WAVE FUNCTION CALCULATIONS ON SMALL MOLECULES

by

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CONTENTS

ABSTRACT

The ab initio calculation of wave functions for small polyatomic molecules is now feasible but is time-consuming, expensive and limited in accuracy. The most frequently used approach is that of molecular orbital (MO) theory, using the self-consistent field (SCF) method with a linear combination of atomic orbitals (LCAO) approximation to the MO's. On the other hand, semi-empirical methods have been widely used and have yielded extremely interesting results in spite of the fact that they have often been based on flimsy theoretical foundations. The first and best known calculations of this type were of course initiated by Hückel and refer to the π-electrons of conjugated molecules. Later semi-empirical SCF LCAO MO calculations, in which electron interaction effects are more properly taken into account, were done on π-electron systems. Then the Hückel type LCAO MO method, and later the approximate SCF MO scheme, were applied to more general systems.

In this work a new semi-empirical SCF scheme is presented in which an attempt is made to produce a method as close to ab initio procedures as possible. A particular basis of orthogonalised orbitals is chosen to render valid, with a reasonable degree

of accuracy, the integral approximations made. The use of a particular set of integral approximations allows the simulation of the results of non-empirical calculations. The semi-empirical calculations described in this work are less empirical than any previously performed on more general systems; this allows the scheme to be built on a sounder basis than other semi-empirical schemes which include all electrons. Results are presented to show that with a relatively simple method of estimating the larger two-electron integrals, over an orthogonal basis, reasonable results can be obtained for small polyatomic molecules. As well as giving good results the method is used as a basis for examining the foundations of more empirical calculations.

Two approaches are used to obtain wave functions, the SCF MO LCAO and the self-consistent group function (SCGF) method. It is found that SCGF method has several advantages over the ordinary SCF MO LCAO method in the performance of semi-empirical calculations.

CHAPTER ONE

INTRODUCTION

The Theory of Self-Consistent Molecular Orbital and Group Function Methods

The general aim of this work was to perform semi-empirical calculations on molecules, including all electrons.

This chapter describes the two methods, SCFMO and SCGF, which have been used in this work to obtain approximate solutions to the Schrödinger equation

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

where $\hat{H}$ is the Hamiltonian operator for the electronic part of the system*

$$\hat{H} = \sum_i h(i) + \tfrac{1}{2}\sum_{i,j} 1/r_{ij} \tag{2}$$

$$h(i) = -\tfrac{1}{2}\nabla^2(i) + V(i)$$

$$V(i) = -\sum_n Z_n/r_{in}$$

i denotes an electronic coordinate and n a nuclear coordinate

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* For typographical convenience a letter with a roof, e.g. $\hat{H}$, denotes an operator.

(atomic units are used e=1, m=1, h/2π=1).

The MO method is an extension of the Bohr theory of electronic configurations from atoms to molecules. Each electron is assigned to a one-electron wave function or MO. An approximate N-electron wave function is then built up as an antisymmetrised product (AP) of MO's.

$$\Phi = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots\cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots\cdots & \psi_N(2) \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(N) & \psi_2(N) & \cdots\cdots & \psi_N(N) \end{vmatrix} \qquad (3)$$

Φ may also be represented as

$$\Phi = (N!)^{-\frac{1}{2}} \sum_{P} (-1)^{P} P\bigl(\psi_1(1)\psi_2(2) \ldots \psi_N(N)\bigr)$$

in which the sum P is over all permutations of the N! distinct electrons amongst themselves and $(-1)^P$ is +1 if the permutation involves an even number of pair interchanges, -1 if it involves an odd number. The MO's are products of a function depending on the space coordinates of the electron only and a function depending on the spin coordinates only[†]

$$\psi_\kappa(i) = \phi_\kappa(x_i;y_i;z_i)\ \eta_\kappa(i)$$

where

$$\eta_\kappa(i) = \left\{ \begin{matrix} \alpha(i) \\ \beta(i) \end{matrix} \right.$$

The spatial functions and the spin functions are assumed orthonormal

$$\begin{aligned} \int \phi_i{}^*(1)\phi_j(1)\ dx_1 &= \delta_{ij} \\ \int \eta_i(s_1)\eta_j(s_1)\ ds_1 &= \delta_{ij} \end{aligned} \qquad (4)$$

If the original space orbitals are not mutually orthogonal then they can always be transformed to an orthogonal basis. The form of the wave function (3) requires that all the MO's must be linearly independent, since otherwise the determinant vanishes. So only two MO's can contain the same spatial function and they must then have different spins; such a pair of MO's are said to form a closed electron shell. A closed shell structure then refers to an AP completely composed of closed shells. Most molecules in the ground state have a closed shell structure in the MO approximation.

[†] The term MO is here used to denote the spin-orbital product - not just the spatial factor.

In the group function method, various lone pairs and bond pairs are recognised from the start and the wave functions is written as an antisymmetrised product of localised two-electron functions. More generally one considers also many-electron groups of electrons (such as a π-electron system).

The closed shell molecular wave function is written

$$\Phi_{A,B,\ldots}(1,2,\ldots N) = M \sum_P (-1)^P P\left(\Phi_A(1,\ldots N)\Phi_B(N_A+1,\ldots N_A+N_B)\ldots\right) \quad (5)$$

Φ_R is called a group function for the N^R electrons of group R. It is assumed that the group functions are individually antisymmetric in the variables to which they refer. A completely antisymmetrical function results when the summation in (5) excludes the sub-group of permutations which leave every electron in its original group. If there are ν permutations in the remaining distinct cosets, the normalising factor M is $(\nu!)^{-\frac{1}{2}}$, provided the group functions are normalised and orthogonal in the sense

$$\int \Phi_R^*(1,i,j,\ldots)\Phi_S(1,k,\ell,\ldots)\, d\tau_1 = 0 \qquad (R\neq S)$$

The wave function for group R, Φ_R, is written as a linear combination of N^R-electron basis functions for the electrons of group R, ϕ_μ^R

$$\Phi_R = \sum_{\mu=1}^{m} \bar{c}_\mu^R \, \phi_\mu^R \qquad (6)$$

where the ϕ_μ^R are constructed from orbitals $r_1, r_2, \ldots$ of group R (e.g. a Slater determinant or suitably coupled set of determinants). r_i are basis orbitals of group R (e.g. suitably orthogonalised AO's or hybrids).

Variation Theorem

For a normalised trial wave function Ψ we can calculate

$$E = \int \Psi^* \hat{H} \Psi \, d\tau$$

which is the expectation value of the energy of the system in state Ψ. By the variation theorem this expectation value cannot be less than the exact energy of the system in its lowest energy state

$$E \geq E_1 \qquad (7)$$

Proof Expanding the trial function Ψ in terms of the complete set of orthonormal eigenfunctions of $\hat{H}$, and assuming that Ψ is normalised then

$$\Psi = \sum_{i}^{m} c_i \, \psi_i$$

and

$$E = \sum_{i,j}^{m} c_i^* \, c_j \, H_{ij}$$

where

$$H_{ij} = \int \psi_i^*(1)\ \hat{H}\ \psi_j(1)\ d\tau_1$$

Now since

$$\hat{H}\ \psi_j = E_j\ \psi_j$$

$$H_{ij} = E_j \int \psi_i^*(1)\psi_j(1)\ d\tau_1 = E_j\ \delta_{ij}$$

So

$$E = \sum_j^m c_j^*\ c_j\ E_j \tag{8}$$

But as Ψ is normalised, substitution in $\int \Psi^*\Psi\ d\tau = 1$, multiplication by E_1 and subtraction from (8) gives

$$E - E_1 = |c_2|^2\ (E_2-E_1) + |c_3|^2\ (E_3-E_1) + \ldots$$

But every term on the right is positive since E_1 is the lowest energy value and (7) therefore follows.

In the variation method Ψ contains parameters which can be varied until E has its lowest value for the particular type of function chosen. This is an extremely useful method since we know that variation of parameters in the wave function cannot give a lower energy than the exact energy, so that it is reasonable to assume that lowering the energy produces a better wave function which is a more adequate description of the system. There are no analogous theorems for such properties as dipole moment or charge distribution so that it would be very difficult to use these properties to decide upon a good wave function.

The SCF MO method for closed shell systems

The SCF MO method for closed shell systems has been developed by Roothaan(1), Hall(2) and McWeeny(3).

The total energy for the closed shell system is

$$E = \int \Phi^* \hat{H} \Phi \, d\tau$$

where $\hat{H}$ is given by equation (2) and Φ by equation (3).

$$E = \int \Phi^* \sum_i \hat{h}(i) \, \phi \, d\tau + \int \Phi^* \left(1/2 \sum_{i,j}{}' 1/r_{ij}\right) \Phi \, d\tau$$

$$= I + G$$

Now

$$I = \frac{1}{N!} \int \sum_P (-1)^P P\left(\psi_1(1)\psi_2(2)\ldots\psi_N(N)\right)^* \sum_i \hat{h}(i) \sum_Q (-1)^Q Q\left(\psi_1(1)\psi_2(2)\ldots\psi_N(N)\right) d\tau_1 d\tau_2 \ldots d\tau_N$$

Since each permutation P simply affects the labelling of the variables of integration we have N! identical terms

$$I = \int \left(\psi_1(1)\psi_2(2)\ldots\psi_N(N)\right)^* \sum_i \hat{h}(i) \sum_Q (-1)^Q Q\left(\psi_1(1)\psi_2(2)\ldots\psi_N(N)\right) d\tau_1 d\tau_2 \ldots d\tau_N$$

Now since $\sum_i \hat{h}(i)$ is a sum of one-electron operators, any non-trivial permutation Q produces two non-coincidences of spin orbitals, one of which must integrate to zero by equation (4), so

$$I = \sum_i \int \psi_i(1)\ \hat{h}(1)\ \psi_i(1)\ d\tau_1 = \sum_i h_i$$

since all the factors multiplying these terms integrate to unity by equation (4).

