potential, determined from appearance potentials in halogen mixtures,[222] are listed.

Methyl fluoride: Frost and McDowell[208] list the third ionization potential as a_1 in their table, but their accompanying text indicates that this is a misprint, and that the third highest orbital has e symmetry, as in the other methyl halides, and in agreement with all versions of MO theory considered.

Hydrogen cyanide and methyl cyanide: The computed orbital energies indicate that the first two ionization potentials may be too close to be resolved. This prediction could be verified by determining how many distinct ionization potentials are resolved in the photoelectron spectra, which have not yet been observed.

D. CONCLUSIONS

The SCF-MO-CNDO theory leads to the prediction of fairly accurate ionization potentials when empirical electron-repulsion integrals and bonding parameters are used, and is definitely more reliable than the EHT. The theory is, of course, a drastic semi-empirical approximation to the complete SCF-MO theory, in which an extended basis set is used and all electron-interaction integrals are evaluated explicitly. Even in the latter theory, ionization potentials are not predicted exactly (Table 7.4), due to errors in Koopmans' theorem. It is therefore not surprising that some of the predicted orbital energies in the semi-empirical SCF-MO theory are somewhat in error, or even in the wrong order for a given molecule. The computed orbital energies provide support, but not conclusive evidence, for a given assignment of the ionization potentials of a molecule, when this order has not been determined experimentally.

CHAPTER 8

BONDING ENERGIES

A. CALCULATION OF BONDING ENERGIES FROM SCF-MO-CNDO THEORY

The complete Hamiltonian for a molecule can be partitioned (Chapter 1) into electronic and nuclear terms:

$$\overset{o}{H} = \overset{o}{H}_e + \overset{o}{T}_n + \overset{o}{V}_{nn} \qquad (1.5)$$

where $\overset{o}{H}_e$ is the electronic Hamiltonian with eigenvalue E_e, $\overset{o}{T}_n$ is the nuclear kinetic energy, and $\overset{o}{V}_{nn}$ is the internuclear potential energy. The total molecular energy is often partitioned into electronic, vibrational, and rotational terms.[207]

$$E = E_{elect} + E_{vib} + E_{rot} \qquad (8.1)$$

E_{elect} is the total electronic energy, given by

$$E_{elect} = E_e + V_{nn} \qquad (8.2)$$

where V_{nn} is the expectation value of the internuclear potential energy for a fixed nuclear configuration.

At $0^{o}K$, the rotational and translational energies vanish, and only the vibrational zero-point energy[230]

$$\overset{o}{E}_{vib} = \frac{h}{2} \sum_i \nu_i \qquad (8.3)$$

remains; the summation extends over all vibrational normal modes.[230] For most of the small molecules considered, all the vibrational frequencies, and their degeneracies, are known.[230-232] At $0^{o}K$, therefore, the energy of an isolated molecule is

$$E = E_e + V^o_{nn} + \frac{h}{2}\sum_i \nu_i \qquad (8.4)$$

For a closed-shell molecule with a single-determinant wave function

$$\Psi = \mathrm{Det}\left| \psi_1\alpha \quad \psi_1\beta \quad \ldots\ldots\ldots \quad \psi_n\beta \right| \qquad (1.9)$$

E_e can be expressed as a summation over the occupied orbitals,[1]

$$E_e = \sum_i (J_i + E_i) \qquad (8.5)$$

E_i is the orbital energy eigenvalue, which may be written

$$E_i = \sum_{k,l} C^*_{ki} \; C_{li} \; F_{kl} \qquad (2.11)$$

when the molecular orbitals are linear combinations of atomic orbitals. The C_{ki} are orbital coefficients, and F is the Hartree-Fock Hamiltonian matrix. Similarly,

$$J_i = \sum_{k,l} C^*_{ki} \, C_{li} \, H_{kl} \qquad (8.6)$$

where H is the core Hamiltonian matrix. On substituting equations (2.11) and (8.6) into equation (8.5),

$$E_e = \sum_{k,l} (H_{kl} + F_{kl}) \sum_i C^*_{ki} \; C_{li} \qquad (8.7)$$

The population matrix elements, P_{kl}, were defined previously as

$$P_{kl} = 2\sum_{i} C^{*}_{ki}\, C_{li} \tag{2.15}$$

so that

$$E_e = \frac{1}{2} \sum_{k,l} P_{kl}\,(H_{kl} + F_{kl}) \tag{8.8}$$

the form used by Pople, Santry and Segal.[42,43] In matrix form, this becomes

$$E_e = \frac{1}{2}\,\mathrm{tr}\ P\,(H + F) \tag{8.9}$$

From equations (8.2) and (8.9) the total electronic energy is

$$E_{elect} = \frac{1}{2}\,\mathrm{tr}\ P\,(H + F) + V_{nn} \tag{8.10}$$

For computation, it is convenient to use the equivalent form

$$E_{elect} = \frac{1}{2}\,\mathrm{tr}\ PH + \sum_{i} E_i + V_{nn} \tag{8.11}$$

since the energy eigenvalues E_i are determined together with the orbital coefficients.

The SCF-MO-CNDO theory has been applied by other authors only to the calculation of the relative energies of different nuclear configurations[44-46] or electronic states[67,68] of single molecules, although Dewar et al. have computed heats of formation using their PNDDO approximation.[64,69] To calculate relative energies for single molecules, it is sufficient to consider the relative values of the total electronic energy, E_{elect}.

In order to find bonding or dissociation energies, or heats of formation, however, the choice of the energy zero implied by equation (8.11) must be examined.

For an all-valence-electron SCF-MO theory, the right hand side of equation (8.10) vanishes if

(i) the molecule has no valence-shell electrons, so that the one-electron density matrix P is zero, and E_e vanishes, and

(ii) the atomic cores are at infinite distance apart, so that V_{nn} vanishes.

In chemistry, however, one is interested not in the energy required to remove all the electrons and atomic cores to infinite separation, but rather in the bonding energy, or atomization energy, required to separate the molecule into neutral atoms in their ground state at infinite distance apart.[75] This bonding energy may be expressed as

$$E_B = \sum_A E_A - E_{elect} \qquad (8.12)$$

where E_A is the valence shell electronic energy of atom A, and E_B is positive for a stable molecule.

For a diatomic molecule, E_B is equal to the heat of dissociation, D_e, measured from the minimum of the potential energy curve.[207] For a harmonic oscillator,

$$E_B = D_e = D_o + \frac{1}{2} h\nu \qquad (8.13)$$

where D_o is the observed heat of dissociation from the vibrational ground state, and ν is the vibrational frequency.[207] In general, the bonding energy is related to the experimental heat of formation at 0^oK,

$$E_B = \Delta H_{f0} + \sum_A (\Delta H_{f0}(A)) + E^o_{vib} \tag{8.14}$$

where ΔH_{f0} is the molecular heat of formation in the gas phase at 0^oK, and $\Delta H_{f0}(A)$ is the heat of formation of the monatomic gas of element A.[231] If the heats of formation are only available at some temperature, T^oK, equation (8.14) is formally replaced by

$$E_B = -\Delta H_{f\tau} + \sum_A (\Delta H_{f\tau}(A)) + E_{vib} - \int_0^T \Delta C_p \, d\tau \tag{8.15}$$

The integral is neglected if the required heat capacity data are not known.

The theoretical bonding energy is found by substituting equation (8.2) into equation (8.12)

$$E_B = \sum_A E_A - E_e - V_{nn} \tag{8.16}$$

The atomic energy, E_A, formally represents the energy required to remove all the valence-shell electrons from atom A, just as E_e represents the energy required to remove the valence-shell electrons from the molecule. The successive ionization of electrons, from both atoms and molecules, requires increasing amounts of energy for two reasons:

(i) the electrostatic repulsion of other electrons acting on the electron to be ionized decreases. This effect is incorporated into any

SCF theory, since the variation of the electrostatic potential with charge distribution is explicitly included in the SCF equations.

(ii) as electrons are removed, the remaining electrons are less screened from the nucleus, as implied by the Slater rules[7,70] for screening constants, so that the orbitals which they occupy are reorganized to have a greater probability density near the nucleus, and the expectation value of the nuclear attraction is increased. This effect is not accounted for in SCF-MO calculations with a minimum basis, since the orbital parameters are assigned fixed values. The parameters evaluated from atomic spectra in Chapter 3 are valid only for valence states close to electroneutrality. If the energy required to remove all the valence electrons from an atom is calculated from these parameters, it differs from the sum of experimental ionization potentials[81] by, for example, 24.5 ev. for C, and 171.0 ev. for F.

If, in calculating the bonding energy from equation (8.16), atomic energies were equated to the sum of the appropriate experimental ionization potentials, the effect of orbital reorganization would be included only in the atomic energy, and not in the molecular energy, so that the bonding energy would be seriously in error. In order to remove this error, the atomic and molecular energies must be calculated using the same approximations and parameters, so that there is a cancellation of errors in the bonding energies.

In the CNDO approximation, the energy of an atomic state is given by

$$E = C^{o} + \sum_{k} n_k \bar{U}_{kk} + \frac{1}{2} (\sum_{k} n_k) (\sum_{k} n_k - 1) g_{AA} \qquad (3.18)$$

where n_k is the number of electrons in the k^{th} orbital, and the summations extend over all the valence-shell orbitals. Since the energy must now be expressed relative to the core state, with all valence electrons removed, the additive constant becomes zero, and for a state with n_s s - electrons and n_p p - electrons,

$$E = n_s \bar{U}_{ss} + n_p \bar{U}_{pp} + (n_s + n_p) (n_s + n_p - 1) g_{AA} \qquad (8.17)$$

B. INTERNUCLEAR POTENTIAL ENERGY

An explicit form has not yet been given for the internuclear potential energy, V_{nn}. If the atomic cores are assumed to be point charges, or non-polarizable non-penetrating spherical charge distributions, then V_{nn} is simple the classical electrostatic repulsion between point charges,

$$V_{nn} = \sum_{A>B} Z_A Z_B R_{AB}^{-1} \qquad (8.18)$$

in atomic units, as assumed by Pople, Santry, and Segal.[43,45] The net electrostatic interaction between any two atoms is then

$$E_{AB} = V_{nn} + P_{AA} V_{AB} + P_{BB} V_{BA} + P_{AA} P_{BB} g_{AB} \qquad (8.19)$$

The interatomic core-attraction integral, V_{AB}, has been chosen so that the penetration integrals vanish (Chapter 4),

$$V_{AB} = -Z_B g_{AB} \qquad (4.16)$$

Thus for two neutral atoms, with atomic populations P_{AA} and P_{BB} equal to the atomic core charges Z_A and Z_B, the use of the point-charge expression, equation (8.18), leads to a net electrostatic repulsion,

$$E^o_{AB} = Z_A Z_B \left(R^{-1}_{AB} - g_{AB}\right) \qquad (8.20)$$

which makes it impossible to predict accurate bonding energies for any reasonable choice of parameters.

For hydrogen, for example, the population matrix, as shown previously, is

$$P = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \qquad (7.6)$$

so that equation (8.10) for the total electronic energy becomes

$$E_{elect} = H_{11} + H_{12} + F_{11} + F_{12} + V_{nn} \qquad (8.21)$$

Equation (4.18) and equation (2.28), for the matrix elements H_{11} and H_{12} respectively, become for hydrogen

$$H_{11} = U_{11} - g_{12} \qquad (8.22)$$

and

$$H_{12} = -\beta^o_H S_{12} \qquad (8.23).$$

Combining these with equations (7.7) and (7.8) for F_{11} and F_{12}, the electronic energy is

$$E_e = 2U_{11} + \frac{1}{2} g_{11} - \frac{3}{2} g_{12} - 2\beta^o_H S_{12} + V_{nn} \qquad (8.24)$$

and the bonding energy is

$$E_B = 2\beta_H^o S + \frac{3}{2} g_{12} - \frac{1}{2} g_{11} - V_{nn} \qquad (8.25)$$

since for hydrogen, the atomic energy E_H equals the local core- Hamiltonian matrix element U_{11}. If the internuclear potential energy has the point-charge form (8.18), the bonding energy is then

$$E_B = 2\beta_H^o S + \frac{3}{2} g_{12} - \frac{1}{2} g_{11} - R_{AB}^{-1} \qquad (8.26)$$

If equation (8.26) is solved simultaneously with equation (7.9) for the ionization potential of hydrogen,

$$I = 7.171 + \beta_H^o S + \frac{1}{2} g_{12} \qquad (7.9)$$

then for the experimental bonding energy and ionization potential, g_{11} determined from the Pariser approximation,[72] and $Z_H' = 1.2$; the inter-atomic electron-repulsion integral $g_{12} = 28.052$ ev., and the bonding parameter $\beta_H^o = -5.748$ ev. These values are absurd, however, since g_{12} is much higher than even the theoretical g_{11} for hydrogen, 20.408 ev., and the bonding parameter has the wrong sign, which implies that the anti-bonding orbital is the occupied orbital.

If, on the other hand, the bonding parameter is chosen to give the correct dissociation energy for reasonable values of g_{12}, then the bonding parameter is 14.074 ev., and 10.759 ev., when g_{12} is determined by the Mataga, and by the Ohno formula respectively. The calculated ionization potentials are then 20.53 ev., and 19.78 ev., in the two cases, in very poor agreement with the experimental value of 15.45 ev.

The point- charge form for V_{nn} is therefore unsatisfactory. Dewar and Klopman[64] have suggested that this is because the method of assignment of atomic parameters fails to allow for the reorganization of atomic orbitals, and changes in the effective nuclear charges, upon molecule formation, and that this error must be compensated by altering the form of V_{nn}.

The simplest satisfactory assumption is that the net electrostatic interaction between two neutral atoms, E^{o}_{AB}, vanishes, so that

$$V_{nn} = \sum_{A>B} Z_A Z_B g_{AB} \qquad (8.27)$$

as assumed by Chung and Dewar for pi-electron systems.[232] The electrostatic interaction between any two atoms is then simply the interaction of net charges.

$$E_{AB} = (P_{AA} - Z_A)\ (P_{BB} - Z_B)\ g_{AB} \qquad (8.28)$$

With this choice of V_{nn}, accurate bonding energies and ionization potentials can be obtained for reasonable parameter values. For hydrogen, substitution of equation (8.27) into equation (8.25) leads to the bonding energy

$$E_B = 2\beta^{o}_{H}S + \frac{1}{2}(g_{12} - g_{11}) \qquad (8.29)$$

which may be solved simultaneously with equation (7.9) for the ionization potential to give $g_{12} = 10.766$ ev. and $\beta^{o}_{H} = 4.293$ ev., (for $Z'_H = 1.2$), as in Chapter 7.

Dewar and Klopman[64] have objected to the use of equation (8.27) in calculations including all valence electrons, since they have found that a net repulsive interaction between neutral atoms at short internuclear distances is necessary in order to predict potential energy minima. In this thesis, however, it is found that equation (8.27) leads to satisfactory prediction of bonding energies at experimental bond lengths.

The final formula used to compute bonding energies from the semi-empirical SCF-MO theory is found by substituting equations (8.11) and (8.27) into equations (8.16) so that

$$E_B = \sum_A E_A - \frac{1}{2} \mathrm{tr}\, PH - \sum_i E_i - \sum_{A>B} Z_A Z_B g_{AB} \qquad (8.30),$$

where E_A is given by equation (8.17).

C. EXTENDED HUCKEL THEORY BONDING ENERGIES

In the Extended Huckel Theory, E_e cannot be evaluated from equation (8.9), since the one-electron Hamiltonian, $\hat{h}_{eff}$, is not separated into core and electron-repulsion terms. Hoffmann and Lipscomb[114,146] equated the total electronic energy of closed-shell molecules to twice the sum of occupied orbital energies, as in the Huckel pi-electron theory.[15,16]

$$E_{elect} = 2 \sum_i E_i \qquad (8.31)$$

From equations (8.31) and (8.12), the bonding energy is given by

$$E_B = \sum_A E_A - 2 \sum_i E_i \tag{8.32}$$

The internuclear potential energy, V_{nn}, is not included in this calculation of the bonding energy, since Hoffmann[114] found that the EHT predicts potential energy minima for most stable molecules (although not hydrogen), which vanish when V_{nn} is included. He assumed therefore that

> "the method of guessing the matrix elements simulates within the electronic energies the presence of nuclear repulsions at small distances,"[114]

and suggested that this effect is due to a rough cancellation of electron-electron and nuclear-nuclear repulsions, neither of which is included explicitly in the EHT. Allen and Russell[145] have shown that bond angles are predicted correctly from Hartree-Fock calculations, using a simple sum of orbital energies as in equation (8.31), except for highly ionic molecules; so that the EHT may also be expected to predict bond angles correctly. This does not apply, however, to bond lengths.[145]

As in the SCF theory, the atomic and molecular energies must be calculated using the same approximations and parameters, so that there is a cancellation of errors in the bonding energy. By analogy with equation (8.31), the valence-shell energy of an atom with n_s s-elections and n_p p - electrons is

$$E_A = n_s h_{ss} + n_p h_{pp} \tag{8.33}$$

Hoffmann and Lipscomb[114,146] have used instead

$$E_A = (n_s - 1)\cdot h_{ss} + (n_p + 1)\, h_{pp} \tag{8.34}$$

for boron and carbon, since they found that the ratios of bonding energies for different boron hydrides are correctly predicted using equation (8.34) in a preliminary calculation[146] with all off-diagonal matrix elements given by

$$h_{kl} = KS_{kl}, \qquad K = 21 \text{ ev.} \tag{8.35}$$

This procedure is not justified, however, since equation (8.33) and <u>not</u> equation (8.34) refers to the ground state of an atom. Table (8.1) shows that the procedure of Hoffmann and Lipscomb is not only theoretically invalid, but also leads to much less accurate bonding energies than are obtained using equation (8.33).

D. EXPERIMENTAL BONDING ENERGIES

The principle source for the experimental data concerning bonding energies is the JANAF Interim Thermochemical Tables.[231] The disscoiation energies of some diatomic molecules are listed directly. For other molecules, the bonding energies of some diatomic molecules are listed directly. For other molecules, the bonding energies have been calculated from equation (8.14), where the molecular and atomic heats of formation have been extrapolated to $0^{o}K$ in the tables, assuming ideal-gas heat capacities.[231] The vibrational frequencies of most of the small

TABLE 8.1

COMPARISON OF EHT BONDING ENERGIES ($Z'_H = 1.0$) WITH THOSE CALCULATED AS PER HOFFMANN AND LIPSCOMB

	This work	As per Hoffmann & Lipscomb	Exptl.
CH_4	19.552	29.291	18.18 ev.
C_2H_2	19.792	39.270	17.53
C_2H_4	24.883	44.361	24.36
C_2H_6	30.781	50.259	30.82
C_3H_8	42.037	71.254	43.56
BH_3	16.398	22.889	12.1
B_2H_6	23.475	36.457	26.00

molecules considered are listed, as well as their degeneracies.[231] Anharmonicity corrections have been neglected, since the effect on E_B is only 0.004 ev. for hydrogen, and less for most other diatomics,[231] and is unknown for most polyatomics.

For molecules not listed in the JANAF tables, the heats of formation are taken from other sources, and the vibrational frequencies from the compilation of Herzberg.[230,232] The heats of formation of the following molecules at 298°K are taken from National Bureau of Standards data: BrCl, ICl, C_2H_6, C_3H_8, ICN, CH_3CN, CH_3Cl, CH_3Br, and CH_3I. The heats of formation of Group IV, V, and VI hydrides were determined by Gunn and Green[235] using an explosive decomposition method, and the dissociation energies of ClF, BrF, and IF were found from appearance potentials by Irsa and Friedman.[222]

The vibrational energy of propane was extrapolated from that of methane and ethane, since the vibrational frequencies are not all known.[230] The unknown vibrational frequencies of IF and BrCl were assumed to be equal to the arithmetic mean of the corresponding pure halogen frequencies, since this approximation is accurate within 50 cm^{-1} for the other four interhalogen molecules.[231,233]

The experimental bonding energies of the binary hydrides used to calibrate the bonding parameters have been rounded off to their probable precision. For other molecules, the bonding energies are given to 0.001 ev. from the experimental data, although this exaggerates their precision in many cases.

E. CALIBRATION OF BONDING PARAMETERS

Bonding parameters for the semi-empirical SCF-MO theory have been calibrated from the bonding energies of binary hydrides, as described in Chapter 4. The variation of calculated bonding energies with bonding parameters in the neighbourhood of the experimental bonding energy is shown in Tables (8.2) and (8.3) for the parameter sets M2 and O2 respectively. The chosen bonding parameters, which give the experimental bonding energies, have been rounded off to the nearest tenth of an electron volt, since greater precision would be inconsistent with the precision of most of the experimental bonding energies. For other parameter sets, the variation of calculated bonding energies with bonding parameters is similar and the final bonding parameters have been listed in Table (4.2)

The exact electronic energy of a molecule can be written[236] as

$$E_{elect} = E_{HF} + E_{corr} + V_{nn} \qquad (8.36)$$

where E_{HF} is the Hartree-Fock energy for the best single-determinant wave function and E_{corr} is the correlation energy. In the semi-empirical theory described here, the parameters are adjusted to give the correct bonding energies, including correlation energy, even though the wave function is a single determinant.

In order to determine the bonding energy of a molecule accurately from a single-determinant wave function, without using empirical parameters, it would be necessary to first determine E_{HF} from a complete SCF-MO calculation, and then either to calculate the exact energy by super-

TABLE 8.2

CALIBRATION OF BONDING PARAMETERS FOR SCF-MO THEORY WITH CNDO APPROXIMATION (PARAMETER SET M2)

	β_A^o	E_B	β_A^o	E_B	Final β_A^o	E_B	β_A^o	E_B	β_A^o	E_B	Exptl. E_B
LiH	1.0	2.740	0.8	2.632	0.7	2.579	0.6	2.525	0.0	2.209	2.6 ev.
BeH_2	5.0	8.298	4.1	7.012	4.0	6.870	3.9	6.727	3.0	5.450	6.9
BH_3	6.0	12.994	5.7	12.344	5.6	12.128	5.5	11.911	5.0	10.831	12.1
CH_4	9.0	20.446	8.3	18.571	8.2	18.304	8.1	18.038	8.0	17.772	18.18
NH_3	9.0	13.313	8.9	13.155	8.8	12.999	8.7	12.842	8.0	11.762	12.93
H_2O	13.0	10.290	12.9	10.196	12.8	10.101	12.7	10.007	12.5	9.820	10.06
HF	18.0	6.443	17.3	6.148	17.2	6.106	17.1	6.064	17.0	6.025	6.11
SiH_4	6.0	16.127	5.3	14.261	5.2	13.994	5.1	13.728	5.0	13.463	13.87
PH_3	7.0	12.255	6.1	10.630	6.0	10.450	5.9	10.271	5.0	8.668	10.47
H_2S	7.0	8.113	6.6	7.646	6.5	7.530	6.4	7.413	6.0	6.950	7.5
HCl	10.0	5.216	9.0	4.660	8.9	4.605	8.8	4.550	8.0	4.109	4.61
GeH_4	5.0	14.044	4.5	12.708	4.4	12.441	4.3	12.175	4.0	11.376	12.5
AsH_3	5.0	9.618	4.8	9.252	4.7	9.069	4.6	8.887	4.0	7.796	9.1
H_2Se	6.0	6.961	5.8	6.725	5.7	6.608	5.6	6.490	5.0	5.789	6.6

TABLE 8.2 cont.

	β_A^o	E_B	β_A^o	E_B	Final β_A^o	E_B	β_A^o	E_B	β_A^o	E_B	Exptl. E_B
HBr	8.0	4.387	7.3	3.992	7.2	3.935	7.1	3.879	7.0	3.823	3.92
SnH_4	4.0	11.968	3.7	11.208	3.6	10.955	3.5	10.702	3.0	9.440	11.0
SbH_3	5.0	8.748	4.8	8.401	4.7	8.229	4.6	8.056	4.0	7.022	8.3
H_2Te	7.0	6.812	6.2	5.935	6.1	5.825	6.0	5.716	5.0	4.628	5.8
HI	7.0	3.357	6.8	3.247	6.7	3.192	6.6	3.137	6.0	2.809	3.20

TABLE 8.3

CALIBRATION OF BONDING PARAMETERS FOR SCF-MO THEORY WITH CNDO APPROXIMATION (PARAMETER SET 02)

	β^o_A	E_B	β^o_A	E_B	Final β^o_A	E_B	β^o_A	E_B	β^o_A	E_B	Exptl. E_B
LiH	0.0	2.933	-0.7	2.645	-0.8	2.606	-0.9	2.567	-1.0	2.529	2.6 ev.
BeH_2	4.0	7.693	3.5	7.019	3.4	6.884	3.3	6.751	3.0	6.352	6.9
BH_3	6.0	14.169	5.1	12.237	5.0	12.022	4.9	11.809	4.0	9.891	12.1
CH_4	8.0	20.091	7.4	18.501	7.3	18.235	7.2	17.970	7.0	17.441	18.18
NH_3	8.0	14.075	7.4	13.140	7.3	12.985	7.2	12.831	7.0	12.524	12.93
H_2O	11.0	10.499	10.6	10.132	10.5	10.040	10.4	9.949	10.0	9.585	10.06
HF	15.0	6.479	14.2	6.160	14.1	6.121	14.0	6.082			6.11
SiH_4	5.0	14.585	4.8	14.055	4.7	13.790	4.6	13.525	4.0	11.941	13.87
PH_3	6.0	11.767	5.4	10.700	5.3	10.523	5.2	10.346	5.0	9.993	10.47
H_2S	6.0	7.930	5.7	7.585	5.6	7.470	5.5	7.355	5.0	6.784	7.5
HCl	8.0	4.734	7.9	4.680	7.8	4.626	7.7	4.572	7.0	4.194	4.61
GeH_4	5.0	15.247	4.1	12.884	4.0	12.623	3.9	12.362	3.0	10.032	12.5
AsH_3	5.0	10.683	4.2	9.234	4.1	9.053	4.0	8.874	3.0	7.088	9.1
H_2Se	6.0	7.828	5.0	6.663	4.9	6.547	4.8	6.431	4.0	5.510	6.6
HBr	7.0	4.309	6.4	3.976	6.3	3.921	6.2	3.865	6.0	3.755	3.92

TABLE 8.3 cont.