For the electron repulsion terms the reduction is the same except that since $1/r_{ij}$ is a two-electron operator the only permutations Q which result in non-zero terms are the identity and single interchanges.

$$G = \int \big(\psi_1(1)\psi_2(2)\ldots\psi_N(N)\big)^* \ (1/2 \sum_{i,j}{}' 1/r_{ij}) \sum_Q (-1)^Q$$
$$\times\ Q\ \big(\psi_1(1)\psi_2(2)\ldots\psi_N(N)\big) d\tau_1 d\tau_2 \ldots d\tau_N$$
$$= \tfrac{1}{2} \sum_{i,j} \Big(\int \psi_i^*(1)\psi_j^*(2)\ \frac{1}{r_{12}}\ \psi_i(1)\psi_j(2) d\tau_1 d\tau_2$$
$$- \int \psi_i^*(1)\psi_j^*(2)\ \frac{1}{r_{12}}\ \psi_i(2)\psi_j(1) d\tau_1 d\tau_2\Big)$$

$$= \tfrac{1}{2} \sum_{i,j} (j_{ij} - k_{ij})$$

So

$$E = \sum_i h_i + \tfrac{1}{2} \sum_{i,j} (j_{ij} - k_{ij}) \qquad (9)$$

For the closed shell case the MO's occur in pairs with the same space functions and different spin functions. We can reduce equation (9) further by integrating over spin coordinates. We define the following integrals over space coordinates only:

$$H_i = \int \phi_i^*(1)\, \hat{h}(1)\, \phi_i(1)\, d\tau_1$$

$$J_{ij} = \int \phi_i^*(1)\phi_j^*(2)\, \frac{1}{r_{12}}\, \phi_i(1)\phi_j(2)\, d\tau_1 d\tau_2$$

$$K_{ij} = \int \phi_i^*(1)\phi_j^*(2)\, \frac{1}{r_{12}}\, \phi_i(2)\phi_j(1)\, d\tau_1 d\tau_2$$

When the spin integration is performed h_i is always equal to H_i, j_{ij} is always equal to J_{ij} and k_{ij} is equal to K_{ij} if ϕ_i and ϕ_j have the same spin factor, and zero otherwise. So contributions to H_i, J_{ij} and K_{ij} arise from the following combinations of spin factors:

	ϕ_i^*	ϕ_j^*	ϕ_i	ϕ_j
h_i	α		α	
	β		β	
j_{ij}	α	α	α	α
	β	β	β	β
	α	β	α	β
	β	α	β	α
k_{ij}	α	α	α	α
	β	β	β	β

So the energy expression (9) reduces to

$$E = 2 \sum_{i} H_i + \sum_{i,j} (2J_{ij} - K_{ij}) \tag{10}$$

To obtain the AP for which the energy is a minimum we have to minimise (10) by varying the MO's with the constraint that the MO's form an orthonormal set.

If we use the approximation that our MO's are linear combinations of atomic orbitals (LCAO)

$$\phi_i = \sum_{p} \chi_p T_{pi} \tag{11}$$

where the χ_p's are normalised atomic orbitals (AO's)

$$\int \chi_p^*(1)\chi_p(1)\, d\tau_1 = 1$$

then we have to find the coefficients T_{pi} for which the energy of the AP is a minimum. Writing equation (11) in matrix notation†

$$\underline{\phi} = \underline{\chi}\, \underline{T}$$

where

$\underline{\phi}$ is $(\phi_1\alpha, \phi_1\beta, \phi_2\alpha, \phi_2\beta, \ldots \phi_n\alpha, \phi_n\beta)$

$\underline{\chi}$ is $(\chi_1, \chi_2, \chi_3, \ldots \chi_m)$

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† For typographical convenience an underscored letter denotes a matrix

and $\underline{T}$ is an m×n matrix, each column containing the AO coefficients of a given MO.

We then define

$$\underline{R} = \underline{T}\,\underline{T}^{\dagger}$$

$$\underline{P} = 2\,\underline{R}$$

where P is the charge and bond order matrix$^{(4)}$. The orthonormality requirements may then be written

$$\underline{R}^2 = \underline{R} \qquad (12)$$

for then

$$\underline{T}\,\underline{T}^{\dagger}\,\underline{T}\,\underline{T}^{\dagger} = \underline{T}\,\underline{T}^{\dagger}$$

is satisfied when

$$\underline{T}^{\dagger}\,\underline{T} = \underline{1}$$

and it can be shown that (12) is both necessary and sufficient for the existence of a T with this property.

Introducing expression (11) into the expression for the energy (10) we get

$$E = 2 \sum_{p,q} \sum_{i} T_{pi}{}^{*}\, T_{qi} \int \chi_p{}^{*}(1)\, \hat{h}(1)\, \chi_q(1)\, d\tau_1$$
$$+ \sum_{p,q,r,s} \sum_{i,j} T_{pi}{}^{*}\, T_{qj}{}^{*} T_{ri} T_{sj} \big(2(pr|qs)-(ps|qr)\big)$$

where

$$(pr|qs) = \iint \chi_p^*(1)\chi_r(1)\,\frac{1}{r_{12}}\,\chi_q^*(2)\chi_s(2)\;d\tau_1 d\tau_2$$

Now since by definition

$$R_{qp} = \sum_{i=1}^{n} T_{qi}T_{pi}^* \qquad \text{(n occupied orbitals)}$$

then

$$E = 2\sum_{p,q} R_{qp}H_{pq} + \sum_{p,q,r,s} R_{rp}R_{sq}\,\big(2(pr|qs)-(ps|qr)\big)$$

where

$$H_{pq} = \int \chi_p^*(1)\;\hat{h}(1)\;\chi_q(1)\;d\tau_1$$

Now if we define

$$\big(J(R)\big)_{rs} = \sum_{t,u} R_{tu}(rs|ut)$$

$$\big(K(R)\big)_{rs} = \sum_{t,u} R_{tu}(rt|us)$$

then we have

$$E = \sum_{p,q} R_{qp}H_{pq} + \sum_{p,r} R_{rp}\{2\big(J(R)\big)_{pr} - \big(K(R)\big)_{pr}\}$$

or

$$E = 2\;\mathrm{tr}\;\underline{R}\;\underline{H} + \mathrm{tr}\;\underline{R}\;\underline{G} \qquad (13)$$

where

$$\underline{G} = 2\ \underline{J}(\underline{R}) - \underline{K}(\underline{R})$$

Now we must minimise the energy expression (13) by the variation of the matrix $\underline{R}$ subject to the idempotency condition (12). Assume that we have an initial $\underline{R}$ matrix satisfying equation (12) and consider a variation

$$\underline{R} \rightarrow \underline{R} + \underline{\delta R}$$

then to first order

$$E^{(1)} = 2\ \mathrm{tr}\ \underline{\delta R}\ \underline{H} + \mathrm{tr}\ \underline{\delta R}\ \underline{G} + \mathrm{tr}\ \underline{R}\ \underline{\delta G}$$

Now

$$\mathrm{tr}\ \underline{\delta R}\ \underline{G} = \mathrm{tr}\ \underline{R}\ \underline{\delta G}$$

since

$$G_{rs} = \sum_{t,u} R_{tu}\bigl(2(rs|ut) - (rt|us)\bigr)$$

$$\begin{aligned}
\mathrm{tr}\ \underline{R}\ \underline{\delta G} &= \sum_{r,s} R_{sr}\ \delta G_{rs} \\
&= \sum_{r,s}\ \sum_{t,u} R_{rs}\ \delta R_{tu}\bigl(2(rs|ut) - (rt|us)\bigr) \\
&= \sum_{t,u} \delta R_{tu}\ \sum_{s,r} R_{sr}\bigl(2(ut|rs) - (tr|us)\bigr) \\
&= \sum_{t,u} \delta R_{tu}\ G_{ut} \\
&= \mathrm{tr}\ \underline{G}\ \underline{\delta R}
\end{aligned}$$

So

$$E^{(1)} = 2 \text{ tr } \delta\underline{R} \, (\underline{H} + \underline{G}) = 2 \text{ tr } \delta\underline{R} \, \underline{h}^F \qquad (14)$$

where

$$\underline{h}^F = \underline{H} + \underline{G}$$

Now since

$$\underline{R} = \underline{T} \, \underline{T}^{\dagger} = \underline{C}^A \, \underline{C}^{A\dagger} + \underline{C}^B \, \underline{C}^{B\dagger} + \ldots.$$

where

$$\underline{T} = (\underline{C}^A \mid \underline{C}^B \mid \ldots. \mid \underline{C}^N)$$

it follows that

$$\begin{aligned} \text{tr } \underline{R} \, \underline{h}^F &= 2 \sum_x \text{tr } \underline{C}^x \, \underline{C}^{x\dagger} \, \underline{h}^F \\ &= 2 \sum_x \text{tr } \underline{C}^{x\dagger} \, \underline{h}^F \, \underline{C}^x \\ &= 2 \sum_x \varepsilon^x = E_{orb}, \text{ say.} \end{aligned}$$

Here the quantity ε_x is the expectation value for an electron in orbital x of the Hartree-Fock Hamiltonian whose matrix is $\underline{h}^F$, and is called an orbital energy. So to first order the change in energy is equal to the change in the total orbital energy, $E_{orb} = 2 \sum_x \varepsilon^x$:

$$\delta E^{(1)} = \delta E_{orb}$$

Now if we choose the orbitals as eigenvectors of $\underline{h}^F$ we shall automatically minimise E_{orb} by the variation theorem. So the condition for minimum energy $\delta E^{(1)} = 0$ may be satisfied by solving

$$\underline{h}^F \, \underline{C} = E \, \underline{C} \qquad (15)$$

a one-electron eigenvalue problem.