	β_A^o	E_B	β_A^o	E_B	Final β_A^o	E_B	β_A^o	E_B	β_A^o	E_B	Exptl. E_B
SnH_4	3.0	12.491	2.2	11.186	2.1	11.033	2.0	10.882			11.0
SbH_3	5.0	9.693	4.3	8.496	4.2	8.326	4.1	8.155	4.0	7.985	8.3
H_2Te	6.0	6.458	5.5	5.916	5.4	5.808	5.3	5.700	5.0	5.376	5.8
HI	7.0	3.767	6.1	3.277	6.0	3.223	5.9	3.168	5.0	2.683	3.20

position of configurations,[236] or to estimate the correlation energy, as in the approximate theory of Hollister and Sinanoglu.[237] The present method is much simpler, however, and can therefore be applied to larger molecules. Its validity is tested by examining the accuracy of bonding energies calculated in this way for molecules other than those used in the calibration of the bonding parameters.

F. COMPARISON OF CALCULATED BONDING ENERGIES WITH EXPERIMENT

Bonding energies calculated from SCF-MO theory using empirical bonding parameters are shown in Table (8.4), for molecules other than those used in calibration. The energies are fairly accurate on the whole, in contrast to those calculated using the Pople-Segal bonding parameters (Table 8.5), so that the theory includes correlation energy reasonably accurately.

The bonding energies calculated for $Z_H' = 1.2$ are more accurate than those for $Z_H' = 1.0$. When electron-repulsion integrals evaluated from atomic spectra are used, the bonding energies for $Z_H' = 1.2$ (Columns M2 and O2) are more accurate for all the molecules considered, except SO_2, I_2, IF, IBr, CH_3I and (for interatomic g_{AB} calculated from the Mataga formula only) LiF. When theoretical electron-repulsion integrals are used, more accurate bonding energies are predicted for $Z_H' = 1.2$ (Column R2), except for LiF, CH_3F and F_2. The value 1.2 is therefore chosen as the better value for the Slater exponent of hydrogen in the SCF-MO calculations.

TABLE 8.4

BONDING ENERGIES CALCULATED BY SCF-MO THEORY WITH CNDO APPROXIMATION AND EMPIRICAL BONDING PARAMETERS

Parameter Set	M1	M2	01	02	R1	R2	Exptl.
N_2	12.325	10.480	12.402	10.839	12.997	11.566	9.903 ev.
CO	13.838	11.931	13.798	12.166	14.136	12.579	11.225
CS	8.093	7.414	8.660	7.970			7.190
CO_2	22.032	18.981	21.310	18.592	22.578	20.160	16.856
OCS		16.142	17.968	15.984			14.417
CS_2	14.154	13.012	14.262	13.090			11.980
NNO			17.401	14.986	18.899	16.634	11.724
SO_2	11.085	9.494	11.255	9.761			11.177
O_3	11.995	9.804	11.009	9.034			6.345
C_2H_2	19.333	17.724	19.969	18.264	20.003	19.448	17.530
C_2H_4	25.290	24.250	25.609	24.366	25.169	24.831	24.357
C_2H_6	31.603	31.032	31.650	30.799	31.077	30.867	30.818
C_3H_8	46.431	45.230	46.250	44.705	45.699	45.373	43.563
B_2H_6	28.657	27.706	27.523	26.580	28.398	27.652	26.004
LiF	5.970	5.551	6.557	6.290	4.101	3.822	5.940

TABLE 8.4 cont.

Parameter Set	M1	M2	01	02	R1	R2	Exptl.
F_2	2.887	2.060	2.627	1.983	0.991	0.064	1.653
Cl_2	3.491	3.178	3.398	3.170			2.508
Br_2	2.767	2.687	2.774	2.695			1.991
I_2	1.677	1.837	1.750	1.907			1.557
ClF	3.882	3.191	3.604	3.079			2.668
BrF	3.369	2.799	3.216	2.778			2.682
BrCl	2.997	2.804	2.977	2.826			2.334
IF	1.524	1.153	1.570	1.295			2.91
ICl	2.382	2.307	2.405	2.368			2.190
IBr	2.162	2.201	2.212	2.251			1.928
CH_3F	19.558	18.634	19.126	18.234	18.813	17.847	18.384
CH_3Cl	17.680	17.329	17.669	17.211			17.154
CH_3Br	16.808	16.608	16.891	16.532			16.640
CH_3I	15.789	15.733	15.944	15.727			15.931
HCN	16.113	14.705	16.367	14.996	16.410	15.603	13.537
CH_3CN			30.866	28.710			26.586

TABLE 8.4 cont.

Parameter Set	M1	M2	01	02	R1	R2	Exptl.
FCN	19.703	17.167	19.265	17.113	20.114	18.199	13.529
ClCN		15.262	17.159	15.468			12.310
BrCN	16.051		16.183	14.589			—
ICN	14.868	13.333	15.094	13.658			11.159

On comparing the results in Table (8.4) for $Z'_H = 1.2$ and different choices of electron-repulsion integrals, the bonding energies calculated using theoretical integrals are less accurate than those calculated using integrals evaluated from atomic spectra, except for C_2H_6 and B_2H_6, for which the bonding energies calculated using theoretical integrals are more accurate than those obtained using the Mataga formula, but not the Ohno formula.

The bonding energies do not provide a conclusive choice between the Mataga and Ohno formulae for interatomic electron-repulsion integrals, since each leads to more accurate bonding energies for about the same number of molecules. As in the calculation of molecular ionization potentials (Chapter 7), it seems that the exact values of the interatomic integrals do not matter, provided that the atomic integrals, and the atomic limit of the interatomic integrals, are evaluated from atomic spectra.

Table (8.5) shows that the Pople-Segal bonding parameters are completely inadequate for the calculation of total molecular energies, since the predicted bonding energies are higher than the experimental by factors ranging from 3 to 8. The bonding energies calculated using theoretical electron-repulsion integrals (Column RP) are slightly better than the others, but the difference is negligible in view of the magnitude of the errors of all the calculated energies in Table (8.5). It should be noted that, since the bonding energies are too high rather than too low, the errors cannot be blamed on the omission of correlation

TABLE 8.5

BONDING ENERGIES CALCULATED BY SCF-MO THEORY WITH CNDO APPROXIMATION AND POPLE-SEGAL BONDING PARAMETERS

Parameter Set	MP	OP	RP	Exptl.
H_2	14.700	13.209	14.398	4.751 ev.
LiH	9.542	10.509	7.987	2.6
BeH_2	25.117	27.240	23.591	6.9
BH_3	44.931	48.392	43.312	12.1
CH_4	62.505	67.602	61.033	18.18
NH_3	47.787	52.018	45.279	12.93
H_2O	32.552	35.672	31.020	10.06
HF	17.639	19.271	16.366	6.11
N_2	51.344	55.082	48.316	9.903
CO	46.269	49.706	44.377	11.225
CO_2	78.196	83.951	74.404	16.856
NNO	76.386	82.387	70.354	11.724
O_3	45.767	50.183	38.955	6.345
C_2H_2	79.055	85.021	78.328	17.530
C_2H_4	96.015	103.204	93.889	24.357
C_2H_6	113.428	121.945	110.297	30.818
C_3H_8	167.580	179.622	163.209	43.563
B_2H_6	110.206	117.628	105.457	26.004
LiF	15.955	17.300	12.639	5.940
F_2	11.672	12.850	8.308	1.653

TABLE 8.5 cont.

Parameter Set	MP	OP	RP	Exptl.
CH_3F	66.474	71.449	63.159	18.384
HCN	63.955	68.801	61.784	13.537
CH_3CN	118.383	126.709	114.546	26.586
FCN	73.472	78.570	69.548	13.529

energy, but are due simply and solely to the large values of the Pople-Segal bonding parameters.[44]

It is therefore a very questionable procedure to calculate the relative energies of different nuclear configurations with bonding parameters which have not been calibrated to give accurate bonding energies, as in calculations of energy barriers and bending force constants.[44-46] Since the calculated barrier to internal rotation in ethane is quite sensitive to changes in the bonding parameters[44], the use of empirical bonding parameters would lead to very different values for the barrier energies. The energy barriers and bending force constants calculated by Pople, Santry, and Segal[44-46] are somewhat erratic, and are in better agreement with experiment for some molecules than for others. In view of the results in Table (8.5), it is concluded that the fair agreement for some molecules is due to a fortuitous cancellation of errors.

The bonding energies calculated using the Extended Huckel Theory are listed in Table (8.6). The results for some molecules are quite accurate, but the theory is seriously in error for the binary hydrides, and especially hydrogen, just as in the prediction of ionization potentials. For the hydrides, the differences between the results for the two values of Z'_H are insignificant in view of the errors. For organic molecules, however, the bonding energies are predicted relatively accurately by the EHT, and the values for $Z'_H = 1.0$ (Column H1) are more accurate than those for $Z'_H = 1.2$. Thus it seems that the best value for the Slater exponent of hydrogen in molecules is 1.2 in the SCF-MO theory

TABLE 8.6

BONDING ENERGIES CALCULATED BY EXTENDED HUCKEL THEORY

	H1	H2	Exptl.
H_2	35.814	32.096	4.751 ev.
LiH	8.696	8.576	2.6
BeH_2	12.752	12.439	6.9
BH_3	16.398	17.265	12.1
CH_4	19.552	21.697	18.18
NH_3	15.640	17.051	12.93
H_2O	13.191	13.843	10.06
HF	8.923	9.103	6.11
SiH_4	23.418	23.725	13.87
PH_3	16.611	17.231	10.47
H_2S	11.252	11.565	7.5
HCl	6.421	6.469	4.61
GeH_4	23.542	23.583	12.5
AsH_3	16.353	17.011	9.1
H_2Se	11.109	11.281	6.6
HBr	5.545	5.576	3.92
SnH_4	24.261	23.898	11.0
SbH_3	17.172	17.470	8.3
H_2Te	10.925	10.828	5.8
HI	5.840	5.710	3.20

TABLE 8.6 cont.

<table>
<tr><th></th><th>H1</th><th>H2</th><th>Exptl.</th></tr>
<tr><td>N_2</td><td colspan="2">10.182</td><td>9.903</td></tr>
<tr><td>CO</td><td colspan="2">10.760</td><td>11.225</td></tr>
<tr><td>CS</td><td colspan="2">7.780</td><td>7.190</td></tr>
<tr><td>CO_2</td><td colspan="2">19.745</td><td>16.856</td></tr>
<tr><td>OCS</td><td colspan="2">16.832</td><td>14.417</td></tr>
<tr><td>CS_2</td><td colspan="2">12.985</td><td>11.980</td></tr>
<tr><td>NNO</td><td colspan="2">15.785</td><td>11.724</td></tr>
<tr><td>SO_2</td><td colspan="2">17.287</td><td>11.177</td></tr>
<tr><td>O_3</td><td colspan="2">7.133</td><td>6.345</td></tr>
<tr><td>C_2H_2</td><td>19.792</td><td>20.071</td><td>17.530</td></tr>
<tr><td>C_2H_4</td><td>24.883</td><td>26.770</td><td>24.357</td></tr>
<tr><td>C_2H_6</td><td>30.781</td><td>34.298</td><td>30.818</td></tr>
<tr><td>C_3H_8</td><td>42.037</td><td>46.994</td><td>43.563</td></tr>
<tr><td>B_2H_6</td><td>23.475</td><td>25.947</td><td>26.004</td></tr>
<tr><td>LiF</td><td colspan="2">15.503</td><td>5.940</td></tr>
<tr><td>F_2</td><td colspan="2">2.404</td><td>1.653</td></tr>
<tr><td>Cl_2</td><td colspan="2">2.309</td><td>2.508</td></tr>
<tr><td>Br_2</td><td colspan="2">1.610</td><td>1.991</td></tr>
<tr><td>I_2</td><td colspan="2">2.447</td><td>1.557</td></tr>
<tr><td>ClF</td><td colspan="2">4.238</td><td>2.668</td></tr>
<tr><td>BrF</td><td colspan="2">5.392</td><td>2.682</td></tr>
<tr><td>BrCl</td><td colspan="2">2.130</td><td>2.334</td></tr>
</table>

TABLE 8.6 cont.

	H1	H2	Exptl.
IF	6.771		2.91
ICl	2.753		2.190
IBr	2.073		1.928
CH_3F	21.413	23.005	18.384
CH_3Cl	17.272	19.140	17.154
CH_3Br	16.167	18.052	16.640
CH_3I	16.395	18.228	15.931
HCN	16.420	16.442	13.537
CH_3CN	28.070	29.533	26.586
FCN	15.851		13.529
ClCN	14.473		12.310
BrCN	14.113		-
ICN	14.348		11.159

as claimed by Pople and Segal,[44] and 1.0 in the EHT, as used by Hoffmann.[114] Since the value of Z'_H determines the behaviour of the molecular orbitals near a hydrogen nucleus, it should not depend on the theory used to calculate the orbitals, but the difference is probably due to a cancellation of errors in one theory or the other.

It is interesting to compare the bonding energies for BH_3 and B_2H_6 in the two theories. In the SCF-MO theory, the bonding energy of B_2H_6 is predicted as accurately as that of many other molecules, despite the possible uncertainty due to the use of the unstable molecule, BH_3, to calibrate the bonding parameter for boron. The EHT, on the other hand, predicts incorrectly that B_2H_6 in unstable with respect to BH_3, even though the EHT was originally developed for calculations on boron hydrides.[138,146] This is another example of the unreliability of the EHT.

In summary, therefore, the best of the theories considered for the calculation of bonding energies is the SCF-MO-CNDO theory with empirical bonding parameters, a Slater exponent for hydrogen of 1.2, and electron-repulsion integrals evaluated from atomic spectra and either the Mataga or the Ohno formula.

CHAPTER 9

DIPOLE MOMENTS

A. CALCULATION OF DIPOLE MOMENTS

The electric dipole moment of a molecule is defined in terms of its electronic wave function as[6]

$$\underline{\mu} = -e \int \Psi_e^* \, \overset{o}{\underline{r}} \, \Psi_e \, dV + e \sum_A Z_A \underline{R}_A \qquad (9.1)$$

where $\underline{R}_A$ and Z_A are the position and the atomic number of nucleus A, and the dipole operator, $e \, \overset{o}{\underline{r}}$, is a sum of one-electron position operators, multiplied by the electronic charge e,

$$e \, \overset{o}{\underline{r}} = e \, (\overset{o}{\underline{r}} (1) + \ldots . + \overset{o}{\underline{r}} (n)) \qquad (9.2)$$

In molecular orbital theories for valence electrons only, Z_A is interpreted as the charge of the core of atom A, including both the nucleus and the inner-shell electrons. In the molecules considered, the axis along which the dipole moment lies is determined by symmetry, and is chosen as the x-axis, so that

$$\mu = \left| \underline{\mu} \right| = \mu_x = -e \int \Psi_e^* \, \overset{o}{x} \, \Psi_e \, dV + e \sum_A Z_A X_A \qquad (9.3)$$

For a single-determinant wave function, the expectation value of a sum of identical one-electron operators ~~is the sum of the integrals of the one-electron operators~~ is the sum of the integrals of the one-electron operators, over the occupied molecular spin orbitals,[2] so that

$$\mu = -e \sum_{i} n_{i} \int \psi_{i}^{*} \, \overset{o}{x} \, \psi_{i} \, dV + e \sum_{A} Z_{A} X_{A} \tag{9.4}$$

where n_i is the number of occupied spin orbitals corresponding to the i^{th} orbital. In a closed-shell molecule, each molecular orbital is doubly occupied, so that

$$\mu = -2e \sum_{i} \int \psi_{i}^{*} \, \overset{o}{x} \, \psi_{i} \, dV + e \sum_{A} Z_{A} X_{A} \tag{9.5}$$

For molecular orbitals which are linear combinations of atomic orbitals,

$$\mu = -2e \sum_{i} \sum_{k} \sum_{l} c_{ki}^{*} \, c_{li} \int \phi_{k}^{*} \, \overset{o}{x} \, \phi_{l} \, dV + e \sum_{A} Z_{A} X_{A} \tag{9.6}$$

The integrals appearing in equation (9.5) are the matrix elements of $\overset{o}{x}$ with respect to the atomic orbitals, and will be referred to as <u>dipole integrals</u>,

$$X_{kl} = \int \phi_{k}^{*} \, \overset{o}{x} \, \phi_{l} \, dV \tag{9.7}$$

so that the dipole moment is

$$\mu = -e \sum_{k} \sum_{l} P_{kl} X_{kl} + e \sum_{A} Z_{A} X_{A} \tag{9.8}$$

where the P_{kl} are defined by the expansion of the one-electron density matrix in terms of the basis orbitals. (Chapter 2)

In matrix form, equation (9.8) for the dipole moment becomes

$$\mu = -e \, \mathrm{tr} \, PX + e \sum_{A} Z_{A} X_{A} \tag{9.9}$$

Equation (9.9) is an exact expression for a closed-shell single-determinant wave function, and leads to quite accurate dipole moments in complete SCF-MO calculations, when an extended basis set is used, so that the wave function approaches the Hartree-Fock wave function.[30,238] Dipole moments for wave functions from complete SCF-MO calculations with a minimum basis set of Slater orbitals, however, may be much less accurate, since the dipole moment is sensitive to small errors in the wave function.[229]

Equation (9.9) is used to compute dipole moments for the wave functions calculated using the Extended Huckel Theory. For the SCF-MO theory with the CNDO approximation, however, equation (9.9) must be modified in order to preserve invariance with respect to translation of axes. The first non-zero multipole moment tensor of a molecule is independent of the location of the origin of co-ordinates,[239] so that for a neutral molecule, the dipole moment is invariant under a change of origin. This would not be so, however, if the dipole moment were calculated from equation (9.9) in molecular orbital theories in which overlap is neglected, as shown below.

Consider the transformation of co-ordinates

$$x' = x - x_o, \quad y' = y, \quad z' = z \tag{9.10}$$

Under this transformation, equation (9.9) for the dipole moment is transformed to

$$\mu' = -e \operatorname{tr} PX' + e \sum_{A} Z_A X_A' \tag{9.11}$$

in which the transformed dipole integrals, X'_{kl}, are given by

$$X'_{kl} = \int \phi_k^* (\mathring{x} - x_o) \; \phi_l \, d V = X_{kl} - x_o S_{kl} \tag{9.12}$$

The nuclear co-ordinates transform according to equation (9.10), so that

$$\mu' = -e \text{ tr } P(X - x_o S) + e \sum_A Z_A (X_A - x_o) \qquad (9.13)$$

From equations (9.9) and (9.13), the transformation rule for the dipole moment is

$$\mu' = \mu + e x_o (\text{tr } PS - \sum_A Z_A) \qquad (9.14)$$

For molecular orbital theories in which overlap is included, the orthonormality condition for the orbitals was shown to be

$$\sum_k \sum_l C^*_{ki} C_{li} S_{kl} = \delta_{ij} \qquad (2.7)$$

so that the total number of (valence-shell) electrons in a closed-shell molecule is

$$N = 2 \sum_i \sum_k \sum_l C^*_{ki} C_{li} S_{kl} = \sum_k \sum_l P_{kl} = \text{tr } PS \qquad (9.15)$$

and the dipole moment is invariant for a neutral molecule.

If overlap is neglected, however, the orthonormality condition is

$$\sum_k C^*_{ki} C_{kj} = \delta_{ij} \qquad (2.34)$$

and the total number of electrons is

$$N = 2 \sum_i \sum_k C^*_{ki} C_{ki} = \sum_k P_{kk} = \text{tr } P \qquad (9.16)$$

so that the dipole moment transforms as

$$\mu' = \mu + e x_o \text{ tr } P (S - I) \qquad (9.17)$$

Equation (9.9) cannot be used, therefore, to compute the dipole moment when the molecular orbitals have been calculated without overlap.

There are several ways to calculate an approximate dipole moment, which is invariant under translation of axes, for the SCF-MO-CNDO theory.

(i) The dipole moment can be calculated by assuming that the electron population of each atom is a point charge at the nucleus, so that

$$\mu = e \sum_{A} (Z_A - P_{AA}) X_A \qquad (9.18)$$

Equation (9.18) is clearly invariant with respect to translation for a neutral molecule, and is in one sense consistent with the CNDO approximation, since with this approximation, the dipole integrals between different atomic orbitals vanish, and the dipole moment is

$$\mu = -e \sum_{k} P_{kk} X_{kk} + e \sum_{A} Z_A X_A \qquad (9.19)$$

The centre of charge of a pure s or p orbital is at the nucleus, so that for an s-p basis set, equation (9.19) is identical with equation (9.18). However, this is not true for a hybrid basis set since the centre of charge of a hybrid orbital is not at the nucleus. In molecules with lone pairs, the displacement of the centre of the electron population of an atom away from the nucleus makes a substantial contribution to the molecular dipole moment.[55,75,44,46] This atomic polarization effect is not included in the point-charge approximation.

(ii) Pople and Segal[44] neglected all the diatomic dipole integrals in equation (9.8), but included the dipole integrals for different orbitals on the same atom, so that the dipole moment is given by

$$\mu' = -e \sum_k \sum_l P_{kl} X_{kl} \theta_{kl} + e \sum_A Z_A X_A \qquad (9.20)$$

where: $\theta_{kl} = \begin{cases} 1 & \text{if } \phi_k \text{ and } \phi_l \text{ are on the same atom,} \\ 0 & \text{otherwise,} \end{cases}$

as in the NDDO approximation.[43]

Equation (9.20) is invariant to translation, since atomic orbitals of the same atom are orthogonal, and it is also invariant to rotation and hybridization, since the dipole integrals X_{kl} of a given atom transform in the required way.[43]

For a basis of pure s and p orbitals, the only non-zero dipole integral for different orbitals on the same atom is X_{s-p_x}. The term containing this integral represents the atomic polarization effect, which is omitted in the point-charge formula, equation (9.18). For Slater orbitals, whose radial factor is given by equation (4.19), X_{s-p_x} is found by elementary integration to be

$$X_{s-p_x} = \int \phi_s \, \overset{o}{x} \, \phi_{p_x} \, dV = \frac{n'(n' + \frac{1}{2})a_o}{\sqrt{3}\ Z'} \qquad (9.21)$$

(iii) The CNDO approximation can be formally justified (Chapter 2) by ragarding the basis orbitals as approximations to the Lowdin orbitals,[47]

$$\bar{\phi} = \phi \ S^{-1/2} \qquad (2.19)$$

Dixon[63] has suggested that the dipole moment be calculated with reference to the Lowdin basis. The dipole integrals are the matrix elements of a one-electron operator, so that in the Lowdin basis, the X-matrix is transformed[47] to

$$\bar{X} = S^{-1/2} X S^{-1/2} \tag{9.22}$$

and dipole moment is transformed to

$$\bar{\mu} = -e \operatorname{tr} P\bar{X} + e \sum_A Z_A X_A = -e \operatorname{tr} (PS^{-1/2} X S^{-1/2}) + e \sum_A Z_A X_A \tag{9.23}$$

Equation (9.23) is invariant under a change of origin, since the Lowdin basis is orthogonal.

In this thesis, all three methods are used to calculate dipole moments from the SCF-MO theory, and the results are compared with experimental dipole moments. All computed dipole moments are multiplied by the conversion factor 4.80294 from atomic units to Debyes, for comparison with exerpimental values.

B. MEASUREMENT OF DIPOLE MOMENTS

The dipole moment of a molecule can be determined by observing its microwave Stark effect, which is the splitting of its rotational spectrum caused by a static electric field. The theory of the microwave Stark effect, and of its use in the measurement of dipole moments is discussed in textbooks on microwave spectroscopy[240-242] for the several cases of linear molecules, symmetric rotors, asymmetric rotors, and molecules with hyperfine structure due to nuclear quadrupole coupling. Dipole moments can now be measured using the microwave Stark effect to an accuracy[243] of 0.001 to 0.003 D.

Dipole moments can also be measured by dielectric constant measurements on bulk matter, but the results are less accurate, as evidenced by the wide variation of reported values for the same molecules.[244] This is partly due to the fact that many of the measurements are made in solution, and dipole moments are quite sensitive to solvent effects.[244] Also, the measured values represent averages over vibrational states and over naturally occurring isotopic species, whereas the values determined using the microwave Stark effect are for individual molecules in specific vibrational states. Values obtained by measurement of spectral intensities[244] are less accurate than those determined from the microwave Stark effect, since intensities are harder to measure accurately than spacings between spectral lines. Other special methods[244] have only been used for a few molecules. Dipole moment values, therefore, have been taken from measurements of the microwave Stark effect for vibrational ground states whenever possible.

For some molecules, only the dipole moments of deuterated species have been measured using the microwave Stark effect. The values for the deuterated species have been taken as the dipole moments of the molecules, and any possible isotope effects have been neglected, even though they can be significant for some molecules.[245]

The signs of most experimental dipole moments have not been determined, so that only the magnitudes of the calculated dipole moments can be compared with experiment. An exception is carbon monoxide, for which several authors have studied the sign of the small dipole moment (0.112 D) because of its special chemical interest.[246] The most definite result is that of Ozier et al., who used a molecular beam magnetic resonance experiment to show that the polarity is C^+O^-.

C. COMPARISON OF CALCULATED DIPOLE MOMENTS WITH EXPERIMENT FOR FIRST ROW MOLECULES

The different formulae for the calculation of dipole moments in a molecular orbital theory with neglect of overlap are compared in Table (9.1), for the wave functions computed from the semi-empirical SCF-MO-CNDO theory, with the parameters which were shown to be the best for the prediction of ionization potentials and bonding energies. The point-charge formula is in overall poor agreement with experiment, showing that the prediction of accurate dipole moments requires the inclusion of atomic polarization effects. The results obtained with the Pople-Segal formula show that the inclusion of these effects does lead to substantial improvement of the results, although they are still not very accurate for some molecules. The dipole moments computed from the Dixon formula, using Lowdin orbitals as a basis, are less accurate on the whole, than those calculated from the Pople-Segal formula. The Pople-Segal formula is therefore the best for the calculation of approximate dipole moments, and the errors in the results may be mostly due to errors in the wave function, rather than in equation (9.20).

TABLE 9.1

COMPARISON OF METHODS OF CALCULATION OF DIPOLE MOMENTS(a) FOR FIRST-ROW MOLECULES FROM SCF-MO-CNDO THEORY

Calculation of μ	Point-Charge		Pople and Segal		Dixon		Exptl.	Reference
Parameter Set	M2	02	M2	02	M2	02		
LiH	4.083	6.030	6.699	7.218	7.024	7.479	5.882 D	247
H_3N	0.465	0.962	1.973	2.221	0.643	0.991	1.468	248
H_2O	0.876	1.417	1.803	2.175	0.929	1.391	1.87	249
HF	1.397	1.866	1.899	2.265	1.578	2.003	1.8195	250
CO	1.549	2.097	0.789	1.372	1.308	2.017	-0.112	251,246
NNO		0.838		0.601		0.862	0.166	252
O_3 (b)	0.734	0.893	0.876	0.909	0.429	0.583	0.58	253
C_3H_8 (c)	0.183	0.106	0.084	0.041	0.151	0.082	0.083	254
LiF	6.052	6.818	6.602	7.098	6.833	7.222	6.328	255
CH_3F	2.721	2.812	2.647	2.687	2.391	2.408	1.8555	256
HCN	1.582	1.689	3.015	2.946	1.547	1.501	2.985	257
CH_3CN		2.440		3.709		2.173	3.92	258
FCN	-0.667	-0.427	0.482	0.648	-0.364	-0.165	2.17	259

Notes on Table 9.1

(a) Positive sign indicates polarity A^+B^-, where A is first atom written.

(b) Positive sign indicates central oxygen at positive end.

(c) Positive sign indicates central carbon at positive end.

Table (9.1) also shows that the computed dipole moment is quite sensitive to changes in the interatomic electron-repulsion integrals. The Mataga formula leads to more accurate dipole moments, as computed by the Pople-Segal formula, than the Ohno formula, for all the molecules considered except FCN. This is evidence in favour of the Mataga formula, although only a few of the computed dipole moments are accurate enough to be used as evidence. The variation of the computed dipole moment with the parameters of the SCF-MO-CNDO theory is considered further in connection with Table (9.2).

Dipole moments of first-row molecules, calculated by the Pople-Segal formula, using the different sets of parameters for the SCF-MO-CNDO theory, are shown in Table (9.2). The values of the electron-repulsion integrals have a substantial effect on dipole moments, since they determine the potential energy corresponding to a given charge distribution, which in turn determines the self-consistent charge distribution. Dipole moments, like ionization potentials, are relatively unaffected by changes in the Slater exponent for hydrogen, although there is a substantial effect for some molecules.

For some molecules, the dipole moments computed using the Pople-Segal bonding parameters are quite different from those computed using the empirical bonding parameters. This can be explained by considering the dependence of the molecular energy on the bonding parameters in the SCF-MO-CNDO theory. The energy eigenvalue of the electronic Hamiltonian has the form,

$$E_e = \frac{1}{2} \sum_{k,l} P_{kl} \left(F_{kl} + H_{kl} \right) \tag{8.8}$$

TABLE 9.2

DIPOLE MOMENTS [(a)] OF FIRST-ROW MOLECULES CALCULATED AS PER POPLE AND SEGAL FROM SCF-MO THEORY AND CNDO APPROXIMATION

Parameter Set	M1	M2	MP	01	02	OP	R1	R2	RP	Exptl.
LiH	6.649	6.699	6.218	7.196	7.218	6.284	6.277	6.365	6.192	5.882
H_3N	2.166	1.973	2.212	2.438	2.221	2.382	2.122	1.873	2.104	1.468
H_2O	1.975	1.803	2.190	2.352	2.175	2.378	1.952	1.784	2.142	1.87
HF	2.032	1.899	1.929	2.394	2.265	2.037	1.848	1.741	1.849	1.8195
CO	0.614	0.789	-1.113	1.138	1.372	-1.510	0.419	0.547	-0.961	-0.112
NNO			0.227	0.558	0.601	-0.300	0.517	0.454	0.761	0.166
O_3	0.860	0.876	1.197	0.925	0.909	1.680			1.178	0.58
C_3H_8	0.121	0.084	0.019	0.072	0.041	-0.005	-0.018	0.003	-0.001	0.083
LiF	6.494	6.602	4.926	7.016	7.098	4.934	5.898	5.936	5.079	6.328
CH_3F	2.638	2.647	1.780	2.642	2.687	1.699	2.055	1.943	1.719	1.8555
HCN	3.218	3.015	2.993	3.170	2.946	3.094	2.745	2.581	2.463	2.985
CH_3CN			3.977	4.104	3.709	4.160			3.053	3.92
FCN	0.800	0.482	2.457	0.957	0.648	3.004	1.094	0.908	1.704	2.17

(a) Sign convention as in Table (9.1).

If the bonding parameters are increased, the interatomic matrix elements H_{kl} and F_{kl} are increased in magnitude, so that the molecule can attain a lower energy by increasing the interatomic P_{kl}, i.e., by the transfer of electron density from lone-pair orbitals into bonding orbitals. The large changes in dipole moment can be explained in terms of this effect. For LiF and CH_3F, the decrease in dipole moment with increased bonding parameters is due to a transfer of electron density from the fluorine lone-pair orbitals to the bonding orbitals. In HF, examination of the population matrix shows that this effect is cancelled by an increase in the atomic polarization of the fluorine atom. For FCN, the transfer of electron density away from the fluorine nucleus leads to an increase in the computed dipole moment, since the polarity of the molecule is $\overset{+}{F}C\overset{-}{N}$. For CO, the increase in bonding parameters results in enough charge transfer to reverse the polarity of the computed dipole moments.

Table (9.3) shows that the Extended Huckel Theory greatly exaggerates the polarities of all molecules considered except propane. In the SCF-MO-CNDO theory, the accumulation of electron density on the more electronegative atom is limited by the electrostatic repulsion of the electrons for each other. This is not so in the EHT, since the Hamiltonian matrix elements are independent of the molecular charge distribution, and do not include electron-repulsion terms. Comparison of Tables (9.2) and (9.3) shows that the SCF-MO-CNDO theory predicts more accurate dipole moments than the EHT, regardless of the choice of parameters, and even though the dipole moment must be computed approximately, in order to preserve

TABLE 9.3

DIPOLE MOMENTS[(a)] OF FIRST-ROW MOLECULES CALCULATED FROM EXTENDED HUCKEL THEORY

	Calculated		Exptl.
	H1	H2	
LiH	7.109	7.292	5.882 D
H_3N	2.904	2.471	1.468
H_2O	4.037	3.737	1.87
HF	3.733	3.615	1.8195
CO	3.232		-0.112
NNO	1.880		0.166
O_3	3.444		0.58
C_3H_8	-0.064	0.010	0.083
LiF	7.499		6.328
CH_3F	4.508	4.071	1.8555
HCN	7.497	7.307	2.985
CH_3CN	9.783	8.797	3.92
FCN	4.845		2.17

(a) Sign convention as in Table (9.1).

translational invariance. This shows that the SCF-MO-CNDO theory is a definite improvement over the EHT, in spite of the uncertainties in some of the parameters.

The above conclusions about the accuracy of computed dipole moments are supported by other recent calculations. Pople and Gordon[65] have calculated the dipole moments of a number of organic molecules from the SCF-MO-CNDO theory with theoretical electron-repulsion integrals and Pople-Segal bonding parameters (Parameter Set RP). The overall accuracy of their results is comparable to that for the molecules considered here, and they have used the results as the basis for an analysis of substituent effects in dipole moments.

As for the Extended Huckel Theory, the dipole moments of heterocyclic molecules calculated by Adam and Grimison[159] are much larger than experimental values, as for the small molecules considered here. A similar conclusion about the inadequacy of the charge distributions in the EHT, due to the absence of electron-repulsion terms in the Hamiltonian matrix elements, was previously based on an attempt to correlate the gross atomic charges of the EHT with chemical shifts,[160] and on a comparison of the computed charge distributions with those obtained from electronegativity equalization theory.[260,261] This conclusion is now more firmly based on the predicted values of a molecular property, the dipole moment, which is calculated directly from the ground-state wave function.

D. COMPARISON OF CALCULATED DIPOLE MOMENTS WITH EXPERIMENT FOR MOLECULES CONTAINING NON-FIRST-ROW ATOMS

Dipole moments, calculated from both the SCF-MO-CNDO theory (using the Pople-Segal formula) and the Extended Huckel Theory, are listed in Table (9.4) for molecules containing atoms not in the first row of the periodic table. The EHT predicts exaggerated polarities as for first-row molecules, but now the SCF-MO-CNDO theory also predicts dipole moments which are much higher than the experimental ones, and in some cases higher than those from the EHT.

Santry and Segal[46] have recently considered the effect of the inclusion of d orbitals in the SCF-MO-CNDO theory for second-row elements, using theoretical electron-repulsion integrals and bonding parameters similar to those used by Pople and Segal[44] for first-row elements. They found that the dipole moments of molecules containing second-row atoms include "pd-polarization" terms involving the dipole integrals between p and d orbitals on the same atom. For most such molecules, this pd-polarization is of opposite sign and comparable magnitude to the sp-polarization, so that the inclusion of sp-polarization alone in the computed dipole moment greatly exaggerates the net atomic polarization. They concluded, therefore, that the inclusion of d orbitals is essential to the accurate prediction of dipole moments for molecules containing second-row elements.

This conclusion is further supported by the results of an exact SCF-MO calculation on phosphine by Boyd and Lipscomb,[274] who found that the

TABLE 9.4

CALCULATED DIPOLE MOMENTS$^{(a)}$ FOR MOLECULES WITH NOT ALL FIRST-ROW ATOMS

	SCF-MO-CNDO as per Pople and Segal				Extended Huckel		Exptl.	Reference
Parameter Set	M1	M2	O1	O2	H1	H2		
H_3P	2.730	2.379	2.238	1.906	2.397	1.482	0.578 D	251
H_3As	3.322	2.908	2.812	2.427	1.301	0.257	0.22	262
H_3Sb	2.978	2.587	2.185	1.863	0.235	-0.834	0.116	262
H_2S	2.423	2.152	2.369	2.100	3.569	2.957	0.974	263
H_2Se	2.844	2.565	2.902	2.627	3.353	2.652	0.24,0.62	264,265
H_2Te	3.059	2.789	3.071	2.817	2.829	1.958		
HCl	2.195	2.022	2.345	2.180	3.759	3.477	1.12	266
HBr	1.979	1.813	2.025	1.865	3.651	3.232	0.83	266
HI	2.159	1.979	2.104	1.934	3.624	3.113	0.445	266
CS	1.532	1.614	1.347	1.460	-3.564		1.97	267
OCS		0.241	0.272	0.028	-3.609		0.7124	268

TABLE 9.4 (continued)

	SCF-MO-CNDO as per Pople and Segal				Extended Huckel			
Parameter Set	M1	M2	01	02	H1	H2	Exptl.	Reference
SO_2	1.251	1.273	2.215	2.190	6.219		1.59 D	269
ClF	0.885	0.962	1.295	1.386	3.166		0.881	270
BrF	1.535	1.636	2.138	2.260	4.106		1.29	271
BrCl	0.634	0.646	0.820	0.835	-5.712		0.57	272
IF	2.002	2.113	2.722	2.841	6.028			
ICl	0.726	0.736	1.014	1.021	1.843		0.65	273
IBr	0.112	0.109	0.237	0.233	0.535			
CH_3Cl	2.790	2.667	2.685	2.588	4.000	3.635	1.869	252
CH_3Br	2.620	2.436	2.459	2.304	3.514	3.205	1.797	252
CH_3I	2.720	2.496	2.497	2.297	3.436	3.178	1.647	252
ClCN		0.922	1.206	1.014	7.232		2.802	252
BrCN	1.469		1.596	1.412	8.700		2.94	259
ICN	1.350	1.210	1.516	1.365	8.636		3.71	259

(a) Sign convention as in Table (9.1).

inclusion of d orbitals reduced their computed dipole moment from 2.34 D to 0.86 D, as compared to the experimental value of 0.578 D. They showed by means of electron density difference maps that this effect is due to the transfer of electron density away from the lone-pair region into the bonding region, so that the atomic polarization of the phosphorus atom is reduced.

It is therefore concluded that the omission of d orbitals in the SCF-MO-CNDO calculations is responsible for the fact that the dipole moments in Table (9.4) are very much less accurate than those calculated using the same theory for molecules containing only first-row atoms, since the sp-polarization included in the computed dipole moments is not balanced by dp-polarization. The assignment of parameters for d orbitals in the semi-empirical SCF-MO-CNDO theory is a subject for future research.

Table (9.5) provides a comparison of the different methods of computing dipole moments, from wave functions calculated without overlap, for molecules containing atoms not in the first row of the periodic table. The point-charge formula, which contains no atomic polarization terms, is, on the whole, more accurate than the Pople-Segal formula, since the errors due to the omission of the sp- and pd- polarizations cancel approximately, as shown by Santry and Segal.[46] For series of similar molecules, such as the hydrogen halides, or the methyl halides, the sp-polarization increases with the principal quantum number of the valence-shell electrons of the heavy atom, since the dipole integral P_{s-p_x} increases (equation 9.21).

The dipole moments in Table (9.5) computed from the Dixon formula

TABLE 9.5

COMPARISON OF METHODS OF CALCULATION OF DIPOLE MOMENTS(a) FOR MOLECULES WITH NOT ALL FIRST-ROW ATOMS FROM SCF-MO THEORY AND CNDO APPROXIMATION

Calculation of μ	Point-Charge		Pople and Segal		Dixon		
Parameter Set	M2	02	M2	02	M2	02	Exptl.
H_3P	-0.127	-0.344	2.379	1.906	0.827	0.260	0.578 D
H_3As	-0.064	-0.259	2.908	2.427	1.286	0.712	0.22
H_3Sb	-0.351	-0.796	2.587	1.863	0.707	-0.120	0.116
H_2S	0.408	0.576	2.152	2.100	0.985	0.932	0.974
H_2Se	0.648	0.961	2.565	2.627	1.340	1.435	0.24,0.62
H_2Te	0.662	0.930	2.789	2.817	1.503	1.550	
HCl	1.006	1.296	2.022	2.180	1.453	1.650	1.12
HBr	0.727	0.919	1.813	1.865	1.050	1.122	0.83
HI	0.548	0.659	1.979	1.934	1.154	1.109	0.445
CS	1.234	1.410	1.614	1.460	1.406	1.869	1.97
OCS	-0.891	-1.108	0.241	0.028	-0.448	-0.766	0.7124

TABLE 9.5 (continued)

Calculation of μ	Point-Charge		Pople and Segal		Dixon		
Parameter Set	M2	O2	M2	O2	M2	O2	Exptl.
SO_2	1.633	2.919	1.273	2.190	0.179	1.548	1.59 D
ClF	1.412	1.780	0.962	1.386	0.977	1.401	0.881
BrF	2.160	2.710	1.636	2.260	1.668	2.292	1.29
BrCl	0.744	0.925	0.646	0.835	-3.644	-3.143	0.57
IF	2.859	3.481	2.113	2.841	2.248	2.969	
ICl	1.188	1.441	0.736	1.021	0.833	1.123	0.65
IBr	0.452	0.552	0.109	0.233	0.126	0.253	
CH_3Cl	2.101	2.104	2.667	2.588	2.327	2.235	1.869
CH_3Br	1.697	1.649	2.436	2.304	1.994	1.847	1.797
CH_3I	1.387	1.287	2.496	2.297	1.998	1.781	1.647
ClCN	0.383	0.498	0.922	1.014	-0.109	-0.036	2.802
BrCN		1.094		1.412		0.506	2.94
ICN	1.287	1.462	1.210	1.365	0.415	0.598	3.71

(a) Sign convention as in Table (9.1).

are also more accurate, on the whole, than those from the Pople-Segal formula, although this fact is harder to interpret on simple physical grounds.

In summary, then, the semi-empirical SCF-MO-CNDO theory considered can be used to calculate approximate dipole moments for molecules containing only first-row atoms, if atomic polarization terms are included. The calculation of approximately correct dipole moments, for molecules which contain atoms not in the first row of the periodic table, requires the inclusion of d orbitals. The EHT predicts exaggerated dipole moments for most molecules.

CHAPTER 10

NUCLEAR QUADRUPOLE COUPLING CONSTANTS

A. INTERACTION OF NUCLEAR QUADRUPOLE MOMENTS WITH ELECTRONIC CHARGE DISTRIBUTIONS

The quadrupole coupling constant (QCC) of a nucleus, A, in a molecule is a measure of the interaction of the nuclear quadrupole moment Q with the molecular charge distribution external to the nucleus. The complete interaction of the nuclear charge distribution with the external electrostatic potential V, due to the electrons and the other nuclei, can be expanded in terms of the nuclear multipole moments,[275]

$$\overset{o}{H}_{ne} = ZeV_A + \sum_j P_j \left(\frac{\partial V}{\partial x_j}\right)_A + \frac{1}{2} \sum_{j,k} Q'_{jk} \left(\frac{\partial^2 V}{\partial x_j \partial x_k}\right)_A \ldots \quad (10.1)$$

where the subscript A indicates a quantity evaluated at the nuclear centre of mass. The first term represents the interaction of the total nuclear charge, Ze, with the electrostatic potential at the centre of mass, and is independent of nuclear orientation. The second term in the expansion is formally the interaction of the nuclear dipole moment with the electric field, but this term is zero since nuclei have no electric dipole moments.[276]

The third term is the interaction of the nuclear quadrupole moment tensor with the electric field gradient tensor, and in the absence of an external magnetic field, it is the leading term which depends on the orientation of the nucleus in the molecule.[275] Nuclei with spin quantum numbers $\geqslant 1$ have non-zero quadrupole moments,[275,276] so that the nuclear-electronic interaction energy (equation 10.1) depends on the nuclear orientation, and transitions can occur between different nuclear orientations in the molecules. (Section C)

The electric field gradient at the nucleus is described by the real, symmetric tensor,[275,277]

$$V_{jk} = \left(\frac{\partial^2 V}{\partial x_j \partial x_k} \right)_A \qquad (10.2)$$

The tensor can be referred to its principal axes, so that there are only three non-zero components. Since the potential V is due to charges external to the nucleus, it obeys Laplace's equation,

$$\sum_j V_{jj} = (\nabla^2 V)_A = 0 \qquad (10.3)$$

so that the electric field gradient can be described in terms of two independent parameters, once the principal axes are known. The standard parameters[275,277,278] are the largest component of the tensor, denoted by

$$e\,q = V_{zz} = \left(\frac{\partial^2 V}{\partial z^2} \right)_A \qquad (10.4)$$

and the <u>asymmetry parameter</u>,

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \qquad (10.5)$$

where the principal axes are conventionally chosen so that

$$\left| V_{zz} \right| \geqslant \left| V_{yy} \right| \geqslant \left| V_{xx} \right| \qquad (10.6)$$

The molecules considered here are symmetric rotors, so that the z-axis is the axis of symmetry, and the x- and y-axes are arbitrary axes normal to it. In this case, $V_{xx} = V_{yy}$, the asymmetry parameter vanishes, and the nuclear quadrupole interaction energy depends only on the largest component of the electric field gradient tensor, e q . The term which depends on the orientation of the nucleus in the molecule has the form[277]

$$E_Q = \frac{e^2 Q q}{4I(2I - 1)} \left[3 m_I^2 - I(I + 1) \right] \qquad (10.7)$$

where Q is the scalar quadrupole moment of the nucleus, hereafter referred to as simply the nuclear quadrupole moment.[275-278] I and m_I are the quantum numbers corresponding to the magnitude and the z-component of the nuclear angular momentum. The energy levels are conventionally expressed in terms of the quadrupole coupling constant (QCC),

$$C = \frac{e^2 Q q}{h} \qquad (10.8)$$

which has units of frequency. The QCC's for isotopic species of the same molecule are proportional to the corresponding nuclear quadrupole moments, so that any information about the molecular electronic structure can be obtained from observations for a single isotopic species.

B. CALCULATION OF NUCLEAR QUADRUPOLE COUPLING CONSTANTS

The electrostatic potential acting on a nucleus, A, in a molecule, due to the electrons and the other nuclei, is given by

$$V = -e\int \Psi_e^* \frac{1}{r} \Psi_e \, d\,V + e\sum_{B\neq A} \frac{Z_B}{R_{AB}} \qquad (10.9)$$

where Ψ_e is the electronic wave function, and Z_B is the atomic number of nucleus B. If equation (10.9) is differentiated twice with respect to the nuclear z co-ordinate,

$$eq = V_{zz} = -e\int \Psi_e^* \frac{(3z^2 - r^2)}{r^5} \Psi_e \, d\,V + e\sum_{B\neq A} \frac{Z_B(3z_B^2 - r^2)}{R_{AB}^5} \qquad (10.10)$$

or in spherical polar co-ordinates,[278]

$$eq = -e\int \Psi_e^* \frac{(3\cos^2\theta - 1)}{r^3} \Psi_e \, d\,V + e\sum_{B\neq A} \frac{Z_B(3\cos^2\theta - 1)}{R_{AB}^3} \qquad (10.11)$$

The operator in the integrand is a sum of identical one-electron operators, as is the dipole operator in Chapter 9, so that for a closed-shell single-determinant wave function, with molecular orbitals composed of linear combinations of atomic orbitals,

$$eq = -e\,\mathrm{tr}\,(Pq_A) + e\sum_{B\neq A} Z_B\, q_{AB} \qquad (10.12)$$

where P is the expansion of the one-electron density matrix in terms of the basis orbitals. The matrix q_A describes the electric field gradient of the electrons at the nucleus A, and has elements which are, in the most general case, three-centre integrals,

$$(q_A)_{kl} = \int \phi_k^* \frac{(3\cos^2\theta - 1)}{r^3} \phi_l \, d\,V \qquad (10.13)$$

while q_{AB} is the electric field gradient per unit charge, of nucleus B, at nucleus A,

$$q_{AB} = \frac{3 \cos^2 \theta_B - 1}{R_{AB}^3} \qquad (10.14)$$

The direct computation of electric field gradients, using equation (10.12), involves the evaluation[279] of the three-centre integrals, $(q_A)_{kl}$. A simple semi-empirical approach, originally due to Townes and Dailey,[280] and first explicitly formulated for molecular orbital theory by Gordy et al.,[240] is often used for the interpretation of nuclear quadrupole coupling constants. The electric field gradient is assumed to arise entirely from the electron population of atom A, since the effect of the electrons on each other atom approximately cancels the effect of the nuclei. The net effect due to other atoms is assumed to be small, as the electric field gradient due to the charge at any point decreases as r^{-3}.

The electric field gradient is therefore given by

$$e\,q = -e \sum_{k}^{A} n_k \,(q_A)_{kk} \qquad (10.15)$$

where n_k is the number of electrons in the k^{th} orbital on atom A, and $(q_A)_{kk}$ is the electric field gradient per unit charge due to the electrons in that orbital, defined by equation (10.13). The inner shells, and the valence s orbital, are spherically symmetric and make no net contribution to the electric field gradient at the nucleus, which is due only to the valence p, d, . . .electrons.