However since $\underline{h}^F$ depends on the elements of $\underline{R}$ and hence on the solutions, an iterative procedure is necessary. An initial $\underline{R}$ satisfying equation (12) is chosen and $\underline{h}^F$ calculated, the eigenvalue problem is then solved and the solutions used to set up a new $\underline{R}$ matrix and so to recalculate $\underline{h}^F$. When the $\underline{R}$ formed from the solutions of the eigenvalue equation differs very little from that used in forming $\underline{h}^F$ then the solution is self-consistent and the procedure is terminated.

The SCGF method for closed shell systems

The SCGF method has been developed by Parks and Parr(5) and McWeeny(6). The derivation of the equations which determine the "best" wave function (in the variational sense) will be outlined below.

Different groups are assumed to be "strong orthogonal" in the sense (using the notation discussed earlier in this chapter)

$$\int \Phi_R{}^*(1,i,j,\ldots)\ \Phi_S(1,k,\ell,\ldots)\ d\tau_1 = 0 \qquad (R{\neq}S) \tag{16}$$

This is true provided

$$\int \phi_\mu^{R*}(1,i,j,\ldots)\phi_\nu^S(1,k,\ell,\ldots)\ d\tau_1 = 0$$

which may be ensured by building different group functions from mutually orthogonal sets of orbitals:

$$\int r_i{}^*(1)s_j(1)\ d\tau_1 = 0 \qquad (r{\neq}s)$$

The total energy using a wave function of the form given in equation (5) can be derived using a procedure similar to that employed in the derivation of the SCF MO equations. The total energy

$$E = \int \Phi^*_{A,B,\ldots} \sum_i \hat{h}(i)\ \Phi_{A,B,\ldots}\ d\tau + \int \Phi^*_{A,B,\ldots}|\tfrac{1}{2} \sum_{i,j}{}'(1/r_{ij})|\Phi_{A,B,\ldots}d\tau$$

can be reduced using the orthogonality condition given in equation (16).

$$E = \sum_R \int \Phi_R{}^*\ \hat{H}_0\ \Phi_R\ d\tau + \tfrac{1}{2} \sum_{R,S}{}'\ (J_{RS}-K_{RS})$$

where

$$\hat{H}_0 = \sum_{i(R)} \hat{h}(i) + \tfrac{1}{2} \sum_{i,j(R)}{}' (1/r_{ij})$$

$$J_{RS} = \int \Phi_R{}^* \Phi_S{}^* \sum_{i(R)} \sum_{j(S)} (1/r_{ij}) \Phi_R \Phi_S \, d\tau$$

$$K_{RS} = \int \Phi_R{}^* \Phi_S{}^* \sum_{i(R)} \sum_{j(S)} (1/r_{ij}) \hat{P}(i\leftrightarrow j) \Phi_R \Phi_S \, d\tau$$

where i(R), for example, refers to summation over variables (i) in group R. $d\tau$ represents integration over all variables and the operator $\hat{P}(i\leftrightarrow j)$ interchanges i and j in the functions succeeding it.

The aim is to obtain a good one-configuration approximation to the molecular ground state by optimising each GF, Φ_R. The best approximation is that which minimises the energy of each group in an effective field provided by the other groups. An effective Hamiltonian for group R in the field of all other groups is given by

$$\hat{H}^R_{eff}(1,2,\ldots N) = \sum_{i(R)} \hat{h}^R_{eff}(i) + \tfrac{1}{2} \sum_{i,j(R)}{}' (1/r_{ij}) \qquad (17)$$

where

$$\hat{h}^R_{eff}(i) = \hat{h}(i) + \sum_{S(\neq R)} \left(\hat{J}^S(i) - \hat{K}^S(i)\right)$$

The coulomb and exchange operators $\hat{J}^R(i)$ and $\hat{K}^R(i)$ are given by

$$\hat{J}^R(i) = \int \Phi_R^*(1,2,..,j,..N_R) \sum_{j(R)} (1/r_{ij}) \Phi_R(1,2,..,j,..N_R)\, d\tau$$

$$\hat{K}^R(i) = \int d\tau\, \Phi_R^*(1,2,..,j,..N_R) \sum_{j(R)} (1/r_{ij}) \Phi_R(1,2,..,i,..N_R) \hat{P}(i\rightarrow j)$$

where $d\tau$ represents integration over all variables except i and the operator $\hat{P}(i\rightarrow j)$ replaces i by j in the functions succeeding it. These operators can be reduced further(7), in terms of the one-electron density matrix for group R, $\rho_1^R(i;j)$:

$$\hat{J}^R(i)\psi(i) = \int \frac{\rho_1^R(j;j)}{r_{ij}}\, d\tau_j\, \psi(i)$$

$$\hat{K}^R(i)\psi(i) = \int d\tau_j\, \frac{\rho_1^R(i;j)}{r_{ij}}\, \psi(j) \qquad \text{(an integral operator)}$$

It can be shown(7) that the condition for stationary total energy is

$$\int \Phi_R^*\, \hat{H}^R_{eff}\, \Phi_R\, d\tau = \text{stationary value},$$

that is the energy of each group in the effective field provided by the other groups is a minimum.

The wave function for the group R is written as a linear combination of basis functions for the electrons of group R as in equation (6).

The basis functions (ϕ_μ^R) to be used will depend on the nature of the group but two cases of special importance serve to illustrate the general procedure. For describing a non-localised π-electron system, it is convenient to employ just one ϕ_μ^R, a one-determinant function whose orbitals are linear combinations of the basis orbitals.

$$\Phi_U = \phi^U = (N_U!)^{-\frac{1}{2}} |\overline{U}_1\alpha \, \overline{U}_1\beta \, \overline{U}_2\alpha \, \overline{U}_2\beta \, \ldots.|$$

In order to discuss bond properties in detail, it is necessary to have a more flexible function. For a bond function constructed from two orbitals we can form three independent singlet functions

$$\begin{aligned} \phi_1^R &= (1/\sqrt{2})|r_1\alpha \; r_1\beta| \\ \phi_2^R &= (1/2) \; \{|r_1\alpha \; r_2\beta|-|r_1\beta \; r_2\alpha|\} \\ \phi_3^R &= (1/\sqrt{2}) \; |r_2\alpha \; r_2\beta| \end{aligned} \qquad (19)$$

If all three are admitted the choice of basis orbitals will be arbitrary. If r_1 and r_2 are AO's at opposite ends of a bond the ϕ_μ^R in (19) will represent "covalent" and "ionic" structures.

Variational determination of the coefficients C_μ^R in equation (6) is carried out by an iterative procedure, adjusting the groups one at a atime. To determine the best group function Φ_R at a given stage, all other group functions being specified at that stage, a linear variational problem with Hamiltonian $\hat{H}^{R}_{eff}$ must be solved. This leads of course to the secular equations for the coefficients

$$\sum_{\mu=1}^{m} C^{R}_{\mu} \left((H^{R}_{eff})_{\mu\nu} - \delta_{\mu\nu} E_{R} \right) = 0 \qquad \nu=1,2,\ldots m$$

The wave function for the other groups enter this equation through the operators $\hat{J}^{S}(i)$ and $\hat{K}^{S}(i)$ in equation (18).

With group functions of the form described above it is easy to write down explicit expressions for the matrix elements of the effective Hamiltonian $(H^{R}_{eff})_{\mu\nu}$.

The GF approach has immediate chemical appeal because it stresses the individuality of different bonds and other chemically recognisable groups. It can transcend the limitations of the Hartree-Fock theory because some measure of correlation is admitted within each electronic group.

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CHAPTER TWO

REVIEW OF PREVIOUS WORK

π-Electron Calculations

A very large number of semi-empirical calculations have been performed on π-electron systems. These systems were treated first for historical reasons and because the calculations were comparatively simple. The bonding in conjugated systems had interested chemists ever since Kekulé. The properties of π-electron systems had been extensively investigated and the characteristic properties of these compounds, such as their stability, reactivity and spectra, were of great interest. The calculations were relatively simple as the π group of electrons were treated separately from other electrons. The π-electrons are treated separately from the σ-electrons, the effects of which may be allowed for (in principle) by the use of an effective Hamiltonian

$$\hat{H}_\pi(1,2,\ldots n_\pi) = \sum_{\mu}^{n_\pi} \hat{H}_{\text{core}}(\mu) + \tfrac{1}{2} \sum_{\mu,\nu}^{n_\pi}{}' (1/r_{\mu\nu}) \qquad (1)$$

This assumption is consistent with the use of a wave function of the form

$$\Psi = \hat{A}(\Psi_\sigma \; \Psi_\pi)$$

where Ψ_σ is an antisymmetric function for the sigma part of the system and Ψ_π is an antisymmetric function describing the pi part. The product function is fully antisymmetrised by the operator $\hat{A}$ (see section on group functions in Chapter 1).

A π-electron wave function Ψ_π is then sought which minimises the π-electron energy

$$E_\pi = \int \Psi_\pi^* \hat{H}_\pi \Psi_\pi \, d\tau \Big| \int \Psi_\pi^* \Psi_\pi d\tau \qquad (2)$$

This minimisation problem has been dealt with using an MO form of Ψ_π in Chapter 1 where the problem was reduced to a set of one-electron equations

$$\underline{h}^F \underline{C} = \varepsilon \underline{C} \qquad (3)$$

These SCF equations for the π group alone are deduced using an orthonormal set of AO's. This is reasonable since it is usually assumed in semi-empirical methods that the π MO's are formed from a linear combination of $2p_\pi$ AO's and that the overlap integrals between AO's are zero.

In Hückel theory equation (1) is not used, but the much simpler form

$$\hat{H}_\pi(1,2,\ldots n_\pi) = \sum_\mu \hat{H}^{eff}(\mu)$$

is employed, where $\hat{H}^{eff}(\mu)$ incorporates the effect of the electron repulsion terms in some average way. As the terms which represent the interaction of electrons are not included explicitly in the Hückel method, an iterative procedure is no longer necessary and the problem is reduced to a set of linear equations. Equation (3) can then be written

$$\sum_q C_{qi} (\hat{H}^{eff}_{pq} - \varepsilon_i) = 0 \qquad (i=1,2,\ldots n_\pi)$$

which has non-trivial solutions when the ε_i are the roots of the secular equation

$$|\hat{H}^{eff}_{pq} - \varepsilon_i| = 0$$

where

$$\hat{H}^{eff}_{pq} = \int \chi_p{}^*(1)\ \hat{H}^{eff}(1)\ \chi_q(1)\ d\tau(1)$$

for the atomic orbitals χ_p and χ_q.

The final assumption of Hückel theory concerns the values of the integrals $\hat{H}^{eff}_{pq}$

$$\hat{H}^{eff}_{pp} = \alpha_p$$

where α_p depends only on the nature of the atom p concerned

$$\hat{H}^{eff}_{pq} = \beta_{pq}$$

where β_{pq} is an empirical property of the bond pq and is zero if p and q are not neighbours.

The total energy is assumed to be equal to the total orbital energies, so that for the closed shell case

$$E_\pi = 2 \sum_i \varepsilon_i$$

The Hückel method has been very successfully applied to a very large number of conjugated systems. It has been very useful in correlating properties such as reactivities, bond lengths and electron distribution, and has the advantage of being very simple to use. Perhaps its biggest practical drawback is the fact that it does not give a reasonable interpretation of spectra, singlet and triplet excited levels not being split. Hückel theory also has the disadvantage that the quantities involved, the Hamiltonian matrix elements, are not exactly defined, and no basis set is actually specified. As McWeeny(1) has pointed out, the Hückel parameters for alternant hydrocarbons are to be compared with the elements of the self-consistent Hartree-Fock Hamiltonian in which the C-C bond orders are given a common average value and the "formal" orders between more distant atoms are neglected. In this case however the total energy and excitation energies cannot be expressed as simple sums and differences of orbital energies, and different values for the Hückel parameters are needed in discussing different properties. In systems containing hetero-atoms the nature of the parameters is even less clear.

In the SCF LCAO MO theory, the Hamiltonian of equation (1) is not approximated, that is the electron repulsion is included explicitly and the SCF equations (3) are solved by the procedure outlined in Chapter 1. Approximations are however made in the calculation of the integrals. The one-electron integrals are approximated in the following way

$$
\begin{aligned}
f_{rr} &= \int \chi_r^* \sum_{\mu} \hat{H}_{core}(\mu)\ \chi_r\ d\tau \\
&= \int \chi_r^* \left| -\tfrac{1}{2}\nabla^2 + V_r + \sum_{s(\neq r)} V_s \right| \chi_r\ d\tau \\
&\simeq \omega_r - \sum_{s(\neq r)} Z_s\ \gamma_{rs} \\
f_{rs} &= \int \chi_r^* \left| -\tfrac{1}{2}\nabla^2 + V_r + V_s + \sum_{t(\neq r,s)} V_t \right| \chi_s\ d\tau \\
&= \beta_{rs}
\end{aligned}
$$

where γ_{rs} is the repulsion integral between $2p_\pi$ type charge clouds on r and s

$$\gamma_{rs} = \int \chi_r^*(1)\ \chi_r(1)\ \frac{1}{r_{12}}\ \chi_s^*(2)\chi_s(2)\ d\tau_1 d\tau_2$$

The framework field V_s due to the framework ion s is approximated by that of a charge Z_s (the number of π-electrons contributed by atom s) smeared out with $2p_\pi$-like density, so that the interaction between a π-electron and this field can be approximated by the electronic repulsion integral between two π-charge clouds. ω_r is roughly minus the ionisation potential from the orbital ϕ_r of atom r in the framework, so that ω_r is approximately a characteristic of the atom r in any conjugated framework. Similarly β_{rs} is expected to be characteristic of the bond r-s.

Early calculations using theoretical values for γ_{rs} did not give very good results. Moffit (1951)$^{(2)}$ and Pariser (1954)$^{(3)}$ proposed that these integrals should be estimated from spectroscopic data. If we consider the following energy change

$$\dot{C} + \dot{C} \rightarrow \ddot{C}^- + \ddot{C}^+$$

where the dots are π-electrons, then the energy change in this theoretical reaction is the energy of the components on the right hand side minus the energy of those on the left.

energy on right hand side = $-2\ I_C$ (valence state ionisation potential)

$+ \gamma_{CC}$

energy on left hand side = $-2\ I_C$

Thus ignoring core energy changes the energy change is γ_{CC}. But the energy needed to perform this reaction is $-I_C$ (to ionise an electron) $+ A_C$ (the electron affinity, for the electron to be received by the neutral carbon atom). So γ_{CC} should be equal to $I_C - A_C$. It was therefore proposed that the theoretical value should be adjusted by setting

$$\gamma_{CC} = I_C - A_C$$

and reducing the other repulsion integrals to roughly maintain relative values.

SCF π theory has been very successful, particularly in explaining the electronic spectra of cyclic hydrocarbons. It has been less successful for heterocyclic compounds, mainly due to the difficulty of deciding on good one-electron parameters. It should be noticed that the explicit introduction of electron repulsion does make the calculations considerably more complicated than Hückel calculations.

Calculations including all electrons

As in π-electron calculations the first sigma electron calculations were of the Hückel type with electron repulsion not treated explicitly. Calculations of this type have been performed by Sandorfy(4), Yoshizumi(5), Fukui et al(6-10), Hoffmann(11-14) and Pople and Santry(15,16).

Sandorfy in 1955 performed extended Hückel calculations on saturated hydrocarbons and their derivatives using three different procedures:

(1) inclusion of only the sp_3 orbitals necessary to describe the carbon skeleton;

(2) implicit inclusion of hydrogen atoms by also including sp_3 hybrids directed towards the hydrogen atoms;

(3) explicit inclusion of 1s orbitals on the hydrogen atoms.

Using method (1) Sandorfy found that the effect of an electron attracting substituent X was mainly to alter the charge in the carbon orbital contributing to the C-X bond. As the orbital charges alternate and there are two orbitals on each atom the small alterations of charge on other atoms are further damped.

Using method (2) he found that almost all the charge pulled on to an electron-attracting substituent X comes from the carbon orbital bonded to it and also from the orbitals directed towards hydrogen on that carbon. He found that the charge on the carbon atoms decreased in the order 1^{ary}, 2^{ary}, 3^{ary}.

In method (3), H orbitals were introduced explicitly for the first time into a semi-empirical calculation.

Sandorfy found it difficult to consider actual substituents realistically as new parameters are needed and it is necessary to find a way of introducing lone pairs. This was probably the first time that any charges and bond orders had been derived for the σ-bonded hydrocarbons and their derivatives.

Also in 1956 Yoshizumi considered hydrocarbons and their derivatives by including only the carbon skeleton of sp_3 orbitals (equivalent to method (1) of Sandorfy). Using the polarisabilities of Coulson and Longuet-Higgins he concluded that effect of a small change in α is limited within the neighbouring bond which is in agreement with Sandorfy's results. He therefore predicted that the value of the dipole moment for C_2H_5X was a limiting one. This tendency was observed for $C\ell$ but not for Br and I. He therefore concluded that in the latter cases the effect of heteroatoms could not be expressed properly by a change in α only, so that this method would not be applicable without modification.

Yoshizumi only treated linear compounds. In 1960 Fukui et al treated linear, branched chain and cyclic compounds by the same carbon skeleton method. As they treated non-linear compounds they had of course to introduce new parameters. They calculated the ionisation potentials of paraffins from the C-C orbitals. For the n-paraffins they obtained good agreement with experiment except in the case of ethane. For cycloparaffins the agreement was not so good, and the greater the deviation of the actual C-C-C angle from the normal one the worse the agreement. They concluded that this was because steric factors had been left out of consideration.

They calculated the total electronic energies and obtained approximately the same total energy per CH_2 group for ethane to n-heptane in accord with experimental data on the heats of formation of these compounds. They neglected nuclear repulsion in this calculation and concluded that discrepancies may have been due to this. This seems extremely unlikely, as the energy per CH_2 group in the above molecules would certainly not be approximately the same if nuclear repulsion had been included. This point will be discussed in more detail later in the chapter when Hoffmann's work is examined.

Fukui et al have also performed calculations including the hydrogen atoms explicitly and using sp_3 hybrids. They have done calculations on the σ-structures of unsaturated compounds and have calculated σ-electron densities and σ dipole moments. From the energy gaps (between the highest occupied and lowest unoccupied orbitals) calculated, they concluded that in most of the molecules the gap was easily large enough to accommodate all the π MO's. In some exceptional cases, for instance chlorobenzene, however, they concluded that it is possible that the lowest vacant σ MO may be below the lowest vacant π MO. This may have an important bearing on the nature of chemical reactions and on physical processes such as polarographic reduction.