The integrals $(q_A)_{kk}$ in equation (10.15) can all be related to the integral

$$q_o = (q_A)_{zz} = \int \phi^*_{p_z} \frac{(3 \cos^2 \theta - 1)}{r^3} \phi_{p_z} \, dV \qquad (10.16)$$

If all three p orbitals have the same radial factor, then

$$(q_A)_{xx} = (q_A)_{yy} = -\frac{1}{2} q_o \tag{10.17}$$

The effect of d orbitals in the halogens is negligible, since for all the valence d orbitals,

$$(q_A)_{dd} \leqslant \frac{1}{7} q_o \tag{10.18}$$

and the d populations are small anyway. The electric field gradient is then given by[240]

$$e\, q = -e\, q_o \left(n_z - \frac{n_x + n_y}{2}\right) \tag{10.19}$$

In order to evaluate q_o, an explicit radial form for the orbitals is needed. The overlap integrals in the molecular orbital calculation are computed for Slater orbitals, but Slater orbitals do not provide a suitable representation of the wave function near the nucleus,[7] where the largest contribution to the electric field gradient arises. Also, for the Slater orbital defined by equation (4.19), q_o is found by elementary integration to be

$$q_o = \frac{4}{5} \frac{Z'^3}{n'(n' - \frac{1}{2})(n' - 1)\, a_o^3} \tag{10.20}$$

so that the calculated electric field gradient is very sensitive to the values of the effective atomic number, Z', and the effective principal quantum number, n'. In order to avoid specifying the radial form of the orbitals, therefore, Townes and Dailey[280] suggested that the quadrupole coupling constant due to a single p electron,

$$C_o = -\frac{e^2 Q q_o}{h} \tag{10.21}$$

be evaluated from the fine or hyperfine structure of atomic spectra, just as the parameters for molecular orbital theory are calibrated using atomic spectra. This procedure also avoids the need for an independent determination of the scalar quadrupole moment of the nucleus, Q. The equation used for the semi-empirical evaluation of nuclear quadrupole coupling constants,[240] therefore, is

$$C = C_o \left(n_z - \frac{n_x + n_y}{2}\right) \tag{10.22}$$

where the quadrupole coupling constant per p electron, C_o, is evaluated from atomic spectra. Equation (10.22) has frequently been used to interpret nuclear quadrupole coupling constants in terms of chemical concepts such as ionic character, hybridization, and pi-bonding.[240,241]

A similar equation, applicable to the SCF-MO-CNDO theory for all valence electrons, can be formally derived from the exact formula, equation (10.12), by making certain simplifying approximations.

(i) The off-diagonal matrix elements of the electric field gradient, $(q_A)_{kl}$, which contain the differential overlap of two orbitals as a factor in the integrand, are neglected in accordance with the CNDO approximation. The matrix elements between two different orbitals on atom A vanish by symmetry in any case (for the s-p basis set considered), while the others refer to overlap regions not on atom A, and are relatively small compared to the diagonal matrix elements for orbitals of atom A, since the electric field gradient operator decreases as r^{-3}. Equation (10.12) therefore reduces to

$$e\,q = -e \sum_{k} P_{kk}\,(q_A)_{kk} + e \sum_{B \neq A} Z_B\, q_{AB} \tag{10.23}$$

(ii) The electric field gradient due to the electron population of each other atom in the molecule is assumed to cancel that due to the atomic core.

$$\sum_{k}^{B} P_{kk}\,(q_A)_{kk} = Z_B\, q_{AB} \tag{10.24}$$

In accurate calculations of electric field gradients, this cancellation has been found to be approximately true, and the net effects of other atoms to be small, again because the electric field gradient operator behaves as r^{-3}. Therefore,

$$e\,q = -e \left(\sum_{k}^{A} P_{kk}\,(q_A)_{kk} \right) \tag{10.25}$$

in the SCF-MO-CNDO theory, P_{kk} represents the electron population of the k^{th} orbital, so that equation (10.25) is equivalent to equation (10.15), and the QCC is given by

$$C = C_o \left(P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right) \tag{10.26}$$

In the Extended Huckel Theory,[114] which includes overlap, it was shown (Chapter 5) that the population of an orbital is given by

$$Q_{rr} = P_{rr} + \sum_{s \neq r} P_{rs}\; S_{rs} \tag{5.10}$$

where the S_{rs} are overlap integrals. By analogy with equation (10.22), one might calculate the QCC from

$$C = C_o \left(Q_{zz} - \frac{Q_{xx} + Q_{yy}}{2} \right) \tag{10.27}$$

Cotton and Harris[281] have derived an analogous equation by assuming that the electric field gradient matrix element between the kth orbital on atom A, and the lth orbital on atom B, is approximated by

$$(q_A)_{kl} = S_{kl}\,(q_A)_{kk} \tag{10.28}$$

The off-diagonal matrix elements between pairs of orbitals, both of which are on other atoms, are still neglected.

Gordy et al.[282] have suggested, however, that the effect of the overlap populations be neglected, since the overlap regions are far from the nucleus, so that equation (10.26) should be used even with the EHT. In order to verify this claim, quadrupole coupling constants have been calculated from the EHT using both equations (10.26) and (10.27).

Quadrupole coupling constants have been calculated for Cl^{35}, Br^{79}, I^{127}, and N^{14} in various molecules, since extensive experimental data are available for these nuclei. For the halogens, the values of the quadrupole coupling constant per p electron, C_o, are 109.746, -769.756, and 2292.712 Mc/s, for Cl^{35}, Br^{79} and I^{127} respectively.[277,283-285] The ground state of the nitrogen atom is an S state, so that there is no electric field gradient at the nucleus, and C_o cannot be determined as for the halogens. Jeffrey and Sakurai[278] have proposed the value $C_o = -7.4$ Mc/s for N^{14}, based on a value for $\langle r^{-3} \rangle_{2p}$ interpolated[286] from values derived from the hyperfine structure of other atoms in the first row of the periodic table, and an estimate[287] of Q based on the magnetic hyperfine structure of NO, with certain subsidiary approximations. Other values have been estimated from attempts to correlate quadrupole coupling constants with simple bonding theories,[280] but the value -7.4 Mc/s has been used here, since it was derived independently of the QCC in any molecule.

A possible source of error in equation (10.23) is the Sternheimer effect, or the polarization, due to the non-spherical nucleus and the valence electrons, of the inner shell electrons, which in turn exert an electric field gradient on the nucleus.[288-290] Sternheimer and Foley have considered this effect, and shown that it can lead to variations in the electric field gradient of an order of magnitude or more for ionic crystals. For isolated covalent molecules, the effect is much smaller, and has been estimated at 24% for the Li_2 molecule.[290] In semi-empirical calculations of quadrupole coupling constants, it is assumed that the Sternheimer polarization effects in the molecule are similar to those in the free atom, so that equation (10.22) is valid if C_o is determined from atomic hyperfine spectra.[277] This is another reason for using atomic spectra to calibrate the molecular calculation.

C. MEASUREMENT OF QUADRUPOLE COUPLING CONSTANTS

The interaction of the nuclear quadrupole moment with the electric field gradient depends upon the nuclear orientation in the molecule, so that the QCC can be found by measuring the energy changes associated with transitions between different orientations.

In the gas phase, QCC's can be determined from hyperfine structure in rotational spectra. The theory of nuclear quadrupole effects in rotational spectra is described in textbooks on microwave spectroscopy,[240-242] for linear molecules and symmetric rotors, which have electric dipole moments. Molecules which do not have electric dipole moments have no rotational spectra, so that the QCC cannot be determined in the gas phase. For asymmetric rotors, the nuclear quadrupole effects are more complex, and it is more difficult to determine the QCC using microwave spectroscopy, but such molecules are not considered here.

Quadrupole coupling constants can be measured in the solid state, using pure nuclear quadrupole resonance (NQR),[277] as well as by nuclear magnetic resonance[275] or Mossbauer spectroscopy.[291] The energy levels for pure NQR are given by equation (10.7), for molecules whose asymmetry parameter is zero. The QCC's measured in the solid state for many molecules, however, differ from the gas-phase values for the same molecules by as much as 10% or more.[277,292] A number of reasons have been suggested for these solid-state effects.

(i) The direct effect of the electric field gradient due to other molecules on nucleus A is relatively small in molecular crystals, although it is appreciable in ionic crystals and metals.[277]

(ii) Changes in molecular electronic structure can be induced by intermolecular forces. The ionic character of many molecules increases in the solid state, since this change is favoured by an increase in Madelung energy.[277] In many halides, the halogen atom carries a partial negative charge, so that the increase in the ionic character leads to a lower QCC. For ICl, however, the iodine QCC is higher in the solid state, since the iodine atom carries a partial positive charge.[277]

(iii) In some molecules, intermolecular bonding causes substantial changes in the molecular electronic structure. The increase in the iodine QCC for ICN in the solid state has been attributed to this effect.[292]

Quadrupole coupling constants measured in the gas phase have therefore been used whenever possible for comparison with theory. As with dipole moments, values measured for deuterated species have been quoted when they are the only values available, and any possible isotope effects have been neglected.

For homonuclear diatomics, the experimental QCC's come from pure NQR measurements in the solid state, since gas-phase values cannot be measured for molecules with no dipole moment. The significance of the solid-state QCC for iodine is doubtful, since the measured asymmetry parameter is 0.15, indicating extensive intermolecular bonding in the solid state.[292]

D. COMPARISONS OF CALCULATED QUADRUPOLE COUPLING CONSTANTS FOR HALOGENS WITH EXPERIMENT

Quadrupole coupling constants calculated from the semi-empirical SCF-MO-CNDO theory, using equation (10.26) are listed in Tables (10.1) to (10.3). The QCC's, unlike the dipole moments for the same molecules, are in fair agreement with experiment, despite the absence of d orbitals in the MO calculations. They do not vary greatly with the value of the interatomic electron-repulsion integrals, or of the Slater exponent for hydrogen. The

TABLE 10.1 NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR Cl^{35}

FROM SEMI-EMPIRICAL SCF-MO-CNDO THEORY

Parameter Set	M1	M2	01	02	Exptl.	Referenc
HCl	-83.40	-88.25	-79.32	-82.02	-67.3 Mc/s	293
CH_3Cl	-77.86	-78.63	-78.53	-79.01	-74.77	294
ClF	-125.73	-126.81	-131.59	-132.78	-146.00	270
Cl_2	-105.88	-106.16	-106.68	-106.88	-108.95	295
BrCl	-98.18	-98.27	-97.03	-97.04	-103.6	272
ICl	-94.45	-94.47	-92.65	-92.64	-82.5	273
ClCN		-73.96	-72.59	-69.48	-83.2	296

TABLE 10.2 NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR Br^{79}

FROM SEMI-EMPIRICAL SCF-MO-CNDO THEORY

Parameter Set	M1	M2	01	02	Exptl.	Referenc
HBr	644.5	657.9	630.2	642.7	530.5 Mc/s	293
CH_3Br	598.6	607.6	609.1	616.7	577.15	294
BrF	944.4	952.4	997.8	1007.3	1089.0	271
BrCl	805.2	806.9	822.9	824.5	876.8	272
Br_2	750.4	750.8	754.4	754.7	764.86	297
IBr	721.3	721.2	718.5	718.4	722	298
BrCN	628.1		611.8	588.9	686.5	296

TABLE 10.3 NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR I^{127} FROM SEMI-EMPIRICAL SCF-MO-CNDO THEORY

Parameter Set	M1	M2	01	02	Exptl.	Reference
HI	-1982	-2020	-1975	-2009	-1823.3 Mc/s	293
CH_3I	-1871	-1907	-1919	-1949	-1934	299
IF	-2899	-2920	-3056	-3078		
ICl	-2460	-2463	-2528	-2529	-2930.0	273
IBr	-2306	-2305	-2339	-2338	-2731	298
I_2	-2218	-2214	-2231	-2227	-2156	300
ICN	-2052	-1995	-2024	-1962	-2420	296

TABLE 10.4 NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR Cl^{35} FROM EXTENDED HUCKEL THEORY

Calculation of QCC	From gross orbital populations		From net orbital populations		Exptl.
Z'_H	1.0	1.2	1.0	1.2	
HCl	-42.15	-49.33	-65.79	-75.49	-67.3 Mc/s
CH_3Cl	-52.26	-51.59	-76.49	-75.16	-74.77
ClF	-162.79		-182.40		-146.00
Cl_2	-88.21		-117.40		-108.95
BrCl	-68.44		-95.11		-103.6
ICl	-58.68		-83.28		-82.5
ClCN	-44.80		-65.38		-83.2

results for bromine are as accurate as for chlorine and iodine, so that the approximate form of the orbital used to calculate overlap integrals (equation (4.24)) does not affect the accuracy of the theory.

Quadrupole coupling constants calculated from the EHT, using both equations (10.26) and (10.27), are listed in Tables (10.4) to (10.6). The QCC's for polar molecules calculated from gross orbital populations (equation (10.27)) correspond to exaggerated polarities, since the calculated values are too low, except when the halogen nucleus of interest is bonded to fluorine, so that it carries a partial positive charge and exaggeration of the polarity leads to a high QCC. The results are therefore consistent with the high dipole moments computed from the EHT. (Chapter 9)

The effect of calculating the QCC from net, instead of gross, orbital populations is invariably to increase the QCC. The halogen atoms are predominantly σ-bonded so that there is a greater overlap population, and a smaller total population, in the $p\sigma$ -orbital than in the $p\pi$ -orbital. The calculated QCC depends on the difference between the $p\sigma$ - and $p\pi$ - populations, so that it is increased if the overlap population is not counted. Tables (10.4) to (10.6) show that while those results which are too low are improved by using net orbital populations, others which are too high are made worse. On the whole, more accurate results are obtained using the SCF-MO theory.

TABLE 10.5 NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR Br^{79} FROM EXTENDED HUCKEL THEORY

Calculation of QCC	From gross orbital populations		From net orbital populations		Exptl.
Z'_H	1.0	1.2	1.0	1.2	
HBr	379.2	441.2	576.5	653.7	530.5 Mc/s
CH_3Br	488.7	481.5	681.2	669.9	577.15
BrF	1252.2		1366.9		1089.0
BrCl	777.4		991.2		876.8
Br_2	626.8		842.5		765
IBr	556.4		761.9		722
BrCN	379.0		534.8		686.5

TABLE 10.6 NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR I^{127} FROM EXTENDED HUCKEL THEORY

Calculation of QCC	From gross orbital populations		From net orbital populations		Exptl.
Z'_H	1.0	1.2	1.0	1.2	
HI	-1333	-1521	-1956	-2169	-1823.3 Mc/s
CH_3I	-1666	-1640	-2210	-2180	-1934
IF	-4056		-4584		
ICl	-2529		-3130		-2930.0
IBr	-2086		-2713		-2731
I_2	-1866		-2483		-2153
ICN	-1399		-1876		-2420

E. COMPARISON OF CALCULATED QUADRUPOLE COUPLING CONSTANTS WITH EXPERIMENT FOR NITROGEN

The calculated quadrupole coupling constants for nitrogen are generally in poor agreement with experiment. Table (10.7) shows that the QCC's calculated from the SCF-MO-CNDO theory with empirical bonding parameters bear little relation to experimental values. Many of the calculated values have the wrong sign, corresponding to smaller electron populations along the symmetry axis than normal to it, in contradiction to the experimental results. Most of the QCC's calculated using the Pople-Segal bonding parameters (Table 10.8), on the other hand, have the correct sign, but the values are still in poor agreement with experiment, except for NH_3.

The QCC's calculated from the Extended Huckel Theory (Table 10.9) are also quite different from the experimental values. The values calculated from gross and from net orbital populations are not too different for most molecules, since the overlap populations along the symmetry axis and normal to it are about the same.

Some idea of the reasons for the failure of the approximate MO theories considered to predict accurate QCC's for nitrogen may be obtained from the results of an ab initio calculation of electric field gradients for N_2,[307] using equation (10.12). The results are found to be very sensitive to the basis set, since the electric field gradient per p electron on atom A, eq_0, is proportional to the cube of the orbital exponent, Z' (equation 10.20). The other electronic terms in equation (10.12) are

TABLE 10.7 NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR N^{14} FROM SCF-MO-CNDO THEORY WITH EMPIRICAL BONDING PARAMETERS

Parameter Set	M1	M2	01	02	R1	R2	Exptl.	Reference
NH_3	+2.233	+1.098	+1.444	+0.674	+0.787	-0.502	-4.0842 Mc/s	301
N_2	-0.763	-0.663	-0.565	-0.482	-0.988	-0.911	-4.65	302
$\underline{N}NO$			+5.833	+6.104	+5.394	+5.817	-0.792	303
$N\underline{N}O$			-2.583	-3.007	-4.289	-4.792	-0.238	303
HCN	+5.313	+6.664	+4.994	+6.280	+5.075	+6.108	-4.58	304
CH_3CN			+5.913	+6.676			-4.214	305
FCN	+8.143	+8.823	+8.458	+9.208	+7.708	+8.150	-2.67	259
ClCN		+7.956	+7.061	+7.897			-3.63	296
BrCN	+6.561		+6.365	+7.220			-3.83	296
ICN	+6.104	+7.048	+5.827	+6.680			-3.80	306

TABLE 10.8 NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR N^{14} FROM SCF-MO-CNDO THEORY WITH POPLE-SEGAL BONDING PARAMETERS

Parameter Set	MP	OP	RP	Exptl.
NH_3	-4.111	-3.930	-4.256	-4.0842 Mc/s
N_2	-2.290	-2.290	-2.317	-4.65
$\underline{N}NO$	+0.612	+0.840	+0.437	-0.792
$N\underline{N}O$	+0.152	-0.015	-0.528	-0.238
HCN	-1.923	-1.903		-4.58
CH_3CN	-1.527	-1.482	-1.908	-4.214
FCN	-0.579	-0.468	-0.995	-2.67

TABLE 10.9 NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR N^{14} FROM EXTENDED HUCKEL THEORY

Calculation of QCC	From gross orbital populations		From net orbital populations		Exptl.
Z'_H	1.0	1.2	1.0	1.2	
NH_3	-4.156	-4.840	-6.188	-6.935	-4.0842 Mc/s
N_2	-3.600		-3.476		-4.65
$\underline{N}NO$	-1.418		-1.111		-0.792
$N\underline{N}O$	+1.786		+2.818		-0.238
HCN	-1.660	-1.592	-1.882	-1.791	-4.58
CH_3CN	-0.958	-1.114	-1.004	-1.206	-4.214
FCN	-0.594		-0.509		-2.67
ClCN	-0.649		-0.564		-3.63
BrCN	-0.667		-0.560		-3.83
ICN	-0.785		-0.718		-3.80

relatively insensitive to changes in the basis set, and in fact there is a rough cancellation between them and the nuclear terms, as assumed in the semi-empirical formula, equation (10.22). Another possible source of error in the ab initio calculation of electric field gradients is the Sternheimer polarization of inner shells, although Richardson[307] has estimated that this has an effect of less than 10% in N_2.

In semi-empirical calculations of quadrupole coupling constants, it is hoped that the errors inherent in ab initio calculations of electric field gradients, as well as any error in the uncertain nuclear quadrupole moment of N^{14}, will be eliminated by evaluating C_o from the hyperfine structure of the atomic spectra.[277] The results in this chapter show that this approach works fairly well for halogens, but not for nitrogen. Townes[308] has pointed out that the semi-empirical formula, equation (10.22), is less satisfactory for nitrogen than for the halogens, since it is smaller and its bonding is more complex.

The above analysis suggests that the errors in the calculated QCC's are primarily due to the failure of equation (10.22), but comparison of the orbital populations with those obtained from complete minimum-basis set SCF-MO calculations shows that part of the error lies in the wave functions calculated using the CNDO approximation. In HCN, for example, the dipole moment calculated using the parameter set M2 is accurate within 1%, (Table 9.2), but the orbital populations for the nitrogen atom are 1.93, 0.50 and 1.40 electrons for the valence-shell s, $p\sigma$ and $p\pi$ orbitals respectively, in contrast to gross orbital populations of 1.77, 1.37, and 0.97 calculated using complete SCF-MO theory.[309] Although the total atomic charges predicted by the semi-empirical SCF-MO-CNDO theory are more accurate than those in the EHT, as shown by the calculated dipole moments, the distribution of the valence-shell electronic populations of each atom among the valence orbitals is often quite inaccurate.

The calculated orbital populations are sensitive to the bonding parameters, and the Pople-Segal parameters lead to QCC's which are somewhat better than those obtained using the empirical bonding parameters. This is an example of a situation, often encountered in semi-empirical pi-electron theory, in which parameters chosen for accurate prediction of one molecular property do not lead to the best results for another property. In this case, the dissociation energies are used as the over-riding criterion for the assignment of bonding parameters, since they are more directly calculated from the results of the SCF-MO theory, and since they can be calculated accurately for at least one set of bonding parameters.

In summary, then, the quadrupole coupling constants calculated for halogens using the semi-empirical SCF-MO-CNDO theory are in fairly good agreement with experiment, while those calculated for nitrogen are unsatisfactory. The Extended Huckel Theory leads to somewhat poorer results for halogens, and also fails for nitrogen.

CHAPTER 11

CONCLUSIONS

A. SUMMARY AND DISCUSSION

The object of the present work has been to develop a semi-empirical SCF-MO theory for the approximate prediction, and interpretation, of ground state molecular properties. The CNDO approximation[43] has been used so that the theory can be extended to fairly large molecules without requiring excessive computer time. The predicted values of physical properties have been compared with those calculated from the theoretically based parameters of Pople and Segal,[44,45] and from the Extended Huckel Theory.[114]

The results in Part B show that the physical properties calculated from the SCF-MO-CNDO theory, especially the ionization potentials and bonding energies, are most accurate when the parameters are evaluated as follows:

(i) Atomic core and electron-repulsion integrals are evaluated from atomic valence state energies, as described in Chapter 3.

(ii) Interatomic electron repulsion integrals are calculated either from the Mataga formula, equation (4.6), or the Ohno formula, equation (4.7). The atomic limits of these integrals are evaluated from atomic valence state energies (Chapter 4). The results obtained with the two formulae are about equally accurate, except that the Mataga formula leads to somewhat more accurate dipole moments (Chapter 9).

(iii) Bonding parameters are calibrated using experimental bonding energies (Chapter 4).

(iv) The orbital exponent for hydrogen is taken as 1.2 in the calculation of overlap integrals.

The success of the theory is therefore to be judged by the accuracy of the physical properties calculated using these parameters. (Parameter sets M2 and 02) The ionization potentials are quite accurate, and in some cases more accurate than those from exact SCF-MO calculations, if Koopmans' theorem is assumed to be valid. For a few molecules, the predicted order of orbital energies is incorrect, but on the whole, the agreement with experiment is quite good. The bonding energies of molecules not considered in the calibration of the bonding parameters are also fairly accurate. Quantities which depend on the molecular charge distribution are not as accurately predicted. The dipole moments are accurate for some molecules which contain only first row atoms, although not for all, and the quadrupole coupling constants for halogens are quite accurate, but the principal failures of the theory are the predictions of dipole moments for molecules containing atoms not in the first row of the periodic table, and of quadrupole coupling constants for nitrogen. The reasons for these failures have been discussed in Chapters 9 and 10 respectively.

The results of the semi-empirical theory have also been compared with those calculated using the Pople-Segal parameters, and it has been shown that the latter lead to overestimation of molecular energy quantities. The predicted ionization potentials are too large when calculated with theoretical electron-repulsion integrals, and/or with the Pople-Segal bonding parameters. The bonding energies calculated from the Pople-Segal bonding parameters are very much too large. Even when the bonding parameters are calibrated to give the correct bonding energies for some molecules, the bonding energies of other molecules are predicted more accurately when semi-empirical electron-repulsion integrals are used.

The relative merits of the various parameters are less evident in the predicted values of properties which depend on the charge distribution. The overall accuracy of the dipole moments is about the same for each set of parameters. Halogen quadrupole coupling constants were not calculated using the Pople-Segal parameters, which were found to be inferior for the prediction of ionization potentials and bonding energies in molecules containing first row atoms, and were therefore not extended to heavier atoms. The N^{14} QCC's calculated with theoretical bonding parameters are actually somewhat more accurate than those calculated using empirical bonding parameters, but are still quite inaccurate. The advantage of the semi-empirical theory, therefore, is that it predicts more accurate orbital energies and total molecular energies. The charge distribution is not improved very much.

The Extended Huckel Theory has also been compared with the semi-empirical SCF-MO-CNDO theory. It has been shown that the energy quantities predicted by the EHT are unreliable, since both ionization potentials and bonding energies are fairly accurate for some molecules, but very inaccurate for others. The EHT predicts very high dipole moments for many molecules, and the calculated halogen QCC's also correspond to exaggerated polarities. The calculated nitrogen QCC's are in poor agreement with experiment in the EHT as well as in the SCF-MO theory.

It might be argued that the present comparison of the EHT with the SCF-MO-CNDO theory is unfair, since no attempt was made to improve the parameters of the EHT empirically. The EHT is, however, a semi-empirical theory since the diagonal Hamiltonian matrix elements are determined from atomic valence state ionization potentials, and the multiplicative constant, K, which appears in the off-diagonal elements (equation 5.4) was evaluated to fit experimental data.[114] Since the actual value of K leads to approximately correct ionization potentials and bonding energies for some molecules, any change in K which improved the predictions for other molecules would be at the expense of these.

The natural way to improve the EHT is to vary the matrix elements with the molecular charge distribution, in which case the calculation must be done iteratively. As explained in Chapter 5, the so-called Iterative Extended Huckel Theory[119,132-135] is unsatisfactory on theoretical grounds, so that an attempt to improve the EHT leads naturally to an SCF-MO theory. The EHT with Hoffmann's parameters has therefore been used as an example of a non-iterative semi-empirical theory, for comparison with the semi-empirical SCF-MO-CNDO theory.

The results indicate that the EHT is not as accurate as the semi-empirical SCF-MO-CNDO theory. The computation time required in the latter theory is only 2 to 3 times as long as in the EHT for a given molecule, so that there is no reason to prefer the EHT. The semi-empirical SCF-MO-CNDO theory is therefore the best available theory at this level of approximation.

These conclusions are based on the predicted values of physical properties, whose calculation involves further approximations not inherent in the MO theories considered, but as pointed out in Chapter 6, this is inevitable since the proper evaluation of a theory requires the comparison of calculated quantities with experiment. Also the effect of these extra approximations has been minimized, by considering quantities which can be calculated directly from the ground state wave function.

The emphasis in this thesis has been on the choice of parameters for the semi-empirical theory. The application of the theory to the interpretation of experimental data is illustrated in Chapter 7, where the computed orbital energies are used to support the identification of certain observed ionization potentials with specific molecular orbitals. Now that the semi-empirical theory has been formulated, it can be used more extensively to interpret molecular properties.

In summary, a semi-empirical molecular orbital theory has been developed for the calculation of ground state molecular properties, and its accuracy and limitations have been investigated.

B. SUGGESTIONS FOR FUTURE RESEARCH

There are a number of ways in which the theory developed here can be extended, and applied to different chemical problems. Some possible directions for future research are indicated here, under the headings:

(i) extension of the theory to different types of molecules, and

(ii) interpretation of molecular properties other than those considered here.

Extension of the Theory to Other Molecules

In this thesis, only small molecules, which can be described to a first approximation by a closed-shell wave function built up of s and p orbitals, are considered. An obvious extension of the theory is its application to larger molecules, which primarily requires the use of more computer time and memory. The extensive computation necessary to parametrize and test the theory was restricted to small molecules, but the final theory can be applied to larger molecules, with much shorter computation times than are required for complete SCF-MO calculations (Appendix C). Kaplansky and Whitehead, for example, are currently applying the semi-empirical SCF-MO-CNDO theory to the interpretation of halogen quadrupole coupling constants, in molecules as large as $(C_2H_5)_3N{\cdot}BCl_3$.

A more significant extension of the theory would be the inclusion of valence-shell d orbitals in the basis set. For transition metals, these orbitals are partially occupied in the ground state, and the atomic parameters can be assigned by a procedure similar to that used here. A more difficult problem is the determination of parameters for the valence-shell d orbitals of main group atoms. Santry and Segal[46] have extended the theoretical parameters of Pople and Segal[44,45] to the second row of the periodic table, including d orbitals as well as s and p orbitals. As discussed in Chapter 9, they showed that the computation of approximately correct dipole moments for molecules with second-row atoms requires the inclusion of d orbitals in the basis set, even for molecules whose elementary chemical description does not require d orbitals. It is harder to evaluate suitable semi-empirical parameters for the valence shell d orbitals of main-group elements, since they are not occupied in the atomic ground state, and the required valence state energies have not been accurately determined. Girard and Whitehead are currently considering this problem, for the second row of the periodic table.

A further possible extension of the theory is to molecules which cannot be described in terms of closed shell wave functions. Pople and Segal[45] have formulated the SCF-MO-CNDO equations for open shell configurations, and have carried out calculations using the same parameters as for closed shell molecules. Similarly, the semi-empirical theory can be extended to open shell configurations, although it may be advisable to modify the atomic parameters, since they were derived from the energies of valence states with an equal number of electrons of each spin, as in a closed-shell molecule. A limitation of the open shell SCF-MO-CNDO theory is that it does not resolve configurational degeneracies.[45] The study of singlet-triplet splits, for example, requires the use of a less approximate theory, such as the EMZDO theory proposed by Dixon.[63]

Interpretation of Molecular Properties

The semi-empirical SCF-MO-CNDO theory can also be applied to the interpretation of physical and chemical properties other than those considered here, such as the conformational and stereochemical problems, which have been studied by the EHT. (See Chapter 5) Since the former theory predicts more accurate bonding energies, it might also be expected to predict more accurate energy differences between molecular conformations.

Also, more spectroscopic quantities can be related to the ground state wave function. The isomer shift in the Mossbauer spectrum of a given nucleus depends on the electron density at that nucleus,[291] although a complete study would require the inclusion of d orbitals in the basis set, since the nuclei which exhibit the Mossbauer effect are either transition metals, or heavy main group elements, such as tin or iodine, in which the contribution of d orbitals to the bonding is significant.

If the theory is extended to open-shell configurations, the isotropic hyperfine interaction in electron spin resonance can be calculated from the spin densities at the nuclei.[310]

Another interesting problem is the interpretation of chemical shifts and spin-spin coupling constants in nuclear magnetic resonance. These quantities are <u>not</u> directly related to the ground state wave function, since the energy of a nucleus in a magnetic field must be calculated using second-order perturbation theory, and formally includes terms which depend on all the excited state energies.[310] It is possible, however, to correlate chemical shifts and coupling constants with ground state wave functions in a semi-empirical way, within series of related molecules.[311] Preliminary attempts[160] to correlate chemical shifts with charge densities calculated from the Extended Huckel Theory were abandoned in favour of developing a better semi-empirical molecular orbital theory, using properties directly related to the ground-state wave function. Now that such a theory has been developed, it might be worthwhile to resume attempts to interpret chemical shifts, as well as spin-spin coupling constants, in terms of ground-state wave functions.

Statement of Claims to Original Research

(1) The atomic core and electron repulsion integrals for the semi-empirical SCF-MO-CNDO theory have been evaluated from atomic valence state energies, and from an analysis of the effect of the CNDO approximation on the Hamiltonian matrix elements in SCF-MO theory. (Chapter 3) The atomic limits for the interatomic electron repulsion integrals have been evaluated similarly. (Chapter 4)

(2) Bonding parameters for the semi-empirical SCF-MO-CNDO theory have been calibrated using the experimental bonding energies of binary hydrides, and the theoretical significance of the values found has been discussed. (Chapter 4)

(3) An approximate method has been developed for the calculation of overlap and dipole integrals involving Slater 4s and 4p orbitals. (Chapter 4)

(4) Ionization potentials, bonding energies, dipole moments and nuclear quadrupole coupling constants for a number of molecules have been calculated from the SCF-MO-CNDO theory, using various sets of parameters. The calculated

values have been compared with experiment, and it has been shown that the semi-empirical parameters, evaluated as described in paragraphs (1) and (2) above, lead to results in better agreement with experiment than the theoretically based parameters used by Pople and Segal. (Part B) It has also been shown that the value 1.2 for the orbital exponent of hydrogen leads to more accurate bonding energies, using the semi-empirical SCF-MO-CNDO theory, than the value 1.0, for molecules not used in the calibration of the bonding parameters (Chapter 8).

(5) Ionization potentials, bonding energies, dipole moments and nuclear quadrupole coupling constants have also been calculated by the Extended Huckel Theory and compared with experiment, and it has been shown that the EHT is neither as accurate, nor as reliable, as the semi-empirical SCF-MO-CNDO theory. (Part B)

(6) The calculated ionization potentials, for the parameters which lead to results in best agreement with experiment, have been used to support the identification of certain observed ionization potentials with specific molecular orbitals. (Chapter 7)

(7) It has been shown that the bonding energies calculated from the Extended Huckel Theory by Hoffmann and Lipscomb are not correctly referred to atomic ground states, and that correction of this error leads to bonding energies in better agreement with experiment. (Chapter 8)

(8) It has been shown that dipole moments cannot be calculated from a molecular orbital theory without overlap, in the same way as if overlap is included, since they would then not be invariant with respect to

translation. Several approximate formulae, which have been proposed in the literature for the calculation of dipole moments in molecular orbital theories without overlap, have been shown to have the required invariance properties. The Pople-Segal formula, which includes point-charge and atomic polarization terms, has been shown to be the most accurate for use with the SCF-MO-CNDO theory. (Chapter 9)

APPENDIX A

MOLECULAR GEOMETRIES

The input data for the computations on each molecule consisted of the atomic numbers and nuclear co-ordinates of all the atoms. The co-ordinates were determined from experimental bond lengths and angles, which were taken from the Tables of Interatomic Distances of the Chemical Society,[181] unless otherwise specified. When available, bond distances corresponding to potential minima ("r_e" values) were preferred.

H_2: R_{HH} = 0.74130 A

LiH: R_{LiH} = 1.59535 A

BeH_2: No data available. Assumed linear, R_{BeH} = 1.3431 A as in BeH.

BH_3: No data available. Assumed trigonal planar, R_{BH} = 1.187 A as for terminal H in B_2H_6.

CH_4: Tetrahedral, R_{CH} = 1.0850 A

NH_3: Pyramidal, R_{NH} = 1.0124 A, $\underline{/HNH} = 106.67^\circ$

H_2O: R_{OH} = 0.9572A, $\underline{/HOH} = 104.52^\circ$

HF: R_{HF} = 0.9171 A

SiH_4: Tetrahedral, R_{SiH} = 1.4798 A

PH_3: Pyramidal, R_{PH} = 1.415 A, $\underline{/HPH} = 93.3^\circ$

H_2S: R_{SH} = 1.328 A, $\underline{/HSH} = 92.2^\circ$

HCl: R_{HCl} = 1.2746 A

GeH_4: Tetrahedral R_{GeH} = 1.527 A

AsH_3: Pyramidal, R_{AsH} = 1.5192 A, $\underline{/HAsH} = 91.83^\circ$

H_2Se: $R_{SeH} = 1.460$ A, $\underline{\angle HSeH} = 91.0^{\circ}$

HBr: $R_{HBr} = 1.414$ A

SnH_4: Tetrahedral, $R_{SnH} = 1.701$ A

SbH_3: Pyramidal, $R_{SbH} = 1.7073$ A, $\underline{\angle HSbH} = 91.30^{\circ}$

H_2Te: $R_{TeH} = 1.7$ A, $\underline{\angle HTeH} = 89.5^{\circ}$

HI: $R_{HI} = 1.60904$ A

N_2: $R_{NN} = 1.09758$ A

CO: $R_{CO} = 1.1282$ A

CS: $R_{CS} = 1.5349$ A

CO_2: Linear, $R_{CO} = 1.15979$ A

OCS: Linear, $R_{CO} = 1.16021$ A, $R_{CS} = 1.56014$ A

CS_2: Linear, $R_{CS} = 1.5532$ A

NNO: Linear, $R_{NN} = 1.1257$ A, $R_{NO} = 1.1863$ A

SO_2: $R_{SO} = 1.4321$ A, $\underline{\angle OSO} = 119.536^{\circ}$

O_3: $R_{OO} = 1.278$ A, $\underline{\angle OOO} = 116.8^{\circ}$

C_2H_2: Linear, $R_{CC} = 1.2050$ A, $R_{CH} = 1.0587$ A

C_2H_4: Planar, $R_{CC} = 1.339$ A, $R_{CH} = 1.086$ A, $\underline{\angle HCH} = 117^{\circ}\ 34'$

C_2H_6: Staggered, $R_{CC} = 1.543$ A, $R_{CH} = 1.102$ A, $\underline{\angle HCH} = 109.3^{\circ}$

C_3H_8: Co-ordinates determined by Lide.[254]

B_2H_6: Bridge structure, $R_{BB} = 1.770$ A, $R_{BH} = 1.334$ A (bridge H),
$R_{BH} = 1.187$ A (terminal H), $\underline{\angle HBH} = 121.5^{\circ}$ (terminal)

LiF: $R_{LiF} = 1.56389$ A

F_2: $R_{FF} = 1.4177$ A

Cl_2: $R_{ClCl} = 1.988$ A

Br_2: R_{BrBr} = 2.2836 A

I_2: R_{II} = 2.662 A

ClF: R_{ClF} = 1.6281 A

BrF: R_{BrF} = 1.7556 A

BrCl: R_{BrCl} = 2.138 A

IF: No data available. Assumed $R_{IF} = \frac{1}{2}$ (R_{II} in I_2 + R_{FF} in F_2)
= 2.03985 A

ICl: R_{ICl} = 2.3207 A

IBr: No data available. Assumed $R_{IBr} = \frac{1}{2}$ (R_{II} in I_2 + R_{BrBr} in Br_2)
= 2.4728 A

CH_3F: R_{CF} = 1.38527 A, R_{CH} = 1.1060 A, $\angle HCF = 108.9^\circ$

CH_3Cl: R_{CCl} = 1.78123 A, R_{CH} = 1.0959 A, $\angle HCCl = 108^\circ 0'$

CH_3Br: R_{CBr} = 1.9388 A, R_{CH} = 1.0954 A, $\angle HCBr = 107^\circ 14'$

CH_3I: R_{CI} = 2.1387 A, R_{CH} = 1.0958 A, $\angle HCI = 106^\circ 58'$

HCN: Linear, R_{CH} = 1.06317 A, R_{CN} = 1.15535 A

CH_3CN: Methyl carbon assumed tetrahedral, R_{CH} = 1.10250 A, R_{CC} = 1.45836 A,
R_{CN} = 1.15710 A

FCN: Linear, R_{CF} = 1.262 A, R_{CN} = 1.159 A (Ref. 259)

ClCN: Linear, R_{CCl} = 1.629 A, R_{CN} = 1.163 A

BrCN: Linear, R_{CBr} = 1.790 A, R_{CN} = 1.159 A

ICN: Linear, R_{CI} = 1.995 A, R_{CN} = 1.159 A

APPENDIX B

COMPUTATION OF OVERLAP AND DIPOLE INTEGRALS

The computation of overlap and dipole integrals is based on the procedure of Mulliken et al.[105] for the evaluation of overlap integrals involving Slater orbitals, but the details have been changed sufficiently so that the actual procedure requires further elaboration. Overlap and dipole integrals respectively were defined previously as:

$$S_{kl} = \int \phi_k^* \; \phi_l \; dV \qquad (2.6)$$

and

$$X_{kl} = \int \phi_k^* \; \dot{x} \; \phi_l \; dV \qquad (9.7)$$

The X-axis is choses as the direction along which the dipole moment lies.

The integrals for each pair of atoms are dealt with separately. For each of the two atoms, the p orbitals along and perpendicular to the internulcear axis are referred to as the $p\sigma$ and $p\pi$ orbitals respectively, as in a diatomic molecule. The integrals are first computed for the s, $p\sigma$ and and $p\pi$ orbitals, and then transformed so that they refer to the molecular basis of s, p_x, p_y and p_z orbitals.

The atomic orbitals on each atom have the form

$$\phi^{nlm} = R_{nl}\,(r)\; Y_{lm}\,(\theta, \phi) \qquad (4.18)$$

For Slater orbitals, the radial function is given by

$$R_{nl}\,(r) = Nr^{n' - 1}\, e^{-\,nr/a_o} \qquad (B.1)$$

which is equivalent to equation (4.20), but with

$$\mu = Z'/n' \tag{B.2}$$

The normalization constant in equation (B.1) has the value

$$N = \left(\frac{2\mu}{a_o}\right)^{n' + 1/2} \frac{1}{\sqrt{(2n')!}} \tag{B.3}$$

while the normalized angular functions for s and p orbitals are

$$\begin{aligned} Y_s &= \frac{1}{\sqrt{4\pi}} \\ Y_p &= \sqrt{\frac{3}{4\pi}} \cos\theta \\ Y_p &= \sqrt{\frac{3}{4\pi}} \sin\theta\,(\cos\phi \text{ \underline{or} } \sin\phi) \end{aligned} \tag{B.4}$$

with the internuclear axis as the polar axis. Substituting equations (4.18) and (B.1) into equation (2.6), the overlap integral between the k^{th} orbital of atom A and the 1^{th} orbital of atom B becomes

$$S_{kl} = N_A N_B \int r_A^{n'_A - 1}\, r_B^{n'_B - 1}\, e^{-(\mu_A r_A + \mu_B r_B)/a_o}\, Y_k\, Y_l\, dV \tag{B.5}$$

with all factors, except the angular functions Y_k and Y_l, the same for each pair of orbitals of the two atoms.

Following Mulliken et al. the integrals are evaluated in spheroidal co-ordinates, given by[105]

$$\xi = \frac{r_A + r_B}{R}, \quad \eta = \frac{r_A - r_B}{R}, \quad \phi = \phi_A = \phi_B \tag{B.6}$$

The volume element in these co-ordinates is

$$d\,V = \frac{R^3}{8}\,(\xi^2 - \eta^2)\;d\xi\;\;d\eta\;\;d\,\emptyset \tag{B.7}$$

so that the overlap integral, equation (B.5), becomes

$$S_{k1} = N_A N_B \left(\frac{R}{2}\right)^{n'_A+N'_B+1} \int_0^{2\pi} d\,\emptyset \int_1^{\infty} d\xi \int_{-1}^{1} d\eta\;(\xi+\eta)^{n'_A-1}\,\cdot$$

$$(\xi-\eta)^{n'_B-1}\;e^{-p(\xi+\eta t)}\;Y_k\,Y_1\,(\xi^2-\eta^2) \tag{B.8}$$

where the parameters p and t are defined by

$$p = \frac{\mu_A + \mu_B}{2}\;\frac{R}{a_o} \tag{B.9}$$

and

$$t = \frac{\mu_A - \mu_B}{\mu_A + \mu_B} \tag{B.10}$$

The product of the normalization constants can be expressed in terms of these parameters,

$$N_A N_B = \frac{\left(\frac{2p}{R}\right)^{n'_A+n'_B+1}\;(1+t)^{n'_A+\frac{1}{2}}\;(1-t)^{n'_B+\frac{1}{2}}}{\sqrt{(2\,n'_A)!\;\;(2\,n'_B)!}} \tag{B.11}$$

so that the overlap integral can be written

$$S_{k1} = K\int_1^{\infty} d\xi \int_{-1}^{1} d\eta\;F\,(\xi,\eta)\;G\,(\xi,\eta)\;e^{-p(\xi+\eta t)} \tag{B.12}$$

where

$$K = \frac{p^{n'_A+n'_B+1}\;(1+t)^{n'_A+\frac{1}{2}}\;(1-t)^{n'_B+\frac{1}{2}}}{\sqrt{(2\,n'_A)!\;\;(2\,n'_B)!}} \tag{B.13}$$

$$F(\xi,\eta) = (\xi+\eta)^{n'_A-1} \; (\xi-\eta)^{n'_B-1} \tag{B.14}$$

and

$$G(\xi,\eta) = (\xi^2-\eta^2)\int_0^{2\pi} Y_k \, Y_l \, d\phi \tag{B.15}$$

The function $F(\xi,\eta)$ is the same for each pair of orbitals of the two atoms and can be weitten in polynomial form,

$$F(\xi,\eta) = \sum_{i,j} C_{ij} \, \xi^i \, \eta^j \tag{B.16}$$

where the C_{ij} are determined by comparison of equations (B.14) and (B.16).

The overlap integral is now expressed in terms of the elementary integrals

$$A_i(p) = \int_1^{\infty} \xi^i \, e^{-p\xi} \, d\xi$$

$$B_j(pt) = \int_{-1}^{1} \eta^j \, e^{-pt\eta} \, d\eta \tag{B.17}$$

For example, if $G(\xi,\eta) = 1$, then

$$S_{kl} = K \sum_{i,j} C_{ij} \, A_i \, B_j \tag{B.18}$$

The actual functions $G(\xi,\eta)$ are found by transforming the angular functions into spheroidal co-ordinates and then integrating over ϕ so that

$$
\begin{aligned}
G(\xi,\eta) = \; & \tfrac{1}{2}(\xi^2-\eta^2) && \text{for} \quad S_{s-s} \\
& \tfrac{\sqrt{3}}{2}(1-\xi\eta)(\xi+\eta) && \text{for} \quad S_{s-p\sigma} \\
& \tfrac{\sqrt{3}}{2}(1+\xi\eta)(\xi-\eta) && \text{for} \quad S_{p\sigma-s} \\
& \tfrac{3}{2}(1-\xi^2\eta^2) && \text{for} \quad S_{p\sigma-p\sigma} \\
& \tfrac{3}{4}(\xi^2-1)(1-\eta^2) && \text{for} \quad S_{p\pi-p\pi}
\end{aligned}
\qquad (B.19)
$$

The overlap integrals for which no $G(\xi,\eta)$ is listed are zero. The non-zero overlap integrals are then given by

$$
\begin{aligned}
S_{s-s} &= \frac{K}{2} \sum_{i,j} C_{ij}\,(A_{i+2}B_j - A_iB_{j+2}) \\
S_{s-p\sigma} &= \frac{\sqrt{3}\,K}{2} \sum_{i,j} C_{ij}\,(A_{i+1}B_j + A_iB_{j+1} - A_{i+2}B_{j+1} - A_{i+1}B_{j+2}) \\
S_{p\sigma-s} &= \frac{\sqrt{3}\,K}{2} \sum_{i,j} C_{ij}\,(A_{i+1}B_j - A_iB_{j+1} + A_{i+2}B_{j+1} - A_{i+1}B_{j+2}) \\
S_{p\sigma-p\sigma} &= \frac{3\,K}{2} \sum_{i,j} C_{ij}\,(A_iB_j - A_{i+2}B_{j+2}) \\
S_{p\pi-p\pi} &= \frac{3\,K}{4} \sum_{i,j} C_{ij}\,(A_{i+2}B_j + A_iB_{j+2} - A_iB_j - A_{i+2}B_{j+2})
\end{aligned}
\qquad (B.20)
$$

If one or both atoms are hydrogen, the equations for the integrals involving the corresponding p orbitals are not applicable.

The dipole integrals are computed in terms of integrals in the local co-ordinate system.

$$X'_{kl} = \int \phi_k^* \; x' \; \phi_l \; d\,V$$

$$Y'_{kl} = \int \phi_k^* \; y' \; \phi_l \; d\,V$$

$$Z'_{kl} = \int \phi_k^* \; z' \; \phi_l \; d\,V \qquad \text{(B.21)}$$

where x' is the co-ordinate along the internuclear axis from the origin at A, and y' and z' are co-ordinates perpendicular to it. In terms of the spheroidal co-ordinates, defined by equation (B.6),

$$x' = (1 + \xi\eta) \; \frac{R}{2}$$

$$y' = \frac{R}{2} \sqrt{(\xi^2 - 1)\;(1 - \eta^2)} \quad \cos\phi$$

$$z' = \frac{R}{2} \sqrt{(\xi^2 - 1\;(1 - \eta^2)} \quad \sin\phi \qquad \text{(B.22)}$$

so that the non-zero integrals are

$$X'_{s-s} = \frac{KR}{4} \sum_{i,j} C_{ij} \left(A_{i+2}B_{j} + A_{i+3}B_{j+1} - A_{i}B_{j+2} - A_{i+1}B_{j+3}\right)$$

$$X'_{s-p\sigma} = \frac{\sqrt{3}\,KR}{4} \sum_{i,j} C_{ij} \left(A_{i+1}B_{j} + A_{i}B_{j+1} - A_{i+3}B_{j+2} - A_{i+2}B_{j+3}\right)$$

$$\begin{aligned} X'_{p\sigma-s} = \frac{\sqrt{3}\,KR}{4} \sum_{i,j} C_{ij} \big(&A_{i+1}B_{j} + 2A_{i+2}B_{j+1} + A_{i+3}B_{j+2} - A_{i}B_{j+1} - 2A_{i+1}B_{j+2} \\ &- A_{i+2}B_{j+3}\big) \end{aligned}$$

$$X'_{p\sigma-p\sigma} = \frac{3KR}{4} \sum_{i,j} C_{ij} \left(A_{i}B_{j} + A_{i+1}B_{j+1} - A_{i+2}B_{j+2} - A_{i+3}B_{j+3}\right)$$

$$\begin{aligned} X'_{p\pi-p\pi} = \frac{3KR}{8} \sum_{i,j} C_{ij} \big(&-A_{i}B_{j} - A_{i+1}B_{j+1} + A_{i+2}B_{j} + A_{i+3}B_{j+1} + A_{i}B_{j+2} \\ &+ A_{i+1}B_{j+3} - A_{i+2}B_{j+2} - A_{i+3}B_{j+3}\big) \end{aligned}$$

$$\begin{aligned} Y'_{s-p\pi} = Z'_{s-p\pi} = \frac{\sqrt{3}\,KR}{8} \sum_{i,j} C_{ij} \big(&-A_{i+1}B_{j} - A_{i}B_{j+1} + A_{i+3}B_{j} + A_{i+2}B_{j+1} \\ &+ A_{i+1}B_{j+2} + A_{i}B_{j+3} - A_{i+3}B_{j+2} - A_{i+2}B_{j+3}\big) \end{aligned}$$

$Y'_{p\sigma-p\pi} = Z'_{p\sigma-p\pi} = X'_{p\pi-p\pi}$ (above)

$$\begin{aligned} Y'_{p\pi-s} = Z'_{p\pi-s} = \frac{\sqrt{3}\,KR}{8} \sum_{i,j} C_{ij} \big(&-A_{i+1}B_{j} + A_{i}B_{j+1} + A_{i+3}B_{j} - A_{i+2}B_{j+1} \\ &+ A_{i+1}B_{j+2} - A_{i}B_{j+3} - A_{i+3}B_{j+2} + A_{i+2}B_{j+3}\big) \end{aligned}$$

$$\begin{aligned} Y'_{p\pi-p\sigma} = Z'_{p\pi-p\sigma} = \frac{3KR}{8} \sum_{i,j} C_{ij} \big(&-A_{i}B_{j} + A_{i+1}B_{j+1} + A_{i+2}B_{j} - A_{i+3}B_{j+1} \\ &+ A_{i}B_{j+2} - A_{i+1}B_{j+3} - A_{i+2}B_{j+2} + A_{i+3}B_{j+3}\big) \end{aligned} \tag{B.23}$$

The overlap and dipole integrals must now be transformed so that they refer to the molecular basis orbitals. The three valence-shell p orbitals of an atom transform as vectors under a rotation about the nucleus, while the s orbital is unaffected. If a_x, a_y, and a_z are the direction cosines of the internuclear axis from A to B, with respect to the molecular co-ordinate system, then the overlap integrals in the molecular basis are given by

$$
\begin{aligned}
S_{s-s} &= S_{s-s} \\
S_{s-p_i} &= -a_i\, S_{s-p\sigma} \\
S_{p_i-s} &= a_i\, S_{p\sigma-s} \\
S_{p_i-p_j} &= (\delta_{ij} - a_i a_j)\, S_{p\pi-p\pi} - a_i a_j\, S_{p\sigma-p\sigma}
\end{aligned}
\qquad (B.24)
$$

where the subscripts i and j represent either x, y, or z.