It should be noted that it is very dangerous to obtain molecular properties by the addition of separately calculated σ and π molecular properties. Thus accurate SCF LCAO minimal basis calculations on formaldehyde (to be discussed later) predict that the π-electron density is greater on the carbon atom than on the oxygen atom. This is of course contrary to what is usually assumed. Of course the effect of the σ-electrons on the π-electrons should be taken into account in a self-consistent procedure.

One of the dangers of semi-empirical procedures is that we only get from the calculations what we expect. This is illustrated by the case of formaldehyde mentioned above, where the semi-empirical one-electron parameters for carbon and oxygen are so chosen that the oxygen atom will have greater π-electron charge than the carbon atom. This weakness of course can only be overcome by approximate procedures which retain as much as possible of the exact procedures.

Pople and Santry have also performed calculations involving the explicit introduction of hydrogen atoms and using sp_3 hybrids. For saturated hydrocarbons they derived sufficient conditions for a transformation to completely localised orbitals for C-H and C-C bonds and they then used a perturbation approach to study the extent and causes of partial delocalisation of the bonding electrons. They found that long range bond orders, a measure of electron delocalisation, could be quite large and could extend over several bonds. They also applied the method to unsaturated hydrocarbons including both σ and π electrons in contrast to Fukui et al. This perturbation technique does predict that the electronic charge on the hydrogen atom decreases in the series ethane, ethylene and acetylene in agreement with SCF LCAO MO minimal basis calculations and with experimental evidence. It will be seen below that this is not true in Hoffmann's extended Hückel calculations. Like Sandorfy, Yoshizumi and Fukui et al, Pople and Santry used the Longuet-Higgins and Roberts(17) method of estimating off-diagonal Hamiltonian matrix elements

$$H_{ij} = K\, S_{ij}$$

where S_{ij} is the overlap integral between orbitals ϕ_i and ϕ_j.

Hoffmann has performed calculations including hydrogen atoms explicitly and using s and p orbitals rather than sp_3 hybrids. He treated a very large number of organic and inorganic compounds, both saturated and unsaturated, linear and cyclic, homo and hetero. He treated molecules as large as decalin and anthracene.

As Hoffmann treated general polyatomic molecules (not only hydrocarbons) he needed specific values for the diagonal elements of the Hamiltonian matrix elements H_{ii}. The H_{ii} were chosen as valence state ionisation potentials. The off-diagonal matrix elements were calculated using the Wolfsberg-Helmholtz(18) approximation

$$H_{ij} = 0.5K\,(H_{ii}+H_{jj})\,S_{ij}$$

where S_{ij} is the overlap integral between orbitals i and j.

The method predicts the bond distance in methane very accurately when the nuclear repulsion term is excluded from the total energy calculation. If the nuclear repulsion term is included then the minimum disappears completely. We have seen earlier in this chapter that good results have been obtained using the Hückel method and calculating the total energy simply as a sum of orbital or one-electron energies. Slater(19) has pointed out that the sum of the one-electron energies of the Hartree-Fock Hamiltonian is equal to the total energy minus the nuclear-nuclear repulsions, plus the electron-electron repulsions. The last two terms cancel roughly and so the sum of the one-electron energies is approximately equal to the true total energy. The predicted bond distances in acetylene, ethylene and ethane however are less satisfactory and the water molecule is predicted to be linear. The calculations fail to predict any strain energy in small rings and tend to overestimate steric repulsions. This finally leads to incorrect isomerisation energies for pentanes and hexanes. The theory does in general lead to the correct assignment of equilibrium conformation and predicts barriers to rotation in ethane and other molecules, though the barriers are very inaccurate and even their qualitative behaviour from one molecule to another is often wrong. Many of the charges and bond orders for the molecules have been calculated for the first time. Hoffmann is apparently confident of the charge distributions since simple Hückel theory indicates that these are quite insensitive to the choice of parameters. Results to be presented later suggest that the predicted charges should be viewed with some suspicion. Simple Hückel theory only indicates that the charges in alternant hydrocarbons are insensitive to a change of parameters, but this is surely because the charges are mainly dependent on the topology of the molecule. This is not the case for molecules containing heteroatoms and when hydrogen atoms are included explicitly all the calculations become equivalent to such calculations. Thus Hoffmann's charges in the molecules methane, ethane, ethylene and acetylene are not in agreement with the results of exact SCF LCAO MO minimal basis calculations or with experimental evidence. This point is discussed further in Chapter 6.

In π-electron calculations the major step taken after the Hückel method had been introduced was the use of semi-empirical SCF LCAO MO theory. In calculations involving σ- or both σ- and π-electrons the analagous step was taken by Pople, Santry and Segal(20,21).

Pople, Santry and Segal examined the invariance of various approximate SCF procedures under simple transformations of the AO basis set, such as rotation of axes or replacement of s and p orbitals by hybrid orbitals. They believe that it is important that any approximate theory should be independent of choice of axes system as in the full SCF theory. They also believe that the approximate theory should be invariant with respect to the hybridisation of AO's. In order to satisfy these criteria they suggested that the approximate coulomb integrals for p orbitals on centres A and B should be independent of orientation

$$(2p_x^A\ 2p_x^A|2p_x^B\ 2p_x^B) = (2p_y^A\ 2p_y^A|2p_y^B\ 2p_y^B) = (2p_z^A\ 2p_z^A|2p_z^B\ 2p_z^B)$$

but the actual integrals do not of course have this property and the imposition of such equalities represents a dangerous over-simplification. The only real invariance requirement is that all physical properties are invariant against the change of description in which one set of basis orbitals is replaced by a new set, related to the old by a non-singular linear transformation (as for instance in changing the axes with respect to which the p orbitals are defined, or in changing from a non-orthogonal to an orthogonal basis). This does not imply that approximations made in one basis will be equally valid when applied to the corresponding quantities in another basis. In fact the invariance of physical properties would almost certainly require that the approximations should be different. There is no physical law requiring invariance of approximations.

They concluded that there are only two internally consistent approximations to the full SCF equations. These are the use of (i) only (aa|bb) two-centre integrals, that is the complete neglect of differential overlap (CNDO), and (ii) neglect of differential overlap except for two-centre integrals of type (aa'|bb'), where a and a' (or b and b') are orbitals on the same centre, that is neglect of diatomic differential overlap (NDDO). Also if β_{ij} is chosen to be proportional to the overlap integral S_{ij}, then the constant of proportionality must be independent of the type of orbital i or j and only dependent on the nature of the two participating atoms. This criterion is not satisfied by the Wolfsberg-Helmholtz(9) approximation used by Hoffmann. It is satisfied by the Longuet-Higgins and Roberts(17) approximation

$$\beta_{ij} = \beta_{AB} S_{ij}$$

where β_{AB} depends only on the nature of the atoms a and b and i and j are orbitals on centres a and b respectively.

In the CNDO method Pople, Santry and Segal suggest that further approximations have to be made to restore invariance under hybridisation or other local rotations, as discussed above, which is destroyed when CNDO is assumed. It has to be assumed that γ_{ij} depends only on the atoms to which orbitals i and j belong and not on the type of orbitals involved. They assumed that all $\gamma_{\mu_A \nu_B}$ are equivalent irrespective of the nature of the orbitals μ_A and ν_B, and are equal to $\gamma_{2S_A 2S_B}$.

The calculations predict reasonable bond angles though like Hoffmann's extended Hückel calculations they do not predict bond distances reasonably. The charges on the hydrogen atoms in the series methane, ethane, ethylene, acetylene are in agreement with experimental evidence except for the fact that methane and ethane have almost the same charge on the hydrogen. This point will be discussed in more detail in Chapter 6. The theory predicts barriers to rotation in molecules such as ethane and though the absolute values of the barriers are much too low the relative magnitudes in a series of molecules are correct. It was seen earlier that this was not the case with Hoffmann's extended Hückel calculations.

Pople and Segal performed a large number of semi-empirical SCF calculations. The approximations used in π-electron calculations are not necessarily applicable to calculations including σ-electrons.

Thus in σ-electron calculations the CNDO approximation involves the neglect of one and two-centre repulsion integrals of the form (aa'|bb') where a and a', and b and b', are orbitals on the same centre. This is not the case in π theory since there is only one orbital on each centre.

Pople, Santry and Segal appear to require by their invariance procedure described above that the approximations used should be the same regardless of the basis set used. This invariance of approximations does not appear to be essential as it is obvious that CNDO is only a reasonable approximation for an orthogonal basis set and not just for any basis. Thus over a Slater AO basis of s and p orbitals the CNDO approximation would involve the neglect of integrals as large as 0.25 - 0.35 atomic units which would obviously be very unsatisfactory. When these integrals are transformed to a symmetrically orthogonalised hybrid basis they are reduced in value and their neglect becomes more reasonable, though still questionable, since the largest of them, of the form (aa'|aa'), are approximately 0.075 atomic units or 2 electron volts. So in fact even using an orthogonal basis it would appear desirable to retain integrals of the form (aa'|bb'). This point will be discussed in more detail in Chapter 5 where the effect of various approximations is examined.

However in spite of these two objections the method does give reasonable results, as has been seen above, and it is useful to examine why this is so.

Pople and Segal have calculated the one-electron Hamiltonian matrix elements in the following way:

(a) α's are calculated using spectroscopic data and so a reasonable difference between the α's for s and p orbitals on one centre and for α's on different centres are obtained.

(b) β's are calculated by fitting CNDO diatomic calculations with variable β to give results closest to those of the exact minimal basis calculations. In this way the β's are chosen to be reasonably close to the exact values over an orthonormal basis as can be seen in the Tables below giving Pople and Segal's one-electron integrals for water and the exact integrals for the non-orthogonal and orthogonal bases for comparison (the effective Hamiltonian approximation has been used, since Pople and Segal do not include the 1s orbital explicitly).

Pople and Segal's One-Electron Hamiltonian for Water

h_1	h_2	2s	$2p_x$	$2p_y$	$2p_z$
-3.471	-0.124	-0.374	-0.156	-0.203	0
	-3.471	-0.374	-0.156	0.203	0
		-6.313	0	0	0
			-5.715	0	0
				-5.715	0
					-5.715

Exact One-electron Hamiltonian for Water (Non-Orthogonal Basis)

h_1	h_2	2s	$2p_x$	$2p_y$	$2p_z$
-3.9198	-1.7401	-2.8193	-1.1532	-1.3890	0
	-3.9198	-2.8193	-1.1532	1.3890	0
		-5.9154	0	0	0
			-5.3794	0	0
				-5.4434	0
					-5.2878

Exact One-electron Hamiltonian for Water (Symmetrically Orthogonalised Basis)

h_1	h_2	2s	$2p_x$	$2p_y$	$2p_z$
-3.2839	-0.1489	-0.4570	-0.2324	-0.2122	0
	-3.2839	-0.4570	-0.2324	0.2122	0
		-5.7845	0.0932	0	0
			-5.3245	0	0
				-5.4281	0
					-5.2878

It is clear that Pople and Segal's one-electron integrals correspond most closely to the values calculated for an orthogonal basis, for which the CNDO approximation is reasonable. Also their prescription for estimating the one-electron matrix elements by fitting diatomic CNDO to exact calculations compensates to some extent for the errors introduced by the use of the CNDO approximation.

The β values used, which simulate values over an orthogonalised basis, remain reasonable parameters for molecules other than diatomics, as noted by Löwdin(22). Thus for a diatomic with hybrid orbitals on the two centres

$$h_1 = S_1 + \lambda p_{x_1} \qquad h_2 = S_2 - \lambda p_{x_2}$$

the orthogonalised hybrids are (to first order in overlap)

$$\bar{h}_1 \simeq h_1 - \tfrac{1}{2} S\, h_1 \quad \text{and} \quad \bar{h}_2 \simeq h_2 - \tfrac{1}{2} S\, h_2$$

for then

$$S_{\bar{h}_1\bar{h}_2} = S - \tfrac{1}{2}S - \tfrac{1}{2}S = 0$$

(to first order in overlap). So β over the orthogonalised basis is given by

$$\bar{\beta} \simeq \beta - S\,\alpha$$

Now consider the effect of bringing up a point charge. The α term alters by $\int |\phi_1|^2 V \, dv = X$ and the β term by $\int \phi_1^* \phi_2 V \, dv$, that is approximately SX. So we have

$$\alpha \rightarrow \alpha + X$$

$$\beta \rightarrow \beta + SX$$

So

$$\begin{aligned} \bar{\beta} &\simeq \beta + SX - S(\alpha + X) \\ &\simeq \beta - S\alpha \end{aligned}$$

This explains why $\bar{\beta}$ can be taken over from diatomic to polyatomic molecules since to first order it does not alter with external molecular environment.

The success of the Pople Segal calculations is apparently not due to the invariance restrictions but rather is achieved in spite of them. The calculations give reasonable results because they simulate the use of an orthogonal basis, for which the CNDO approximation is reasonable, and they have to some extent allowed for the use of the CNDO approximation, and the more drastic approximation of setting all γ_{AB} equal, by fitting the β values used to give results close to exact diatomic calculations.

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CHAPTER THREE

AIMS AND REVIEW OF PRESENT WORK

In recent years ab initio calculations on diatomic molecules and semi-empirical calculations including all electrons have been performed. These semi-empirical calculations have been described in the previous chapter. They have either not considered electron repulsion explicitly (extended Hückel calculations) or incorporated a large number of approximations and semi-empirical elements. The success of the Parr-Pariser-Pople semi-empirical π-electron theory encourages the study of minimal basis calculations including all electrons with the aim of producing a more complete semi-empirical theory than those which have so far been used. This is the aim of the present study.

With this aim in view, it is first necessary to perform ab initio minimal basis calculations on simple polyatomic systems. Two main methods were used: (i) SCF LCAO MO calculations, and (ii) "group function" calculations in which individual bonds, inner shells, etc. are dealt with as localised units. The computational background is to a large extent common to both methods. Since computational facilities have so far been severely limited, the necessary pilot calculations have employed integrals accurately calculated elsewhere, or else less accurate integrals which may often serve for comparative calculations using the different quantum mechanical methods. When accurate and approximate integrals are both available it has been possible to gain valuable insight into the effects of approximation.

The calculations have been performed with a view to eventually producing a semi-empirical scheme. It is of course obvious that unless a large proportion of the two-electron integrals are neglected the number of parameters becomes completely unwieldy even for the smallest molecules. It is therefore necessary to choose an orbital basis in which most of the two-electron integrals take very small values. It remains to be seen whether or not a basis can be found in which the CNDO, or the less stringent NDDO approximation, gives a reasonable representation of the facts, when there are several AO's on each centre. Experience suggests that such a basis will consist of orthogonal orbitals possessing maximum localisation. The problem of making reasonable integral approximations is inseparable from that of how best to choose a basis in which the orbitals will exhibit orthogonality and a high degree of localisation.

The s,p,d,... orbitals on each centre although orthogonal by symmetry, do not exhibit high localisation; 2s and 2p AO's for example occupy roughly the same region of space and are orthogonal only because of their nodal properties. It is, however, possible to improve the localisation by mixing; for example the four sp^3 hybrids are concentrated mainly in four tetrahedrally disposed regions and are thus not only orthogonal but also substantially "non-overlapping". Various criteria have been devised for defining such orbitals, but in this work suitably chosen hybrids were considered adequate, as well as having strong chemical appeal. Thus in qualitative valence theory chemical bonds are commonly associated with overlapping pairs of hybrids and so by choosing these we retain close contact with the simple pictorial concepts. Hybrids on different centres are not of course orthogonal, those which point towards each other having a particularly large overlap; they may, however, be symmetrically orthogonalised by the Löwdin(1) prescription and then remain as close to the simple hybrids (in the least squares sense(2)) as is permitted by orthogonality.

The following approximations, which are often used in performing semi-empirical calculations, have been examined:

(i) Neglect of 'inner-shell' electrons:

  (a) allowing for inner-shell electrons by replacing the complete one-electron Hamiltonian by an effective Hamiltonian

  (b) replacing the inner-shell electrons by point charges centred at the nuclei.

(ii) Neglect of certain two-electron integrals over an orthogonalised basis set:

  (a) CNDO approximation, the neglect of all but $(\phi_i\phi_i|\phi_j\phi_j)$ integrals

  (b) NDDO approximation, the neglect of all but $(\phi_i\phi_i'|\phi_j\phi_j')$ integrals, where ϕ_i, ϕ_i' (and ϕ_j, ϕ_j') are different orbitals on the same centre.

In Parr-Pariser-Pople π-electron theory the approximation

$$(\phi_i\phi_j|\phi_k\phi_\ell) = \delta_{ij}\,\delta_{k\ell}\,(\phi_i\phi_i|\phi_k\phi_k)$$

is used.

In π-electron calculations there is only one orbital on each centre, but when all electrons are included the situation is different because the charge density $(\phi_i\phi_j)$ may involve different orbitals on the same centre. Approximation (a) would then involve the neglect of most one-centre integrals. For this reason this approximation seems rather too drastic when all electrons are included. So calculations using an NDDO approximation (b) have also been performed and the effects of the two approximations have been compared.

The approximation of integrals by the Mulliken method(3) and by the fitting of Slater orbitals with Gaussian orbitals(4) have also been examined. Experience gained in the use of these approximations and in the use of exact two-electron integrals has then been used in an attempt to produce a much simpler scheme for the approximation of the two-electron integrals over an orthogonalised hybrid basis. This approximation, which has involved the study of the effect of orthogonalisation on the two-electron integrals, has been used in performing a large number of semi-empirical calculations.

All previous approximate SCF schemes have taken all or part of the one-electron Hamiltonian matrix from experimental data. The usual procedure is to take the one-centre parts of the "core" Hamiltonian (for an electron in the presence of a single nucleus and inner shell electrons) from atomic data and to obtain from these a complete framework Hamiltonian by allowing in some way for the attraction of other atomic centres in the molecule. This procedure appears to be unsatisfactory for two reasons:

(a) The one-centre contributions are estimated without ever specifying the basis orbitals. Consequently, it is not clear how the data (referring to free atoms) is related to the quantities appearing in the theory (referring to atoms or ions in a molecular environment).

(b) If one assumes that the empirical one-centre terms refer to orthonormalised AO's (for which the neglect of certain two-electron integrals may be a reasonable approximation) then the addition of "framework corrections" must be over the same basis. This actually involves the calculation of the whole framework Hamiltonian matrix over the non-orthogonal basis (including three-centre parts) and transformation to an orthogonal basis.

In the calculations so far performed, efforts have been made to calculate all <u>one</u>-electron integrals accurately for the reasons discussed above and for the following reasons:

(i) These integrals, unlike the two-electron integrals, are not disturbed by the approximate admission of correlation effects.

(ii) There are not many of these integrals and the problem of calculating them only increases as N^2 as the dimension of the problem, N, increases.