The transformation of the dipole integrals to the molecular basis involves two steps:

(i) The co-ordinates are rotated about nucleus A, with both the p orbitals and the position operators transforming as vectors.

(ii) The origin is moved from nucleus A, with co-ordinates (x_A, y_A, z_A), to the molecular origin, with the dipole integrals transforming as

$$X_{kl} \longrightarrow X_{kl} + x_A S_{kl} \qquad (B.25)$$

The non-zero dipole integrals in the molecular basis, for the x component of the position operator, are then given by

$$
\begin{aligned}
X_{s-s} &= a_x X'_{s-s} + x_A S_{s-s} \\
X_{s-p_i} &= (\delta_{xi} - a_x a_i) Y'_{s-p\pi} - a_x a_i X'_{s-p\sigma} + x_A S_{s-p_i} \\
X_{p_i-s} &= a_x a_i X'_{p\sigma-s} + (\delta_{xi} - a_x a_i) Y'_{p\pi-s} + x_A S_{p_i-s} \\
X_{p_i-p_j} &= a_x a_i a_j (Y'_{p\pi-p\sigma} - X'_{p\pi-p\sigma} - X'_{p\pi-p\pi} - Y'_{p\sigma-p\pi}) + a_i \delta_{xj} Y'_{p\sigma-p} \\
&\quad + a_x \delta_{ij} X'_{p\pi-p\pi} - a_j \delta_{xi} Y'_{p\pi-p\sigma} - x_a S_{p_i-p_j}
\end{aligned}
\tag{B.26}
$$

where again the subscripts i and j represent either x, y, or z.

Finally, the dipole integral between the s and the p_x orbitals of the same atom is given by equation (9.21).

The computational procedure is modified slightly for atoms of principal quantum number 4. The orbitals of such an atom are approximated using equation (4.25), and the overlap and dipole integrals are then computed as linear combinations of the appropriate integrals involving 3s and 5s, or 3p and 5p, orbitals.

APPENDIX C

COMPUTER PROGRAMMES

The computations for this thesis were performed on an IBM 7044 computer at the McGill University Computer Centre. The programme was written in FORTRAN IV language, and the programmes used are listed here. The programmes are not applicable to the hydrogen molecule, for which computation was done by hand.

The largest part of the computation time, for both the SCF-MO-CNDO and EHT programmes, is required for matrix diagonalization, and is proportional to the cube of the size of the basis set. Approximate computation times, on the IBM 7044, for a basis of N atomic orbitals, are $N^3/4000$ minutes for the SCF-MO-CNDO theory (for an average 10-12 iterations), and $N^3/10,000$ minutes for the EHT.

```
$IBFTC CNDO
      DATA MAT,MOR/20,32/
C     MAIN PROGRAM FOR  SCF-MO-CNDO CALCULATION
C     MAT,MOR = MAXIMUM NO. ATOMS,VALENCE-SHELL ATOMIC ORBITALS(S AND P)
      DIMENSION G(20,20),IAT(20),PAA(20),X(3,20)
C     G = ELECTRON-REPULSION INTEGRALS,IAT = ATOMIC NUMBERS
C     PAA = ELECTRON POPULATIONS OF ATOMS,X = NUCLEAR COORDINATES
      DIMENSION C(32,32),F(32,32),H(32,32),P(32,32),P1(32,32),
     1P2(32,32),S(32,32),D(32,32),W(32,32),U(32,32),SS(32)
C     C = LCAO COEFFICIENTS, F = TOTAL HARTREE-FOCK HAMILTONIAN
C     H = CORE HAMILTONIAN, P = POPULATION MATRIX , P1 AND P2 =
C     POPULATION MATRICES FROM PREVIOUS ITERATIONS, S = OVERLAP MATRIX,
C     D = DIPOLE INTEGRAL MATRIX, W,U, AND SS = VARIABLES  IN SUBROUTINE
C     DIPOLE
      DIMENSION NAME(5)
C     NAME = NAME OF MOLECULE (MAXIMUM 30 LETTERS)
      COMMON ZH
C     ZH = ORBITAL EXPONENT FOR HYDROGEN
      LOGICAL SCF,CHECK,BVARY
C     SCF = TRUE IF CALCULATION HAS CONVERGED TO SELF-CONSISTENCY
C     CHECK = TRUE IF INTERMEDIATE MATRICES TO BE PRINTED FOR DEBUGGING
C     BVARY = TRUE IF BONDING PARAMETERS TO BE VARIED
      READ(5,500)CHECK,BVARY,ZH,BETAHO
C     BETAHO = PARAMETER USED IN SUBROUTINE CORE
    1 READ(5,501)NA,NH,NE,NB,BMAX,DB,NAME
C     NA = NO.ATOMS NOT HYDROGEN,NH=NO. HYDROGENS, NE = NO.VALENCE
C     ELECTRONS
C     FOR BINARY HYDRIDES NB. = NO. VALUES FOR BONDING PARAMETER OF
C                  MAIN ATOM, BMAX = MAXIMUM VALUE,DB = INCREMENT
      IF(.NOT.BVARY) NB=1
      CALL CLOCK(ITIME)
C     SUBROUTINE CLOCK IS PART OF MCGILL COMPUTER SYSTEM-TIMES PROGRAM
      NAT=NA+NH
      NOR=4*NA+NH
C     NAT = NO.ATOMS,NOR = NO.OF VALENCE SHELL ORBITALS(S AND P)
C
C     READ INPUT DATA-ATOMIC NUMBERS AND NUCLEAR COORDINATES
C     HYDROGENS MUST BE READ IN LAST
      READ(5,502)(J,IAT(J),(X(I,J),I=1,3),JJ=1,NAT)
      WRITE(6,601) NAME,NAT,NH,NE
      WRITE(6,602)(IAT(J),(X(I,J),I=1,3),J=1,NAT)
      WRITE(6,603)
C     COMPUTE ELECTRON-REPULSION,OVERLAP AND DIPOLE INTEGRALS
      CALL REPUL(G,IAT,MAT,NA,NAT,X)
      CALL INTGRL    (IAT,X,MAT,MOR,NA,NAT,NOR,S,D,ZH)
      WRITE(6,600)ZH
      IF(.NOT.CHECK) GO TO 7
      WRITE(6,604)
      CALL PRINT(G,MAT,NAT)
      WRITE(6,605)
      CALL PRINT(S,MOR,NOR)
      WRITE(6,606)
      CALL PRINT (D,MOR,NOR)
    7 DO 26 IB=1,NB
```

```
C     ASSIGN VARIABLE BONDING PARAMETER FOR BINARY HYDRIDES
      IF(BVARY)BETAAO=BMAX-DB*FLOAT(IB-1)
C     COMPUTE CORE MATRIX AND INITIAL F-MATRIX
      CALL CORE(H,G,S,IAT,BETAAO,BETAHO,MAT,MOR,NA,NAT,NOR)
      CALL START(F,G,H,IAT,    ITER,MAT,MOR,NA,NOR,SCF)
      IF(.NOT.CHECK) GO TO 10
      WRITE(6,607)
      CALL PRINT(H,MOR,NOR)
      WRITE(6,609)
      CALL PRINT(F,MOR,NOR)
C     START ITERATIVE SOLUTION OF SECULAR EQUATIONS
   10 CALL EVALUE(F,MOR,MOR,C,MOR,MOR,NOR,1.0E-6,1)
C     SUBROUTINE EVALUE IS PART OF MCGILL COMPUTER SYSTEM
C     FINDS EIGENVALUES AND EIGENVECTORS OF A REAL SYMMETRIC MATRIX
C     INPUT MATRIX = F,EIGENVALUES OUTPUT ON DIAGONAL OF F
C     EIGENVECTORS = C, MOR = DIMENSION OF MATRIX F, NOR =ORDER
C     ACCURACY = 1.0 E-6, FINAL PARAMETER INDICATES EIGENVECTORS NEEDED
C
C     SORT ORBITALS BY ENERGY AND COMPUTE POPULATION MATRIX
      CALL SORT(F,C,NOR,MOR)
      CALL COULSN(C,P,NOR,NE,MOR)
      IF(.NOT.CHECK) GO TO 14
      WRITE(6,612)ITER
      CALL  PRINT(P,MOR,NOR)
C     TEST FOR SELF-CONSISTENCY
   14 CALL TEST (P,P1,P2,1.0E-4,ITER,MOR,NOR,SCF)
      IF(SCF) GO TO 16
C     IF NOT SELF-CONSISTENT,COMPUTE NEW HAMILTONIAN MATRIX
      CALL POPLE(F,G,H,IAT,MAT,MOR,NAT,NOR,P,PAA)
      IF (ITER-50)10,10,1
C     PRINT ENERGY LEVELS,LCAO COEFFICIENTS, POPULATIONS
   16 WRITE(6,616)ITER
      WRITE(6,617)(F(I,I),I=1,NOR)
      WRITE(6,618)
      CALL PRINT(C,MOR,NOR)
      WRITE(6,620)
      CALL PRINT(P,MOR,NOR)
      WRITE(6,622) (PAA(I),I=1,NAT)
C     COMPUTE DIPOLE MOMENT AND BONDING ENERGY
      CALL DIPOLE(D,IAT,P,PAA,S,X,MAT,MOR,NA,NAT,NOR,SS,W,U,IB)
      CALL ENERGY(F,G,H,IAT,P,MAT,MOR,NA,NAT,NOR,NE)
      CALL CLOCK(JTIME)
      TIME=FLOAT(JTIME-ITIME)/60.
   26 WRITE(6,625)TIME
      GO TO 1
  500 FORMAT(2L1,2F4.1)
  501 FORMAT(4I3,2F4.1,20X,5A6)
  502 FORMAT(2I2,3F10.5)
  600 FORMAT(29H SLATER EXPONENT FOR HYDROGEN,F5.2)
  601 FORMAT(1H1,5A6/I4,6H ATOMS,I4,10H HYDROGENS,I4,
     1 24H VALENCE-SHELL ELECTRONS)
  602 FORMAT(14HKATOMIC NUMBER,6X,12HCO-ORDINATES/(5X,I2,6X,3F10.5))
  603 FORMAT(50HJSCF-LCAO-MO METHOD WITH ZERO DIFFERENTIAL OVERLAP)
  604 FORMAT(26HKREPULSION INTEGRAL MATRIX)
  605 FORMAT(15HKOVERLAP MATRIX)
```

```
  606 FORMAT(28HKDIPOLE MATRIX (X-COMPONENT))
  607 FORMAT(24HKCORE HAMILTONIAN MATRIX)
  609 FORMAT(16HKINITIAL FMATRIX)
  612 FORMAT(24HKPOPULATION MATRIX AFTER,I3,11H ITERATIONS)
  616 FORMAT(I3,20H ITERATIONS REQUIRED)
  617 FORMAT(14HKENERGY LEVELS/(3X,14F9.4))
  618 FORMAT(18H LCAO COEFFICIENTS)
  620 FORMAT(18HKPOPULATION MATRIX)
  622 FORMAT(21HKTOTAL ATOMIC CHARGES/(14F9.4))
  625 FORMAT(5HKTIME,F7.1,8H SECONDS)
      END



$IBFTC HOFMAN
      DIMENSION X(3,25),NAT(25),S(50,50),D(50,50),P(50,50),
     1H(50,50),E(50,50),C(50,50),SDIAG(50,50),NAME(5)
C     MAIN PROGRAM FOR EXTENDED HUCKEL THEORY CALCULATION
C     X = NUCLEAR CO-ORDINATES,NAT = ATOMIC NUMBER, S = OVERLAP MATRIX,
C     D = DIPOLE MATRIX, P = POPULATION MATRIX, H = HAMILTONIAN MATRIX
C     E = TRANSFORMED HAMILTONIAN MATRIX IN TERMS OF LOWDIN ORBITALS
C     WHICH IS DIAGONALIZED TO GIVE  ORBITAL ENERGIES
C     C = LCAO COEFFICIENTS
C     SDIAG = DUPLICATE OF OVERLAP MATRIX
C     NAME = NAME OF MOLECULE (MAXIMUM 30 LETTERS)
      EQUIVALENCE(SDIAG,E),(H,C)
      COMMON/ALPHA/AS(53),AP(53),EATOM(53)
C     AS, AP = VALENCE-STATE IONIZATION POTENTIALS, EATOM = ISOLATED
C     ATOM ENERGIES ACCORDING TO EHT
   18 FORMAT(F4.1)
   19 FORMAT(3I3,31X,5A6)
   20 FORMAT(1H1,5A6/I3,6H ATOMS,I3,10H HYDROGENS,I3,18H VALENCE ELECTRO
     1NS/18H HYDROGEN EXPONENT,F4.1)
   21 FORMAT(2I2,3F10.5)
      READ(5,18) ZH
    1 READ(5,19) NA,NH,NEL,NAME
C     ZH = ORBITAL EXPONENT FOR HYDROGEN, NA = NO. ATOMS NOT HYDROGEN,
C     NH = NO. HYDROGENS, NEL = NO. ELECTRONS, NAH = NO. ATOMS, N = NO.
C     VALENCE-SHELL ORBITALS (S AND P)
      NAH=NA+NH
      WRITE(6,20) NAME,NAH,NH,NEL,ZH
C     READ IN INPUT DATA-ATOMIC NUMBERS AND CO-ORDINATES
C     HYDROGEN ORBITALS MUST BE READ IN LAST
      READ(5,21)(I,NAT(I),(X(J,I),J=1,3),I=1,NAH)
      N=4*NA+NH
C     ASSIGNMENT OF DIAGONAL HAMILTONIAN MATRIX ELEMENTS
      WRITE(6,61)
      DO 80 I=1,NA
      NATI=NAT(I)
      H(4*I-3,4*I-3)=-AS(NATI)
      H(4*I-2,4*I-2)=-AP(NATI)
      H(4*I-1,4*I-1)=-AP(NATI)
      H(4*I  ,4*I  )=-AP(NATI)
   80 WRITE(6,62)NAT(I),(X(J,I),J=1,3),AS(NATI),AP(NATI)
      IF(NH.EQ.0) GO TO 83
```

```
      KA=4*NA+1
      WRITE(6,63)AS(1)
      DO 81 K=KA,N
      I=K-3*NA
      H(K,K)=-AS(1)
   81 WRITE(6,64)(X(J,I),J=1,3)
   61 FORMAT(8HKELEMENT,5X,12HCO-ORDINATES,10X,17HCOULOMB INTEGRALS)
   62 FORMAT(1H ,I3,3F10.5,2(F7.3,3H EV))
   63 FORMAT(41HKHYDROGEN CO-ORDINATES(COULOMB INTEGRAL =,F7.3,4H EV))
   64 FORMAT(3F10.5)
C     ASSIGN OVERLAP AND DIPOLE MATRIX ELEMENTS
   83 CALL INTGRL(NAT,X,25,50,NA,NAH,N,S,D,ZH)
      DO 98 I=1,N
      DO 98 J=1,N
   98 SDIAG(I,J)=S(I,J)
C     ASSIGN OFF-DIAGONAL HAMILTONIAN MATRIX ELEMENTS
      DO 82 I=2,N
      JA=I-1
      DO 82 J=1,JA
      H(I,J)=0.875*(H(I,I)+H(J,J))*S(I,J)
   82 H(J,I)=H(I,J)
C     SOLUTION OF SECULAR EQUATIONS INCLUDING OVERLAP
      CALL LOWDIN
      COMMON SDIAG,H,N
C     PRINT LCAO COEFFICIENTS AND ORBITAL ENERGIES
      WRITE(6,71)
   71 FORMAT(1H ,18H LCAO COEFFICIENTS)
      CALL PRINT(C,50,N)
      WRITE(6,72)
   72 FORMAT(1HK,14H ENERGY LEVELS/1H )
      WRITE(6,84)(I,E(I,I),I=1,N)
   84 FORMAT(I3,F10.4,4H  EV)
C     CALCULATE BONDING ENERGIES
      NOC=NEL/2
      ETOT=0.
      DO 85 I=1,NOC
   85 ETOT=ETOT+2.*E(I,I)
      WRITE(6,86)ETOT
      ESEP=0.
      DO 90 I=1,NAH
      NATI=NAT(I)
   90 ESEP=ESEP-EATOM(NATI)
      EATZN=ESEP-ETOT
      WRITE(6,92)ESEP,EATZN
   92 FORMAT(28H ENERGY OF SEPARATED ATOMS =,F10.4,4H  EV/
     124H ENERGY OF ATOMIZATION =,F10.4,4H  EV)
   86 FORMAT(1H0,13H TOTAL ENERGY,F10.4,4H  EV)
C     CALCULATION OF DIPOLE MOMENT AND POPULATION ANALYSIS
      CALL COULSN(C,P,N,NEL,50)
      CALL DIPOLE(D,NAT,P,X,25,50,NAH,N)
      CALL POPAN(P,S,NAT,NA,NH)
      GO TO 1
      END
```

```
$IBFTC ALPH
      BLOCK DATA
C     STORES VALENCE STATE IONIZATION POTENTIALS AND ISOLATED ATOM
C     ENERGIES FOR EXTENDED HUCKEL THEORY
      COMMON/ALPHA/AS(53),AP(53),EATOM(53)
      DATA AS/13.595,0.,5.390,9.916,14.916,21.012,25.588,32.297,
     139.391,0.,5.140,8.948,12.270,17.307,18.612,21.135,25.227,
     20.,4.340,5.655,10*0.,14.588,18.578,17.403,20.811,23.735,0.,
     34.180,5.478,10*0.,12.590,16.158,16.255,19.733,20.833/
      DATA AP/2*0.,3.543,5.958,8.425,11.273,13.946,17.274,20.862,
     10.,3.037,4.519,6.466,9.190,10.733,12.396,15.037,0.,2.726,
     23.958,10*0.,6.751,9.432,9.359,11.675,13.101,0.,2.601,3.651,
     310*0.,6.185,8.326,8.751,11.038,12.670/
      DATA EATOM/13.595,0.,5.390,19.832,38.257,64.570,93.014,
     1133.690,183.092,0.,5.140,17.896,31.006,52.994,69.423,
     291.854,125.639,0.,4.340,11.310,10*0.,35.927,56.020,62.883,
     388.322,112.975,0.,4.180,10.956,10*0.,31.365,48.968,58.763,
     483.618,105.016/
      END



$IBFTC ATOMIC
      BLOCK DATA
C      STORES SEMI-EMPIRICAL ATOMIC PARAMETERS FOR SCF-MO-CNDO THEORY
C     SUBSCRIPT = ATOMIC NUMBER
      COMMON/ATOM/USS(53),UPP(53),GAA(53),GSTAR(53)
C     USS,  UPP = LOCAL CORE-HAMILTONIAN DIAGONAL MATRIX ELEMENTS FOR
C     S, P ORBITALS
      DATA USS/13.595,0.,
     1 4.999,15.543,30.371,50.686,70.093,101.306,129.544,0.,
     2 4.502,13.083,22.828,36.494,58.610,66.796,86.774,0.,
     3 3.170,9.842,10*0.,25.032,35.844,50.151,66.005,76.413,0.,
     4 3.555,9.430,10*0.,23.056,26.981,47.427,64.464,76.905/
      DATA UPP/ 2*0.,
     1 3.673,12.280,24.702,41.530,57.848,84.284,108.933,0.,
     2 3.247,9.603,18.592,30.375,50.940,58.008,75.681,0.,
     3 3.115,7.696,10*0.,19.807,29.973,44.485,57.927,65.412,0.,
     4 2.804,7.074,10*0.,17.663,21.869,40.923,57.144,69.091/
C      GAA = ATOMIC ELECTRON-REPULSION INTEGRALS FROM VALENCE-STATE
C      ENERGIES
      DATA GAA/12.848,0.,
     1 3.469,5.935,8.000,10.207,11.052,13.625,15.054,0.,
     2 2.982,4.623,5.682,6.964,9.878,9.205,10.292,0.,
     3 3.702,3.977,10*0.,5.936,6.608,8.399,9.121,8.823,0.,
     4 2.495,3.749,10*0.,5.530,4.297,7.657,8.985,9.448/
C      GSTAR = ATOMIC LIMIT OF INTERATOMIC ELECTRON-REPULSION INTEGRALS
      DATA GSTAR/12.848,0.,
     1 3.458,5.953,8.048,10.333,11.308,13.907,15.233,0.,
     2 3.031,4.656,5.680,7.015,9.886,9.260,10.366,0.,
     3 3.560,3.979,10*0.,5.942,6.634,8.361,9.156,8.838,0.,
     4 2.384,3.761,10*0.,5.582,4.304,7.761,9.039,9.382/
      COMMON/CORECH/KORE(53)
C       KORE = CORE CHARGES
```

```
      DATA KORE/1,0,1,2,3,4,5,6,7,0,1,2,3,4,5,6,7,0,1,2,10*0,3,4,5,6,7,
     1 0,1,2,10*0,3,4,5,6,7/
      END


$IBFTC ATOMIC
      BLOCK DATA
C     STORES ATOMIC PARAMETERS FOR  SCF-MO-CNDO THEORY USED BY POPLE AND
C     SEGAL
C      SUBSCRIPT = ATOMIC NUMBER
      COMMON/ATOM/USS(53),UPP(53),GAA(53),GSTAR(53)
C      USS, UPP = LOCAL CORE - HAMILTONIAN DIAGONAL MATRIX  ELEMENTS FOR
C     S,  P  ORBITALS
      DATA USS/17.380,0.,6.319,20.403,41.720,70.271,106.056,149.075,
     1 199.327,44*0./
      DATA UPP/2*0.,4.471,17.020,36.127,61.792,94.015,132.796,
     1 178.135,44*0./
C     GAA = THEORETICAL ATOMIC ELECTRON-REPULSION INTEGRALS
      DATA GAA/20.4075,0.,6.4252,9.6378,12.8503,16.0629,19.2755,22.4881,
     1 25.7007,44*0./
      DATA GSTAR/53*0./
      COMMON/CORECH/KORE(53)
C      KORE = CORE CHARGES
      DATA KORE/1,0,1,2,3,4,5,6,7,0,1,2,3,4,5,6,7,0,1,2,10*0,3,4,5,6,7,
     1 0,1,2,10*0,3,4,5,6,7/
      END
```

```
$IBFTC CORE
      SUBROUTINE CORE(H,G,S,IAT,BETAAO,BETAHO,MAT,MOR,NA,NAT,NOR)
C     ASSIGNS CORE HAMILTONIAN MATRIX FOR SCF-MO-CNDO CALCULATION
C     THIS VERSION VARIES BONDING PARAMETER FOR CENTRAL ATOM IN
C     BINARY HYDRIDES-NOT APPLICABLE TO OTHER MOLECULES
C     BETAAO = BONDING PARAMETER OF CENTRAL ATOM,BETAHO OF HYDROGEN
C     I AND J ARE ATOM INDICES, K AND L ARE ORBITAL INDICES
      COMMON/ATOM/USS(53),UPP(53),GAA(53),GSTAR(53)/CORECH/
     1KORE(53)
      DIMENSION H(MOR,MOR), S(MOR,MOR), IAT(MAT), G(MAT,MAT)
C     DIAGONAL CORE MATRIX ELEMENTS-ATOMIC TERMS
C     HYDROGEN ORBITALS LAST AS IN MAIN PROGRAM
      DO 1 I=1,NA
      IATI=IAT(I)
      H(4*I-3,4*I-3)=-USS(IATI)
      H(4*I-2,4*I-2)=-UPP(IATI)
      H(4*I-1,4*I-1)=-UPP(IATI)
    1 H(4*I  ,4*I  )=-UPP(IATI)
      IF(NOR.EQ.4*NA) GO TO 3
      K1=4*NA+1
      DO 2 K=K1,NOR
    2 H(K,K)=-USS(1)
C     DIAGONAL ELEMENTS-ADD INTERATOMIC TERMS
    3 DO 4 K=1,NOR
      I=MAX0((K+3)/4,K-3*NA)
      DO 4 J=1,NAT
      IF(J.EQ.I) GO TO 4
      IATJ=IAT(J)
      H(K,K)=H(K,K)-FLOAT(KORE(IATJ))*G(I,J)
    4 CONTINUE
C     OFF DIAGONAL CORE MATRIX ELEMENTS
      BETAO=0.5*(BETAAO+BETAHO)
      DO 10 K=5,NOR
      DO 10 L=1,4
      H(K,L)=-BETAO*S(K,L)
   10 H(L,K)=H(K,L)
      IF(NOR.EQ.5) GO TO 25
      DO 20  K=6,NOR
      LL=K-1
      DO 20 L=5,LL
      H(K,L)=-BETAHO*S(K,L)
   20 H(L,K)=H(K,L)
   25 WRITE(6,30) BETAHO,BETAAO
   30 FORMAT(31H1BONDING PARAMETER FOR HYDROGEN,
     1F5.1,19H EV, FOR OTHER ATOM,F5.1,3H EV)
      RETURN
      END
```

```
$IBFTC CORE
      SUBROUTINE CORE(H,G,S,IAT,BETAAO,BETAHO,MAT,MOR,NA,NAT,NOR)
C     ASSIGNS CORE HAMILTONIAN MATRIX FOR SCF-MO-CNDO CALCULATION
C     THIS VERSION STORES FIXED BONDING PARAMETERS
C     BETAHO IS USED TO ASSIGN CORRECT SET OF BONDING PARAMETERS IN THIS
C     VERSION
      DIMENSION H(MOR,MOR), S(MOR,MOR), IAT(MAT), G(MAT,MAT)
C      BM,BO,BR ARE SETS DETERMINED FOR MATAGA,OHNO,ROOTHAAN
C       REPULSION INTEGRALS RESPECTIVELY,HYDROGEN EXPONENT 1.0
C     BM2,BO2,BR2 FOR HYDROGEN EXPONENT 1.2
C     BPS ARE POPLE-SEGAL BONDING PARAMETERS
      DIMENSION BM(53),BM2(53),BO(53),BO2(53),BR(9),BR2(9),BPS(9)
      DATA BR/5.4,0.,2.5,4.3,6.2,9.1,11.2,16.1,22.6/
      DATA BR2/5.2,0.,3.8,5.2,6.5,9.,10.6,14.7,20.4/
      DATA BM/4.9,0.,0.4,3.8,5.8,6.7,9.6,14.2,19.2,4*0.,5.0,6.0,
     16.7,9.3,14*0.,4.3,4.6,5.7,7.3,14*0.,3.4,4.5,5.7,6.5/
      DATA BM2/5.4,0.,0.7,4.,5.6,8.2,8.8,12.8,17.2,4*0.,5.2,6.,
     16.5,8.9,14*0.,4.4,4.7,5.7,7.2,14*0.,3.6,4.7,6.1,6.7/
      DATA BO/3.9,0.,-0.9,3.2,5.2,7.8,8.,11.7,15.7,4*0.,4.6,5.3,
     15.8,8.1,14*0.,3.8,4.,5.,6.4,14*0.,1.9,3.9,5.1,5.8/
      DATA BO2/4.3,0.,-0.8,3.4,5.,7.3,7.3,10.5,14.1,4*0.,4.7,5.3,
     15.6,7.8,14*0.,4.,4.1,4.9,6.3,14*0.,2.1,4.2,5.4,6./
      DATA BPS/3*9.,13.,17.,21.,25.,31.,39./
C     ASSIGN BONDING PARAMETERS TO ORBITALS
C     I AND J ARE ATOM INDICES, K AND L ARE ORBITAL INDICES
      IB=IFIX(BETAHO+0.1)
      DO 100 K=1,NOR
      I=MAX0((K+3)/4,K-3*NA)
      IATI=IAT(I)
      GO TO (10,20,30,40,50,60,70),IB
   10 H(K,K)=BM (IATI)
      IF(K.EQ.1) WRITE(6,15)
      GO TO 100
   20 H(K,K)=BM2(IATI)
      IF(K.EQ.1) WRITE(6,25)
      GO TO 100
   30 H(K,K)=BO (IATI)
      IF(K.EQ.1) WRITE(6,35)
      GO TO 100
   40 H(K,K)=BO2(IATI)
      IF(K.EQ.1) WRITE(6,45)
      GO TO 100
   50 H(K,K)=BR (IATI)
      IF(K.EQ.1) WRITE(6,55)
      GO TO 100
   60 H(K,K)=BR2(IATI)
      IF(K.EQ.1) WRITE(6,65)
      GO TO 100
   70 IF(IATI.GT.9) GO TO 99
      IF(K.EQ.1) WRITE(6,75)
      H(K,K)=BPS(IATI)
  100 CONTINUE
C     OFF-DIAGONAL CORE MATRIX ELEMENTS
      DO 200 K=2,NOR
```

```
      LL=K-1
      DO 200 L=1,LL
      H(K,L)=-0.5*S(K,L)*(H(K,K)+H(L,L))
  200 H(L,K)=H(K,L)
C     DIAGONAL CORE MATRIX ELEMENTS-ATOMIC TERMS
C     HYDROGEN ORBITALS LAST AS IN MAIN PROGRAM
      COMMON/ATOM/USS(53),UPP(53),GAA(53),GSTAR(53)/CORECH/
     1KORE(53)
      DO 1 I=1,NA
      IATI=IAT(I)
      H(4*I-3,4*I-3)=-USS(IATI)
      H(4*I-2,4*I-2)=-UPP(IATI)
      H(4*I-1,4*I-1)=-UPP(IATI)
    1 H(4*I  ,4*I  )=-UPP(IATI)
      IF(NOR.EQ.4*NA) GO TO 3
      K1=4*NA+1
      DO 2 K=K1,NOR
    2 H(K,K)=-USS(1)
C     DIAGONAL ELEMENTS-ADD INTERATOMIC TERMS
    3 DO 4 K=1,NOR
      I=MAX0((K+3)/4,K-3*NA)
      DO 4 J=1,NAT
      IF(J.EQ.I) GO TO 4
      IATJ=IAT(J)
      H(K,K)=H(K,K)-FLOAT(KORE(IATJ))*G(I,J)
    4 CONTINUE
      RETURN
   99 WRITE(6,95)
   95 FORMAT(54HLPOPLE AND SEGAL BONDING PARAMETERS ONLY FOR FIRST ROW)
      CALL EXIT
   15 FORMAT(44HJBONDING PARAMETERS EVALUATED FOR MATAGA 1.0)
   25 FORMAT(44HJBONDING PARAMETERS EVALUATED FOR MATAGA 1.2)
   35 FORMAT(42HJBONDING PARAMETERS EVALUATED FOR OHNO 1.0)
   45 FORMAT(42HJBONDING PARAMETERS EVALUATED FOR OHNO 1.2)
   55 FORMAT(46HJBONDING PARAMETERS EVALUATED FOR ROOTHAAN 1.0)
   65 FORMAT(46HJBONDING PARAMETERS EVALUATED FOR ROOTHAAN 1.2)
   75 FORMAT(35HJPOPLE AND SEGAL BONDING PARAMETERS)
      END
```

```
$IBFTC COULSN
      SUBROUTINE COULSN (C,P,N,NE,M)
C     COMPUTES ONE-ELECTRON DENSITY MATRIX FOR MOLECULAR ORBITAL WAVE
C     FUNCTION
      DIMENSION C(M,M),P(M,M)
      NOC=NE/2
      DO 60 L=1,N
      DO 60 K=1,L
      P(K,L)=0.
      DO 61 I=1,NOC
   61 P(K,L)=P(K,L)+C(K,I)*C(L,I)
      P(K,L)=2.*P(K,L)
   60 P(L,K)=P(K,L)
      RETURN
      END



$IBFTC DIPOLE
      SUBROUTINE DIPOLE (D,IAT,P,PAA,S,X,MAT,MOR,NA,NAT,NOR,
     1SS,W,U,IB)
C     COMPUTES DIPOLE MOMENT FOR LCAO-MO WAVE FUNCTION NORMALIZED
C     WITHOUT OVERLAP BY POINT-CHARGE, POPLE-SEGAL,AND DIXON FORMULAE
C     W = OVERLAP MATRIX TO POWER MINUS ONE-HALF
C     U = EIGENVECTORS OF OVERLAP MATRIX
C     SS = EIGENVALUES TO POWER MINUS ONE-HALF
      DIMENSION D(MOR,MOR),P(MOR,MOR),S(MOR,MOR),W(MOR,MOR)
      DIMENSION PAA(MAT),X(3,MAT),IAT(MAT),U(MOR,MOR),SS(MOR)
      COMMON/CORECH/KORE(53)
C     COMPUTES X-COMPONENT ONLY IN DEBYES
C     ASSIGN CO-ORDINATES SO DIPOLE MOMENT ALONG X-AXIS
C     CORE CHARGE TERM (DCOR) AND ELECTRONIC POINT-CHARGE
C     TERM (DPT)
      DCOR =0.
      DPT=0.
      DO 1 I=1,NAT
      IATI=IAT(I)
      DCOR=DCOR+X(1,I)*FLOAT(KORE(IATI))
    1 DPT=DPT+X(1,I)*PAA(I)
C     ATOMIC POLARIZATION TERM (DPOL)
      DPOL =0.
      DO 2 I=1,NA
    2 DPOL = DPOL+2.*P(4*I-2,4*I-3)*D(4*I-2,4*I-3)
C     DIXON FORMULA FOR ELECTRONIC DIPOLE MOMENT (DDIX)
      IF(IB.GT.1)GO TO 10
C     IF BONDING PARAMETER CHANGED, CAN STILL USE SAME W-MATRIX
      DO 40 K=1,NOR
      DO 40 L=1,NOR
   40 W(K,L)=S(K,L)
      CALL EVALUE(W,MOR,MOR,U,MOR,MOR,NOR,1.0E-6,1)
C     SEE COMMENTS ON SUBROUTINE EVALUE IN MAIN CNDO PROGRAM
      DO 50 K=1,NOR
   50 SS(K)=SQRT(W(K,K))
      DO 4 I=1,NOR
```

```
      DO 4 J=1,NOR
      W(I,J)=0.
      DO 4 K=1,NOR
    4 W(I,J)=W(I,J)+U(I,K)*U(J,K)/SS(K)
   10 DDIX =0.
      DO 5 I=1,NOR
      DO 5 J=1,NOR
      DO 5 K=1,NOR
      DO 5 L=1,NOR
    5 DDIX =DDIX +P(I,J)*W(J,K)*D(K,L)*W(L,I)
C     TOTAL DIPOLE MOMENT IN DEBYES
      DPT = 4.80294*(DCOR-DPT)
      DPOPLE=DPT-4.80294*DPOL
      DDIX=4.80294*(DCOR-DDIX)
      WRITE (6,6)DPT,DPOPLE,DDIX
    6 FORMAT(23HLDIPOLE MOMENT (DEBYES)/4X,17HPOINT-CHARGE TERM,
     16X,F8.3/4X,23HPOPLE AND SEGAL FORMULA,F8.3/4X,
     213HDIXON FORMULA,10X,F8.3)
      RETURN
      END


$IBFTC DIPOLE
      SUBROUTINE DIPOLE (D,IAT,P,X,MAT,MOR,NAT,NOR)
C     COMPUTES DIPOLE MOMENT FOR LCAO-MO WAVE FUNCTION
C     NORMALIZED INCLUDING OVERLAP
C     COMPUTES X-COMPONENT ONLY IN DEBYES
C     ASSIGN CO-ORDINATES SO DIPOLE MOMENT ALONG X-AXIS
      DIMENSION D(MOR,MOR),P(MOR,MOR),X(3,MAT),IAT(MAT),CORE(53)
C     CORE = CORE CHARGES
      DATA CORE    /1.,0.,1.,2.,3.,4.,5.,6.,7.,0.,1.,2.,3.,4.,
     15.,6.,7.,0.,1.,2.,10*0.,3.,4.,5.,6.,7.,0.,1.,2.,10*0.,
     23.,4.,5.,6.,7./
C     CORE CHARGE TERM
      DIPOL =0.
      DO 1 I=1,NAT
      IATI=IAT(I)
    1 DIPOL =DIPOL  + X(1,I)*CORE(IATI)
C     ELECTRONIC TERM
      DO 2 I=1,NOR
      DO 2 J=1,NOR
    2 DIPOL =DIPOL -P(I,J)*D(I,J)
C     CONVERT TO DEBYES AND PRINT
      DIPOL =DIPOL *4.80294
      WRITE (6,3)DIPOL
    3 FORMAT (14HKDIPOLE MOMENT,F8.3, 7H DEBYES)
      RETURN
      END
```

```
$IBFTC ENERGY
      SUBROUTINE ENERGY (F,G,H,IAT,P,MAT,MOR,NA,NAT,NOR,NE)
C     COMPUTES BONDING ENERGY IN SCF-MO-CNDO CALCULATION
      DIMENSION F(MOR,MOR),G(MAT,MAT),H(MOR,MOR),IAT(MAT),
     1P(MOR,MOR),EA(53)
C     EA = ENERGY OF ISOLATED NEUTRAL ATOMS IN CNDO APPROXIMATION
      COMMON/ATOM/USS(53),UPP(53),GAA(53),GSTAR(53)//ZH
      COMMON/CORECH/KORE(53)
C     ELECTRONIC ENERGY
      EEL=0.
      DO 1 K=2,NOR
      LL=K-1
      DO 1 L=1,LL
    1 EEL=EEL+P(K,L)*H(K,L)
      DO 2 K=1,NOR
    2 EEL = EEL+0.5*P(K,K)*H(K,K)
      NOC=NE/2
      DO 3 K=1,NOC
    3 EEL = EEL +F(K,K)
C     CORE REPULSION ENERGY
      ECOR = 0.
      DO 4 I = 2,NAT
      IATI = IAT(I)
      ZI = KORE (IATI)
      JJ = I-1
      DO 4 J =1,JJ
      IATJ = IAT(J)
      ZJ= KORE(IATJ)
    4 ECOR=ECOR + ZI*ZJ*G(I,J)
C     ENERGY OF SEPARATED NEUTRAL ATOMS
      ESEP=0.
      DO 5 I=1,NAT
      IATI=IAT(I)
      Z=KORE(IATI)
    5 ESEP=ESEP-AMIN1(Z,2.)*USS(IATI)-AMAX1(Z-2.,0.)*UPP(IATI)+
     1Z*(Z-1.)*GAA(IATI)/2.
C     BONDING ENERGY
      EDIS = ESEP - EEL - ECOR
      WRITE (6,6) EEL, ECOR, ESEP, EDIS
    6 FORMAT(18HLELECTRONIC ENERGY,F10.4/
     122HJCORE REPULSION ENERGY,F10.4/
     234HJENERGY OF SEPARATED NEUTRAL ATOMS,F10.4/
     322HKENERGY OF ATOMIZATION,F10.4)
      RETURN
      END
```

```
$IBFTC INTGRL
      SUBROUTINE INTGRL  (IAT,X,MAT,MOR,NA,NAT,NOR,S,D,ZH)
C     COMPUTES OVERLAP AND DIPOLE MATRIX ELEMENTS FOR BASIS SET OF S
C     AND  P  ORBITALS FOR MO CALCULATION
C     OVERLAP INTEGRALS BY MULLIKEN ET AL., J.CHEM.PHYS.17,1248
C     (1949)
C     HYDROGEN ORBITALS LAST AS IN MAIN PROGRAM
      DIMENSION IAT(MAT),X(3,MAT),S(MOR,MOR),D(MOR,MOR),
      DIMENSION NQ (53),DENUM2 (4),DELTA(5), EFFN(5),COSINE(3),
     1DKRON(3,3)
      DIMENSION C(10,10),ST(14),SST(3,14)
      DOUBLE PRECISION A(10),B(10),P,T,PT,BPLUS,BMINUS
C     ST=TEMPORARY STORAGE LOCATIONS FOR ATOM-PAIR INTEGRALS IN
C     LOCAL CO-ORDINATE SYSTEM
C     SST USED ONLY IF ONE OR BOTH ATOMS HAS PRINCIPAL QUANTUM
C     NO. 4.
      DATA NQ/2*1,8*2,8*3,18*4,17*5/
      DATA DENUM2 ,DELTA,EFFN/2.,24.,720.,40320.,0.,0.65,4.95,
     115.15,26.85,1.,2.,3.,3.7,4./
      LOGICAL SAME
C     SET OVERLAP(S) AND DIPOLE(D) MATRICES = ZERO
      DO 10 K=1,NOR
      DO 10 L=1,NOR
      S(K,L)=0.
   10 D(K,L)=0.
C     COMPUTE KRONECKER DELTA FOR LATER USE
      DO 15 I=1,3
      DO 16 J=1,3
   16 DKRON (I,J)=0.
   15 DKRON (I,I)=1.
C     ASSIGN ATOMIC NUMBERS(IAT),PRINCIPAL QUANTUM NUMBERS(NQ)
C     AND SLATER EXPONENTS (Z) FOR ATOM PAIR.
      DO 400 I=2,NAT
      IATI=IAT(I)
      NQA=NQ(IATI)
      ZA=(0.65*FLOAT(IATI)-DELTA(NQA))/EFFN(NQA)
      IF (IATI.EQ.1)ZA=ZH
      JJ=I-1
      DO 400 J=1,JJ
      IATJ=IAT(J)
      NQB=NQ(IATJ)
      ZB=(0.65*FLOAT(IATJ)-DELTA(NQB))/EFFN(NQB)
      IF(IATJ.EQ.1) ZB=ZH
C     COMPUTE DISTANCE (R IN ANGSTROMS) AND DIRECTION COSINES
      R=SQRT ((X(1,I)-X(1,J))**2+(X(2,I)-X(2,J))**2+(X(3,I)-
     1X(3,J))**2)
      DO 20 K=1,3
   20 COSINE (K)=(X(K,J)-X(K,I))/R
C     COMPUTE MULLIKEN PARAMETERS
      P=(ZA+ZB)*R/1.05834
      T=(ZA-ZB)/(ZA+ZB)
C     ASSIGN EFFECTIVE PRINCIPAL QUANTUM NUMBERS
      MA=MIN0 (NQA,4)
      MB=MIN0 (NQB,4)
```

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C     COMPUTE A AND B INTEGRALS-DEFINITION IN MULLIKEN PAPER
C     WITH SUBSCRIPT INCREASED BY ONE
      A(1)=DEXP(-P)/P
      SGN=1.
      B(1)=2.
      SAME=IATI.EQ.IATJ
      IF (SAME) GO TO 35
      PT=P*T
      BPLUS=DEXP(PT)/PT
      BMINUS=DEXP(-PT)/PT
      B(1)=BPLUS-BMINUS
C     USE RECURSION FORMULAE FOR REMAINING A AND B INTEGRALS
   35 M=MA+MB+2
      DO 40 K=2,M
      XK=K-1
      A(K)=A(1)+XK*A(K-1)/P
      SGN=-SGN
      IF (SAME) GO TO 39
      B(K)=SGN*BPLUS-BMINUS+XK*B(K-1)/PT
      GO TO 40
   39 B(K)=(1.+SGN)/(XK+1.)
   40 CONTINUE
C     COMPUTE NUMBER OF ATOMS WITH NQ=4 (NR4), AND ASSIGN MA
C     (AND/OR MB) =3 FOR FIRST TERM IN INTEGRALS IF THERE ARE
C     ATOMS WITH PRINCIPAL QUANTUM NUMBER 4
      NR4=0
      IF(NQA.NE.4) GO TO 45
      NR4=1
      NTERM =1
      MA=3
   45 IF (NQB.NE.4) GO TO 50
      NR4=NR4+1
      NTERM =1
      MB=3
C     COMPUTE FACTOR MULTIPLYING SUMMATION FOR INTEGRALS
   50 FACTOR=   P*(P*(1.+T))**MA*(P*(1.-T))**MB*
     1SQRT((1.-T*T)/(DENOM2(MA)*DENOM2(MB)))
C     COMPUTE C-MATRIX
      M0=MA+MB
      M1=M0-1
      M2=M0-2
      DO 60 K=1,M1
      DO 60 L=1,M1
   60 C(K,L)=0.
      C(1,1)=1.
      IF(IATJ.EQ.1) GO TO 70
      SGN=1.
      DO 65 N=1,M2
      IF(N.EQ.MA)SGN=-1.
      DO 65 K=1,N
      L=N+1-K
      C(K+1,L)=C(K,L)
   65 C(K,L+1)=C(K,L+1)+C(K,L)*SGN
C     SET INTEGRAL STORAGE LOCATIONS = ZERO
   70 DO 75 K=1,14
```

```
   75 ST(K)=0.
C     COMPUTE OVERLAP AND DIPOLE INTEGRALS BETWEEN S ORBITALS
      DO 80 K=1,M1
      L=MO-K
      ST(1)=ST(1)+C(K,L)*(A(K+2)*B(L)-A(K)*B(L+2))
   80 ST(6)=ST(6)+C(K,L)*(A(K+2)*B(L)+A(K+3)*B(L+1)-A(K)*B(L+2)
     1-A(K+1)*B(L+3))
      ST(1)=0.5*ST(1)*FACTOR
      ST(6)=0.25*R*ST(6)*FACTOR
C     IF BOTH ATOMS=H,COMPUTE  ONLY THESE TWO INTEGRALS
      IF (MB.EQ.1) GO TO 300
C     COMPUTE INTEGRALS FOR WHICH FIRST ORBITAL IS S,SECOND IS P
      DO 100 K=1,M1
      L=MO-K
      ST(2)=ST(2)+C(K,L)*(A(K+1)*(B(L)-B(L+2))+B(L+1)*(A(K)-
     1A(K+2)))
      ST(7)=ST(7)+C(K,L)*(A(K+1)*B(L)+A(K)*B(L+1)-A(K+3)*B(L+2)-
     1A(K+2)*B(L+3))
  100 ST(11)=ST(11)+C(K,L)*((A(K+1)-A(K+3))*(B(L+2)-B(L))+(A(K)-
     1A(K+2))*(B(L+3)-B(L+1)))
      ST(2)=0.866025404*ST(2)*FACTOR
      ST(7)=0.433012702*ST(7)*FACTOR*R
      ST(11)=0.216506351*ST(11)*FACTOR*R
C     IF NEITHER ATOM =H,COMPUTE REMAINING INTEGRALS
      IF(MA.NE.1) GO TO 200
C     AT THIS POINT ONE ATOM =H.
C     IF QUANTUM NO. OF OTHER ATOM =4,MUST ADD TWO TERMS FOR
C     EACH INTEGRAL
      IF (NR4.EQ.0) GO TO 300
      GO TO (140,150),NTERM
C     TRANSFER FIRST TERMS TO SST AND SET MB=4 FOR COMPUTATION
C     OF SECOND TERMS.
  140 DO 145 K=1,11
  145 SST(1,K)=ST(K)
      NTERM = 2
      MB = 4
      GO TO 50
C     ADD TWO TERMS TO GET TOTAL INTEGRAL AND NORMALIZE
  150 DO  155 K=1,11
  155 ST(K)=(0.7*ST(K)+0.3*SST(1,K))*1.01384531
      GO TO 300
C     COMPUTE REMAINING INTEGRALS
  200 DO 210 K=1,M1
      L=MO-K
      ST(3)=ST(3)+C(K,L)*(A(K+1)*(B(L)-B(L+2))+B(L+1)*(A(K+2)
     1-A(K)))
      ST(4)=ST(4)+C(K,L)*(A(K)*B(L)-A(K+2)*B(L+2))
      ST(5)=ST(5)+C(K,L)*((A(K)-A(K+2))*(B(L+2)-B(L)))
      ST(8)=ST(8)+C(K,L)*(A(K+1)*(B(L)-2.*B(L+2))-A(K)*B(L+1)
     1+A(K+2)*(2.*B(L+1)-B(L+3))+A(K+3)*B(L+2))
      ST(9)=ST(9)+C(K,L)*(A(K)*B(L)+A(K+1)*B(L+1)-A(K+2)*B(L+2)
     1-A(K+3)*B(L+3))
      ST(10)=ST(10)+C(K,L)*((A(K+2)-A(K))*(B(L)-B(L+2))+(A(K+3)
     1 -A(K+1))*(B(L+1)-B(L+3)))
      ST(13)=ST(13)+C(K,L)*((A(K+3)-A(K+1))*(B(L)-B(L+2))+
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```
     1(A(K)-A(K+2))*(B(K+1)-B(K+3)))
  210 ST(14)=ST(14)+C(K,L)*((A(K+2)-A(K))*(B(L)-B(L+2))+(A(K+1)
     1-A(K+3))*(B(L+1)-B(L+3)))
      ST(3)=ST(3)*FACTOR*0.866025404
      ST(4)=ST(4)*FACTOR*1.5
      ST(5)=ST(5)*FACTOR*0.75
      ST(8)=ST(8)*R*FACTOR*0.433012702
      ST(9)=ST(9)*R*FACTOR*0.75
      ST(10)=ST(10)*R*FACTOR*0.375
      ST(12)=ST(10)
      ST(13)=ST(13)*R*FACTOR*0.216506351
      ST(14)=ST(14)*R*FACTOR*0.375
      IF (NR4-1)300,220,250
C     IF QUANTUM NO.OF EITHER ATOM =4, MUST ADD 2 TERMS
  220 GO TO (230,240), NTERM
C     TRANSFER FIRST TERMS TO SST AND SET MA(OR MB)=4 FOR
C     COMPUTATION OF SECOND TERMS
  230 DO 235 K=1,14
  235 SST (1,K)= ST(K)
      IF (NQA.EQ.4) MA=4
      IF (NQB.EQ.4)MB=4
      NTERM=2
      GO TO 50
C     ADD TWO TERMS TO GET TOTAL INTEGRAL
  240 DO 245 K=1,14
  245 ST(K)=(0.7*ST(K)+0.3*SST(1,K))*1.01384531
      GO TO 300
C     IF QUANTUM NO. OF BOTH ATOMS =4, MUST ADD 4 TERMS
C     TRANSFER EACH SET OF TERMS TO SST,CHANGE MA AND/OR MB
C     FOR COMPUTATION OF NEXT SET, AND FINALLY ADD TERMS AND
C     NORMALIZE
  250 IF (NTERM.EQ.4) GO TO 290
      DO 260 K=1,14
  260 SST (NTERM,K)=ST(K)
      NTERM=NTERM+1
      IF(NTERM-3)270,280,270
  270 MB=4
      GO TO 50
  280 MA=4
      MB=3
      GO TO 50
  290 DO 295 K=1,14
  295 ST(K)=(0.09*SST(1,K)+0.21*(SST(2,K)+SST(3,K))+0.49*ST(K))
     1*1.02788231
      GO TO 300
C     OVERLAP AND DIPOLE MATRIX ELEMENTS
C     X-COMPONENT ONLY OF DIPOLE MATRIX
C     MODIFY THIS SECTION IF Y- AND Z- COMPONENTS NEEDED
  300 II=MIN0(4*I-3,I+3*NA)
      JJ=MIN0(4*J-3,J+3*NA)
C     INTEGRALS FOR CASE OF TWO HYDROGENS
      S(II,JJ)=ST(1)
      D(II,JJ)=  ST(6)*COSINE(1)+X(1,I)*S(II,JJ)
      IF (MB.EQ.1) GO TO 400
C     INTEGRALS FOR CASE OF ONE HYDROGEN
```