(iii) The only one-electron integrals which do involve a large amount of computing time are the three-centre nuclear attraction integrals. There are closed analytical expressions for all others. However, the three-centre integrals appear to play a large part in determining the final one-electron Hamiltonian over an orthogonalised basis, and errors in them can have a large effect; attempts to estimate them adequately (e.g. by the Mulliken approximation) were unsuccessful. These integrals have therefore been calculated exactly.

(iv) There has been great difficulty in π-electron theory in obtaining one-electron parameters by semi-empirical procedures. A more systematic approach in which such parameters are calculated exactly is now urgently needed.

After obtaining the basic integrals, exact or approximate, the calculation of SCF MO or group function wave functions is completed. Before discussing results, it is useful to comment on some of the computational details involved.

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CHAPTER FOUR

COMPUTATIONAL DETAILS

In order to perform the calculations described, a large number of computer programs have been developed. The integral programs are slanted towards minimal basis calculations involving hydrogen and first row elements. Thus two types of centres can be chosen, 'heavy atoms' and hydrogens. In calculating the diatomic integrals an appropriate 'sigma-pi' orbital set ($2s$, $2p_{\sigma}$, $2p_{\pi}$, $2p_{\bar{\pi}}$, $1s$) is automatically placed on each pair of heavy centres and rotated to a 'standard orbital' set ($2s$, $2p_x$, $2p_y$, $2p_z$, $1s$) defined by the global coordinate system (see diagram below). A 1s orbital is placed on each hydrogen.

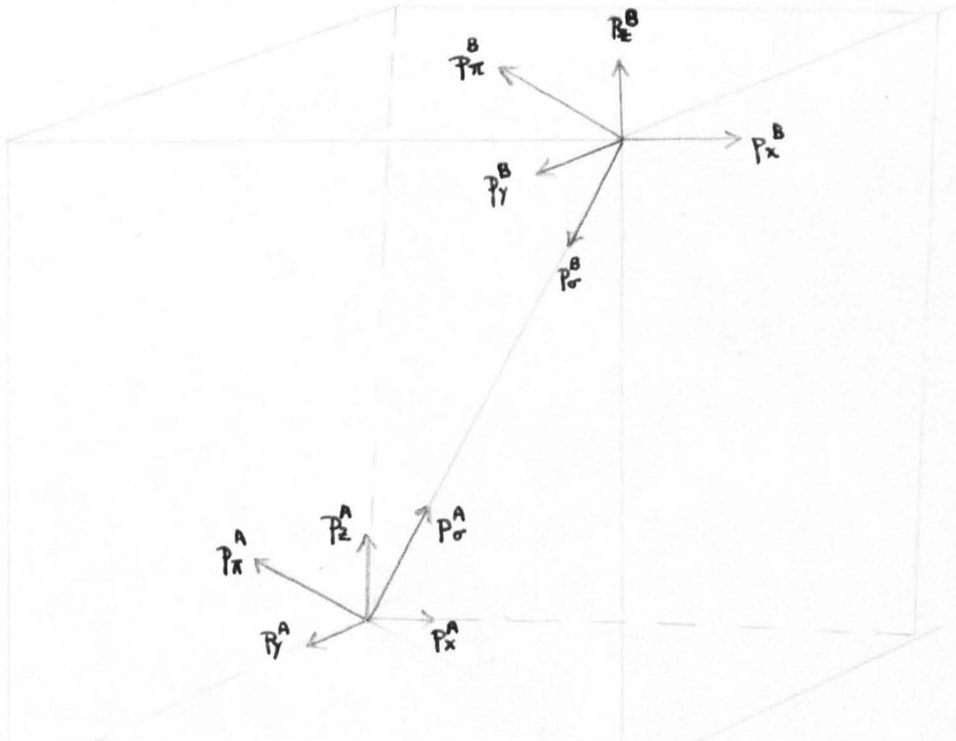
The programs fall into the following parts:

(i) The calculation of the one-electron Hamiltonian integrals

This program calculates the matrix of integrals for the sigma-pi Slater orbital basis on an arbitrary three-dimensional array of centres. Since the integrals are calculated for one pair of centres at a time the problem is split into the evaluation of integrals for a number of diatomic problems. These can easily be calculated by the method of Roothaan(1). The program then transforms to the standard orbital basis or any specified hybrid basis.

Transformation to standard orbital and hybrid basis

In the diagram below, the line AB and the p_z orbitals fix the plane z. p_σ is chosen in the bond direction, p_π perpendicular to AB in plane z and $p_{\bar{\pi}}$ perpendicular to AB and normal to plane z.



If the standard orbitals on centre x are $\underline{\phi}_x = (2s^x, 2p_x^x, 2p_y^x, 2p_z^x, 1s^x)$ and the local rotated orbitals are $\underline{\phi}_x' = (2s^x, 2p_\sigma^x, 2p_\pi^x, 2p_{\bar{\pi}}^x, 1s^x)$, then

$$\underline{\phi}_x' = \underline{\phi}_x \underline{R}$$

where $\underline{R}$ is the matrix of direction cosines of the rotated orbitals with respect to the standard axes. The one-electron integrals in the two bases are then related by (note that $\underline{R}$ is real orthogonal, $\underline{R}^{-1} = \underline{R}^\dagger$)

$$\underline{f}_{AB} = (\underline{\phi}_A^\dagger\, \hat{f}\, \underline{\phi}_B) = \underline{R}_A(\underline{\phi}_A^{\dagger\prime}\, \hat{f}\, \underline{\phi}_B')\underline{R}_B^\dagger = \underline{R}_A\, \underline{f}_{AB}'\, \underline{R}_B^\dagger$$

Considering the p orbitals on centre A as vectors we can determine the 'vectors' of the rotated bases.

(a) $p_\sigma \equiv \vec{AB} \equiv (c_1, c_2, c_3)/R$ (where (c_1, c_2, c_3) are the coordinates of B with respect to A as origin and R is the distance between A and B)

(b) p_π is perpendicular to p_z $(0,0,1)$ and p_σ

$p_\pi \equiv (y_1, y_2, y_3)$

$(p_\pi \cdot p_z) = y_3 = 0$

$(p_\pi \cdot p_\sigma) = y_1 c_1 + y_2 c_2 = 0$

$p_\pi \equiv (\mp c_2, \pm c_1, 0)/A$

(c) $p_{\bar{\pi}} \equiv (z_1, z_2, z_3)$ is perpendicular to p_π and p_σ

$$z_1c_2 - z_2c_1 = 0 \qquad z_1c_1 + z_2c_2 + z_3c_3 = 0$$

$$p_{\bar{\pi}} \equiv (\pm c_1c_3, \pm c_2c_3, \mp(c_1 + c_2))/(AR)$$

where $R = \sqrt{c_1^2 + c_2^2 + c_3^2}$, $A = \sqrt{c_1^2 + c_2^2}$. (The sign convention for p_π and $p_{\bar{\pi}}$ is arbitrary, any choices giving the same final result for the rotation.)

We can then write the specific form of R_A and of R_B which is the same except that p_σ is in the direction of the vector $\vec{BA} = (-c_1, -c_2, -c_3)/R$.

$$R_A = \begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \frac{c_1}{R} & \frac{-c_2}{A} & \frac{-c_1c_3}{AR} & 0 \\ 0 & \frac{c_2}{R} & \frac{c_1}{A} & \frac{-c_2c_3}{AR} & 0 \\ 0 & \frac{c_3}{R} & 0 & \frac{A}{R} & 0 \\ 0 & 0 & 0 & 0 & 1 \end{vmatrix} \qquad R_B = \begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \frac{-c_1}{R} & \frac{-c_2}{A} & \frac{-c_1c_3}{AR} & 0 \\ 0 & \frac{-c_2}{R} & \frac{c_1}{A} & \frac{-c_2c_3}{AR} & 0 \\ 0 & \frac{-c_3}{R} & 0 & \frac{A}{R} & 0 \\ 0 & 0 & 0 & 0 & 1 \end{vmatrix}$$

If B is a hydrogen atom then $\underline{f}_{AB}$ and $\underline{f}_{AB}'$ are 5×1 matrices and

$$\underline{f}_{AB} = \underline{R}_A \, \underline{f}_{AB}'$$

If $\underline{\bar{\Phi}}_x = \underline{\phi}_x \underline{V}_x$ where $\underline{\bar{\Phi}}_x$ is the hybrid basis and $\underline{\phi}_x$ is the standard orbital basis then if A and B are carbon type atoms

$$
\begin{aligned}
\bar{\underline{f}}_{AB} &= (\bar{\underline{\phi}}_A^{\dagger}\ \hat{f}\ \bar{\underline{\phi}}_B) \\
&= \underline{V}_A^{\dagger}\ \underline{f}_{AB}\ \underline{V}_B \\
&= (\underline{V}_A^{\dagger}\ \underline{R}_A)\underline{f}_{AB}'\ (\underline{R}_B^{\dagger}\ \underline{V}_B) \\
&= (\underline{R}_A^{\dagger}\ \underline{V}_A)^{\dagger}\ \underline{f}_{AB}'\ (\underline{R}_B^{\dagger}\ \underline{V}_B)
\end{aligned}
$$

If B is a hydrogen atom then

$$\bar{\underline{f}}_{AB} = (\underline{R}_A^{\dagger}\ \underline{V}_A)^{\dagger}\ \underline{f}_{AB}'$$

Since there are no closed analytical expressions for the three-centre nuclear attraction integrals the program assumes that these have already been calculated. These integrals were at first approximated, but were finally calculated using a three-centre numerical integration program. The method used is to transform each diatomic electron density into elliptical coordinates (ξ, η, ϕ) and to integrate over η and ϕ using the finite-interval Gauss numerical quadrature method and over ξ using the infinite-interval Gauss-Laguerre quadrature.