```
      DO 310 K=1,3
      JJK=JJ+K
      S(II,JJK)=-ST(2)*COSINE(K)
  310 D(II,JJK)=DKRON(1,K)*ST(11)-COSINE(1)*COSINE(K)*
     1(ST(7)+ST(11))+X(1,I)*S(II,JJK)
      IF (MA.EQ.1) GO TO 400
C     INTEGRALS FOR CASE OF NO HYDROGEN
      DO 320 K=1,3
      IIK=II+K
      S(IIK,JJ)=ST(3)*COSINE(K)
      D(IIK,JJ)=DKRON(1,K)*ST(13)+COSINE(1)*COSINE(K)*
     1(ST(8)-ST(13))+X(1,I)*S(IIK,JJ)
      DO 320 L=1,3
      JJL=JJ+L
      S(IIK,JJL)=DKRON(K,L)*ST(5)-COSINE(K)*COSINE(L)*(ST(4)
     1+ST(5))
  320 D(IIK,JJL)=COSINE(K)*COSINE(L)*COSINE(1)*(ST(14)-ST(9)
     1-ST(10)-ST(12))+COSINE(K)*DKRON(L,1)*ST(12)+COSINE(1)*DKRON
     2(K,L)*ST(10)-COSINE(L)*DKRON(1,K)*ST(14)+X(1,I)*S(IIK,JJL)
  400 CONTINUE
C     DIAGONAL ELEMENTS OF OVERLAP AND DIPOLE MATRICES
      DO 410 K=1,NOR
      S(K,K)=1.
      I=MAX0((K+3)/4,K-3*NA)
  410 D(K,K)=X(1,I)
C     ATOMIC POLARIZATION TERMS IN DIPOLE MATRIX
      DO 420 I=1,NA
      IATI=IAT(I)
      NQA=NQ(IATI)
      ZA=(0.65*FLOAT(IATI)-DELTA(NQA))/EFFN(NQA)
  420 D(4*I-2,4*I-3)=0.305516442*(EFFN (NQA)+0.5)/ZA
C     SYMMETRIZE MATRICES
      DO 430 K=2,NOR
      LL=K-1
      DO 430 L=1,LL
      S(L,K)=S(K,L)
  430 D(L,K)=D(K,L)
      RETURN
      END
```

```
$IBFTC LOWDIN
      SUBROUTINE LOWDIN
C     SOLVES SECULAR EQUATIONS INCLUDING OVERLAP BY LOWDIN'S METHOD
C     W = OVERLAP MATRIX TO POWER MINUS ONE HALF
C     U = EIGNEVECTORS OF S, LATER OF E
      DIMENSION  S(50,50),H(50,50),U(50,50),W(50,50),E(50,50),C(50,50)
      COMMON S,H,N
      EQUIVALENCE (S,E),(H,C)
C     COMPUTE W-MATRIX = S TO POWER MINUS ONE-HALF
      CALL EVALUE(S,50,50,U,50,50,N,.0001,1)
C     SUBROUTINE EVALUE IS PART OF MCGILL COMPUTER SYSTEM
C     DIAGONALIZES MATRIX-SEE COMMENTS IN CNDO MAIN PROGRAM
      DO 52 I=1,N
      IF(S(I,I).LT.0.0) GO TO 60
   52 S(I,I)=1./SQRT(S(I,I))
      DO 53 I=1,N
      DO 53 J=1,N
      W(I,J)=0.0
      DO 53 K=1,N
   53 W(I,J)=W(I,J)+U(I,K)*U(J,K)*S(K,K)
C     TRANSFORM HAMILTONIAN MATRIX TO ORTHOGONALIZED BASIS
      DO 54 I =1,N
      DO 54 J =1,N
      E(I,J)=0.
      DO 54 K =1,N
      DO 54 L =1,N
   54 E(I,J)=E(I,J)+W(I,K)*H(K,L)*W(L,J)
C     DIAGONALIZE TRANSFORMED HAMILTONIAN
      CALL EVALUE(E,50,50,U,50,50,N,.0001,1)
C     TRANSFORM LCAO COEFFICIENTS BACK TO ORIGINAL BASIS
      DO 55 I =1,N
      DO 55 J =1,N
      C(I,J)=0.
      DO 55 K =1,N
   55 C(I,J)=C(I,J)+W(I,K)*U(K,J)
C     SORT EIGENVALUES AND EIGENVECTORS IN ORDER OF INCREASING ENERGY
      DO 56 I=2,N
      JA=I-1
      DO 56 J=1,JA
      IF(E(I,I).GE.E(J,J))    GO TO 56
      ET=E(I,I)
      E(I,I)=E(J,J)
      E(J,J)=ET
      DO 57 K=1,N
      CT=C(K,I)
      C(K,I)=C(K,J)
   57 C(K,J)=CT
   56 CONTINUE
      RETURN
   60 WRITE(6,61)
   61 FORMAT(81HONE OF OVERLAP MATRIX EIGENVALUES IS NEGATIVE,INDICATIN
     1G ERROR IN INPUT GEOMETRY)
      CALL EXIT
      END
```

```
$IBFTC POPAN
      SUBROUTINE POPAN(P,S,NAT,NA,NH)
C     PERFORMS MULLIKEN POPULATION ANALYSIS
C     GOP = GROSS ORBITAL POPULATIONS, GAP = GROSS ATOMIC POPULATIONS,
C     OP = OVERLAP POPULATIONS
C     HYDROGEN ORBITALS LAST AS IN MAIN PROGRAM
      DIMENSION P(50,50),S(50,50),NAT(25),OP(25,25),GOP(50),GAP(25)
      NAA=NA+1
      NAH=NA+NH
      NOR=4*NA+NH
C     I,J ATOM INDICES. K,L ORBITAL INDICES.
C     GROSS ORBITAL POPULATIONS
      DO 10 K=1,NOR
      GOP(K)=0.
      DO 10 L=1,NOR
   10 GOP(K)=GOP(K)+P(K,L)*S(K,L)
      WRITE(6,15)(GOP(K),K=1,NOR)
   15 FORMAT(26HKGROSS ORBITAL POPULATIONS/(14F9.4))
C     GROSS ATOMIC POPULATIONS
      DO 20 I=1,NA
      K1=4*I-3
      K4=4*I
      GAP(I)=0.
      DO 20 K=K1,K4
   20 GAP(I)=GAP(I)+GOP(K)
      IF(NH.EQ.0) GO TO 24
      DO 22 I=NAA,NAH
      K=I+3*NA
   22 GAP(I)=GOP(K)
   24 WRITE(6,25)(GAP(I),I=1,NAH)
   25 FORMAT(25HKGROSS ATOMIC POPULATIONS/(14F9.4))
C     ATOMIC OVERLAP POPULATIONS
      DO 30 I=2,NAH
      JJ=I-1
      K1=4*I-3
      K4=4*I
      IF(I.GT.NA) K1=I+3*NA
      IF(I.GT.NA) K4=I+3*NA
      DO 30 J=1,JJ
      L1=4*J-3
      L4=4*J
      IF(J.GT.NA) L1=J+3*NA
      IF(J.GT.NA) L4=J+3*NA
      OP(I,J)=0.
      DO 28 K=K1,K4
      DO 28 L=L1,L4
   28 OP(I,J)=OP(I,J)+2.*P(K,L)*S(K,L)
   30 OP(J,I)=OP(I,J)
      WRITE(6,32)
   32 FORMAT(20HKOVERLAP POPULATIONS)
      CALL PRINT(OP,25,NAH)
      RETURN
      END
```

```
$IBFTC POPLE
      SUBROUTINE POPLE(F,G,H,IAT,MAT,MOR,NAT,NOR,P,PAA)
C     COMPUTES HARTREE-FOCK HAMILTONIAN MATRIX FOR NEW CYCLE OF
C     ITERATION IN SCF-MO-CNDO CALCULATION
C     HYDROGEN ORBITALS AS IN MAIN PROGRAM
      DIMENSION G(MAT,MAT),IAT(MAT),PAA(MAT)
      DIMENSION F(MOR,MOR),H(MOR,MOR),P(MOR,MOR)
C     I AND J ARE ATOM INDICES, K AND L ARE ORBITAL INDICES
      NA=(NOR-NAT)/3
C     DIAGONAL MATRIX ELEMENTS
      DO 3 I=1,NA
      K1=4*I-3
      K4=4*I
      PAA(I)=0.
      DO 2 K=K1,K4
    2 PAA(I)=PAA(I)+P(K,K)
      DO 3 K=K1,K4
    3 F(K,K)=H(K,K)+(PAA(I)-0.5*P(K,K))*G(I,I)
C     DIAGONAL MATRIX ELEMENTS-ADD INTERATOMIC TERMS
      IF(NA.EQ.NAT) GO TO 6
      NAA= NA+1
      DO 5 I=NAA,NAT
      K=I+3*NA
      F(K,K)=H(K,K)+0.5*P(K,K)*G(I,I)
    5 PAA(I)=P(K,K)
    6 DO 9 J=1,NAT
      DO 9 I=1,NAT
      IF(I.EQ.J) GO TO 9
      K1=MIN0(4*I-3,I+3*NA)
      K4=MIN0(4*I  ,I+3*NA)
      DO 7 K=K1,K4
    7 F(K,K)=F(K,K)+PAA(J)*G(I,J)
    9 CONTINUE
C     OFF-DIAGONAL MATRIX ELEMENTS
      DO 10 K=2,NOR
      LL=K-1
      I=MAX0((K+3)/4,K-3*NA)
      DO 10 L=1,LL
      J=MAX0((L+3)/4,L-3*NA)
      F(K,L)=H(K,L)-0.5*P(K,L)*G(I,J)
   10 F(L,K)=F(K,L)
      RETURN
      END
```

```
$IBFTC PRINT
      SUBROUTINE PRINT(ARRAY,M,N)
C     PRINTS NXN MATRIX 14 COLUMNS AT A TIME
      DIMENSION ARRAY(M,N)
      JJ=0
    1 J1=JJ+1
      JJ=MIN0(JJ+14,N)
      WRITE(6,600)(J,J=J1,JJ)
      DO 2 I=1,N
    2 WRITE(6,601)I,(ARRAY(I,J),J=J1,JJ)
      IF(JJ.LT.N) GOTO1
      RETURN
  600 FORMAT(14I9)
  601 FORMAT(1H ,I2,14F9.4)
      END
```

```
$IBFTC REPUL
      SUBROUTINE REPUL(G,IAT,MAT,NA,NAT,X)
C     COMPUTES ELECTRON-REPULSION INTEGRALS FOR SCF-MO-CNDO CALCULATION
C     BY MATAGA APPROXIMATION
      DIMENSION G(MAT,MAT),IAT(MAT),X(3,MAT)
      COMMON/ATOM/USS(53),UPP(53),GAA(53),GSTAR(53)
      DO 1 I=1,NAT
      IATI=IAT(I)
    1 G(I,I)=GAA(IATI)
      DO 2 I=2,NAT
      JJ=I-1
      IATI=IAT(I)
      DO 2 J=1,JJ
      IATJ=IAT(J)
      A=2./(GSTAR(IATI)+GSTAR(IATJ))
      R=SQRT((X(1,I)-X(1,J))**2+(X(2,I)-X(2,J))**2+(X(3,I)-X(3,J))**2)
      G(I,J)=1./(R/14.395+A)
    2 G(J,I)=G(I,J)
      WRITE(6,6)
    6 FORMAT(44HKREPULSION INTEGRALS BY MATAGA APPROXIMATION)
      RETURN
      END
```

```
$IBFTC REPUL
      SUBROUTINE REPUL(G,IAT,MAT,NA,NAT,X)
C     COMPUTES ELECTRON-REPULSION INTEGRALS FOR SCF-MO-CNDO CALCULATION
C     BY OHNO APPROXIMATION
      DIMENSION G(MAT,MAT),IAT(MAT),X(3,MAT)
      COMMON/ATOM/USS(53),UPP(53),GAA(53),GSTAR(53)
      DO 1 I=1,NAT
      IATI=IAT(I)
    1 G(I,I)=GAA(IATI)
      DO 2 I=2,NAT
      JJ=I-1
      IATI=IAT(I)
      DO 2 J=1,JJ
      IATJ=IAT(J)
      A=2./(GSTAR(IATI)+GSTAR(IATJ))
      RSQ=((X(1,I)-X(1,J))**2+(X(2,I)-X(2,J))**2+(X(3,I)-X(3,J))**2)
      G(I,J)=1./SQRT(RSQ/207.32+A*A)
    2 G(J,I)=G(I,J)
      WRITE(6,6)
    6 FORMAT(42HKREPULSION INTEGRALS BY OHNO APPROXIMATION)
      RETURN
      END


$IBFTC REPUL
      SUBROUTINE REPUL(G,IAT,MAT,NA,NAT,X)
C     ASSIGNS THEORETICAL ELECTRON-REPULSION INTEGRALS FOR SCF-MO-CNDO
C     CALCULATION
C     COMPUTATION FOLLOWS ROOTHAAN, J.CHEM.PHYS. 19,1445 (1951)
C     PARAMETERS DEFINED IN ROOTHAAN PAPER
      DIMENSION G(MAT,MAT),X(3,MAT),IAT(MAT),ZETA(9)
      COMMON/ATOM/USS(53),UPP(53),GAA(53),GSTAR(53)//ZH
      DATA ZETA/1.2,0.,0.65,0.975,1.3,1.625,1.95,2.275,2.6/
      ZETA(1)=ZH
      REAL KAP
C     ASSIGN ATOMIC INTEGRALS
      DO 1 I=1,NAT
      IATI=IAT(I)
      IF(IATI.GT.9) GO TO 9
    1 G(I,I)=GAA(IATI)
C     ASSIGN INTERATOMIC INTEGRALS
C     HYDROGENS LAST AS IN MAIN PROGRAM
      DO 6 I=2,NAT
      JJ=I-1
      DO 6 J=1,JJ
      R=SQRT((X(1,I)-X(1,J))**2+(X(2,I)-X(2,J))**2+(X(3,I)-X(3,J))**2)
      IF(J.LE.NA) GO TO 3
C HYDROGEN-HYDROGEN CASE (TAU=0)
      RHO=ZETA(1)*R      /0.52917
      G(I,J)=ZETA(1)*(1.-(1.+RHO*(1.375+RHO*(0.75+RHO/6.)))/EXP(2.*RHO))
     1/RHO
      GO TO 5
C     PARAMETERS FOR ROOTHAAN FORMULAE IN OTHER CASES
```

```
    3 IATI=IAT(I)
      IATJ=IAT(J)
      ZA=ZETA(IATI)
      ZB=ZETA(IATJ)
      Z=0.5*(ZA+ZB)
      RHO=Z*R      /0.52917
      IF(IATI.EQ.IATJ) GO TO 7
      RHOA=ZA*R      /0.52917
      RHOB=ZB*R      /0.52917
      KAP=(ZA*ZA+ZB*ZB)/(ZA*ZA-ZB*ZB)
      IF(I.LE.NA) GO TO 4
C     HYDROGEN-OTHER ATOM CASE
      G(I,J)=(Z/RHO)*(1.-(1.-KAP)**3*((1.-KAP*(5.+KAP*4.))/16.-KAP*RHOA/
     1 8.)*EXP(-2.*RHOA)-(1.+KAP)**2*((15.-KAP*(22.-KAP*(15.-KAP*4.)))/
     2 16.+0.375*(3.-KAP*(3.-KAP))*RHOB+0.25*(2.-KAP)*RHOB**2+RHOB**3/
     3 12.)*EXP(-2.*RHOB))
      GO TO 5
C     CASE OF TWO ATOMS BOTH NOT HYDROGEN
    4 FN(X,Y)=(1.-X)**3*EXP(-2.*Y)*((8.-X*(1.+X*(27.+X*(30.+X*10.))))/
     1 16.+(11.-X*(19.+X*(44.+X*20.)))*Y/32.+(1.-X*(5.+X*4.))*Y**2/16.
     2 -X*Y**3/24.)
      G(I,J)=(Z/RHO)*(1.-FN(KAP,RHOA)-FN(-KAP,RHOB))
      GO TO 5
    7 G(I,J)=(Z    /RHO)*(1.-(80640.+RHO*(131985.+RHO*
     1 (102690.+RHO*(49980.+RHO*(16800.+RHO*(4032.+RHO*
     2 (672.+RHO*64.)))))))/(80640.*DEXP(2.*RHO)))
    5 G(I,J)=27.210*G(I,J)
    6 G(J,I)=G(I,J)
      WRITE(6,8)
    8 FORMAT(41HKREPULSION INTEGRALS BY ROOTHAAN FORMULAE)
      RETURN
    9 WRITE(6,10)
   10 FORMAT(45HKROOTHAAN FORMULAE INCLUDED ONLY FOR HYDROGEN/
     112H+TO FLUORINE)
      CALL EXIT
      END
```

```
$IBFTC SORT
      SUBROUTINE SORT(E,C,N,M)
C     PLACES EIGENVALUES AND EIGENVECTORS IN ORDER OF INCREASING ENERGY
      DIMENSION E(M,M),C(M,M)
      DO 56 I=2,N
      JA=I-1
      DO 56 J=1,JA
      IF(E(I,I).GE.E(J,J))GO TO 56
      ET=E(I,I)
      E(I,I)=E(J,J)
      E(J,J)=ET
      DO 57 K=1,N
      CT=C(K,I)
      C(K,I)=C(K,J)
   57 C(K,J)=CT
   56 CONTINUE
      RETURN
      END


$IBFTC START
      SUBROUTINE START (F,G,H,IAT,    ITER,MAT,MOR,NA,NOR,SCF)
C INITIALIZES SCF-LCAO-MO-CNDO COMPUTATION
      DIMENSION F(MOR,MOR),G(MAT,MAT),H(MOR,MOR),IAT(MAT)
      COMMON/ATOM/USS(53),UPP(53),GAA(53),GSTAR(53)/CORECH/
     1KORE(53)
      LOGICAL SCF
C     ASSIGN INITIAL HARTREE-FOCK HAMILTONIAN MATRIX
C     HYDROGEN ORBITALS LAST AS IN MAIN PROGRAM
      DO 1 K=1,NOR
      DO 1 L=1,NOR
    1 F(K,L)=H(K,L)
      DO 2 I=1,NA
      IATI=IAT(I)
      Z=KORE(IATI)
      F(4*I-3,4*I-3)=-USS(IATI)+(Z-0.5)*G(I,I)
      F(4*I-2,4*I-2)=-UPP(IATI)+(Z-0.5)*G(I,I)
      F(4*I-1,4*I-1)=-UPP(IATI)+(Z-0.5)*G(I,I)
    2 F(4*I  ,4*I  )=-UPP(IATI)+(Z-0.5)*G(I,I)
      IF(NOR.EQ.4*NA) GO TO 4
      NH1=4*NA+1
      DO 3 K=NH1,NOR
    3 F(K,K)=-7.171
C     ASSIGN ITERATION NUMBER = 1 AND SCF CRITERION = FALSE
    4 ITER=1
      SCF = .FALSE.
      RETURN
      END
```

```
$IBFTC TEST
      SUBROUTINE TEST(P,P1,P2,EPS,ITER,M,N,SCF)
C     TESTS FOR CONVERGENCE IN SCF-MO-CNDO CALCULATION
C     USES AITKEN ACCELERATION IF BLOOR CRITERION SATISFIED
C     (SEE BLOOR, CAN.J.CHEM. 42,133(1964))
C     P=CURRENT POPULATION MATRIX,P1 AND P2 ARE PREVIOUS POPULATION
C     MATRICES
C     EPS = ACCURACY REQUIREMENT,ITER = NO. ITERATIONS,
C      SCF = TRUE IF CONVERGENCE REACHED
      DIMENSION P(M,M),P1(M,M),P2(M,M)
      LOGICAL SCF
      IF((ITER/2)*2.EQ.ITER) GO TO 40
C     THIS SECTION USED FOR ODD ITERATIONS
      IF(ITER.EQ.1) GO TO 30
C     CHECK FOR CONVERGENCE
      DO 10 I=1,N
      DO 10 J=1,I
   10 IF(ABS(P(I,J)-P2(I,J)).GT.EPS) GO TO 20
      SCF=.TRUE.
      RETURN
C     IF NOT CONVERGENT, CHECK BLOOR CRITERION FOR APPLICABILITY OF
C     AITKEN ACCELERATION
   20 DO 21 I=1,N
      DO 21 J=1,I
   21 IF(ABS(P(I,J)-P2(I,J)).GT.ABS(P(I,J)-2.*P2(I,J)
     1+P1(I,J))) GO TO 30
C     APPLY AITKEN ACCELERATION
      DO 25 I=1,N
      DO 25 J=1,I
      P(I,J)=P(I,J)-(P(I,J)-P2(I,J))**2/(P1(I,J)
     1-2.*P2(I,J)+P(I,J))
   25 P(J,I)=P(I,J)
C     STORE CURRENT POPULATION MATRIX FOR NEXT ITERATION
   30 DO 35 I=1,N
      DO 35 J=1,N
   35 P1(I,J)=P(I,J)
      GO TO 60
C     THIS SECTION USED FOR EVEN ITERATIONS
C     CHECK FOR CONVERGENCE
   40 DO 45 I=1,N
      DO 45 J=1,I
   45 IF(ABS(P(I,J)-P1(I,J)).GT.EPS) GO TO 50
      SCF=.TRUE.
      RETURN
C     IF NOT CONVERGENT, STORE POPULATION MATRIX FOR NEXT ITERATION
   50 DO 55 I=1,N
      DO 55 J=1,N
   55 P2(I,J)=P(I,J)
   60 ITER=ITER+1
      RETURN
      END
```

```
HYDROGEN CHLORIDE
  2 ATOMS    1 HYDROGENS    8 VALENCE-SHELL ELECTRONS

ATOMIC NUMBER       CO-ORDINATES
    17          0.00000   0.00000   0.00000
     1          1.27460   0.00000   0.00000
SCF-LCAO-MO METHOD WITH ZERO DIFFERENTIAL OVERLAP

REPULSION INTEGRALS BY OHNO APPROXIMATION
SLATER EXPONENT FOR HYDROGEN 1.20
BONDING PARAMETERS EVALUATED FOR OHNO 1.2
10 ITERATIONS REQUIRED

ENERGY LEVELS
   -25.0690 -14.7907 -13.4640 -13.4640  -0.9218
LCAO COEFFICIENTS
          1        2        3        4        5
 1    0.9784  -0.1491   0.0000   0.0000  -0.1431
 2    0.0311   0.7908   0.0000   0.0000  -0.6113
 3    0.0000   0.0000   1.0000   0.0000   0.0000
 4    0.0000   0.0000   0.0000   1.0000   0.0000
 5    0.2043   0.5937   0.0000   0.0000   0.7784

POPULATION MATRIX
          1        2        3        4        5
 1    1.9591  -0.1749   0.0000   0.0000   0.2227
 2   -0.1749   1.2526   0.0000   0.0000   0.9516
 3    0.0000   0.0000   2.0000   0.0000   0.0000
 4    0.0000   0.0000   0.0000   2.0000   0.0000
 5    0.2227   0.9516   0.0000   0.0000   0.7883

TOTAL ATOMIC CHARGES
  7.2117   0.7883


DIPOLE MOMENT (DEBYES)
   POINT-CHARGE TERM           1.296
   POPLE AND SEGAL FORMULA     2.180
   DIXON FORMULA               1.650


ELECTRONIC ENERGY -410.7098
CORE REPULSION ENERGY    56.6678
ENERGY OF SEPARATED NEUTRAL ATOMS -349.4160

ENERGY OF ATOMIZATION    4.6260

TIME    1.3 SECONDS
```

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