(ii) <u>The calculation of coulomb type $(ij|g|i'j')$ integrals</u>

As in (i) the integrals over the sigma-pi basis are calculated(1) and are then transformed to a standard orbital basis or any specified hybrid basis. This two-electron transformation will be discussed in detail in section (iv).

(iii) The calculation of the transformation matrix between the standard basis and the set of orthogonalised hybrids

The transformations involved:

(a) Schmidt orthogonalisation.

$$\underline{\phi}_{\text{Schmidt orth.}} = \underline{\phi}\,\underline{W}$$

All valence orbitals on all atoms are orthogonalised to the inner shell 1s orbitals.

This is necessary in order to keep the 1s orbitals uncontaminated by other orbitals. This has been discussed by McWeeny and Ohno(2) and by Klessinger(3). They have found that when the inner shell orbitals are made to mix with the valence orbitals then the resultant loss of inner-shell energy is not compensated by the gain in bonding energy of the outer shells. The best total energy is obtained by Schmidt orthogonalising the valence orbitals to the inner shell orbitals so that they remain unchanged during symmetric orthogonalisation (see section (c)).

The general equation for the Schmidt orthogonalised function ψ_n which is a linear combination of $\phi_1, \phi_2, \ldots \phi_n$ and is orthogonal to $\phi_1, \phi_2, \ldots {}_{n-1}$ is needed:

$$\psi_n = \phi_n + \sum_{i=1}^{n-1} c_i \phi_i$$

$$< \phi_j | \psi_n > = 0 = S_{jn} + \sum_{i=1}^{n-1} c_i S_{ij} \qquad \text{for } j=1,2,\ldots n-1$$

So we have a set of linear equations to be solved

$$\sum_{i=1}^{n-1} c_i S_{ij} = -S_{jn} \qquad \text{for } j=1,2,\ldots n-1$$

or in matrix notation

$$\underline{c}\ \underline{A} = \underline{B} \tag{1}$$

where $\underline{c}$ is a row matrix of dimension n-1, $\underline{A}$ is a square matrix containing the first n-1 rows and columns of $\underline{S}$, the overlap matrix, and $\underline{B}$ is a row matrix containing the first n-1 elements of the nth row of $\underline{S}$. Equation (1) can be solved to obtain the c_i's by any of the standard methods. In this case $\underline{A}^{-1}$ was determined by diagonalising $\underline{A}$ using Jacobi method to get $\underline{A}_{diag}$, taking the reciprocal of the elements of $\underline{A}_{diag}$ and transforming $\underline{A}^{-1}_{diag}$ with the eigenvectors of $\underline{A}$

$$\underline{A}_{diag} = \underline{V}^{\dagger}\ \underline{A}\ \underline{V}$$

$$\underline{A}^{-1} = \underline{V}\ \underline{A}^{-1}_{diag}\ \underline{V}^{\dagger}$$

$$\underline{c} = \underline{B}\ \underline{A}^{-1}$$

(b) Hybridisation

$$\underline{\phi}_{\text{hybrid}} = \underline{\phi}_{\text{Schmidt orth.}} \, \underline{U}$$

Note that U is in general a non-unitary matrix. In most cases hybrids are set up to point along the bonds and the lone pair hybrids are then determined by orthogonalisation requirements. This is not the case in molecules such as formaldehyde where the hybrids are not uniquely defined by the requirement that they point along the bonds (e.g. s,p-mixing at the oxygen atom). In this case sp_2 hybridisation was arbitrarily assumed for the sake of simplicity.

(c) Symmetric orthogonalisation

$$\underline{\bar{\phi}} = \underline{\phi}_{\text{hybrid}} \, \underline{S}^{-\frac{1}{2}}$$

where $\underline{S}$ is the overlap matrix for the hybrid orbitals. It is desirable to keep the orthogonal orbitals as close as possible to the localised hybrid orbitals. This procedure, first proposed for molecules by Löwdin(4), produces the set of orthogonal orbitals(5) closest (in the least squares sense) to the original AO's.

The total transformation is thus

$$\underline{\bar{\phi}} = \underline{\phi}(\underline{WUS}^{-\frac{1}{2}})$$

The program to get $(\underline{WUS}^{-\frac{1}{2}})$ thus involves the calculation of overlap integrals by a program identical in design to that which calculates the one-electron Hamiltonian. It also involves a general Schmidt orthogonalisation procedure and transformation of the overlap integrals to a Schmidt orthogonalised hybrid basis. The square root of the inverse of the overlap matrix is obtained by diagonalising the matrix to get $\underline{S}_{diag}$, taking the reciprocal square root of the elements of $\underline{S}_{diag}$ and transforming $\underline{S}_{diag}^{-\frac{1}{2}}$ with the eigenvectors of $\underline{S}$:

$$\underline{S}_{diag} = \underline{V}^{\dagger}\,\underline{S}\,\underline{V}$$

$$\underline{S}^{-\frac{1}{2}} = \underline{V}\,\underline{S}_{diag}^{-\frac{1}{2}}\,\underline{V}^{\dagger}$$

(iv) The transformation of one- and two-electron integrals

$$(r|\hat{f}|s) = \sum_{i,j} T_{ri}\,T_{sj}\,(i|\hat{f}|j) \qquad *$$

$$(rs|tu) = \sum_{i,j,k,\ell} T_{ri}T_{sj}\,(ij|k\ell)\,T_{tk}T_{u\ell} \tag{2}$$

---

* In this section a transformation of orbital bases is represented by

$$\underline{R} = \underline{T}\,\underline{I}$$

where $\underline{R}$ and $\underline{I}$ are column vectors of orbitals. Previously in this chapter the convention

$$\underline{\tilde{R}} = \underline{\tilde{I}}\,\underline{\tilde{T}}$$

where $\underline{\tilde{R}}$ and $\underline{\tilde{I}}$ are row vectors had been used.

where $\underline{T}$ is the transformation matrix. The method used is to split the sum into smaller parts, thus for the two-electron integrals the steps involved are

$$C_{ij}^{rs} = T_{ri}T_{sj}$$

$$\gamma_{k\ell}^{rs} = \sum_{i,j} C_{ij}^{rs}\,(ij|k\ell) \tag{3}$$

$$(rs|tu) = \sum_{k,\ell} \gamma_{k\ell}^{rs}\, C_{k}^{tu} \tag{4}$$

and for one-electron integrals

$$< r|\hat{f}|s > = \sum_{i,j} C_{ij}^{rs} < i|\hat{f}|j >$$

This procedure reduces the direct evaluation of expression (2), involving N^8 operations, to two processes (3) and (4) involving N^6 operations, N being the number of orbitals. A further reduction is obtained by storing and calculating only the distinct two-electron integrals e.g. $i \geq j$, $k \geq \ell$, $(ij) \geq (k\ell)$. In this way the number of operations is reduced from N^6 to M^3, where M is N(N+1)/2. As only distinct integrals are stored, they are not implicitly labelled by their position in a matrix but are labelled explicitly by storing them together with a label consisting of four integers stored in a decimal word. This labelling technique allows also for the storing of only non-zero integrals or of any subset of integrals which may be required.

If only distinct integrals are used then as each integral is used it must be multiplied by a numerical factor to allow for the non-distinct integrals which are equal to it. The table below gives the various types of distinct integrals for $i \geqq j$, $k \geqq \ell$ and $(ij) \geqq (k\ell)$ and the non-distinct integrals which are equivalent to them.

Integral	Equivalent Integrals
$(ii\|ii)$	
$(ii\|jj)$	$(jj\|ii)$
$(ij\|ij)$	$(ij\|ji)$ $(ji\|ij)$ $(ji\|ji)$
$(ii\|k\ell)$	$(ii\|\ell k)$ $(k\ell\|ii)$ $(\ell k\|ii)$
$(ij\|k\ell)$	$(ij\|\ell k)$ $(ji\|k\ell)$ $(ji\|\ell k)$
	$(k\ell\|ij)$ $(k\ell\|ji)$ $(\ell k\|ij)$ $(\ell k\|ji)$

The use of only distinct integrals can be allowed for by replacing the expression for C_{ij}^{rs} by

$$C_{ij}^{rs} = T_{ri}T_{sj} + (1 - \delta_{ij})\, T_{si}T_{rj}$$

in expression (3), adding into both $\gamma_{k\ell}^{rs}$ and γ_{ij}^{rs} for an integral $(ij|k\ell)$ if $(ij) \neq (k\ell)$ and summing only over $i \geqq j$ in (3) and $k \geqq \ell$ in (4).

The transformation can be performed to get (i) all integrals over the transformed basis; (ii) only $(r_a s_a|t_b u_b)$ integrals over the transformed basis; and (iii) only $(r_a r_a|s_b s_b)$ integrals over the transformed basis; where r_a is an orbital on centre a.

For diatomic coulomb integrals on centres a and b (see section (iii)) this would involve a transformation with matrices of order (10×10). Since blocks of integrals of the general form

$$\text{(i)}\quad (i_a j_a|k_a \ell_a) \qquad\qquad \text{(ii)}\quad (i_a j_a|k_b \ell_b)$$

$$\text{(iii)}\quad (i_b j_b|k_a \ell_a) \qquad\qquad \text{(iv)}\quad (i_b j_b|k_b \ell_b)$$

are calculated separately, they are also transformed separately. So there is a reduction to at most four transformations involving matrices of order (5×5)

$$(r_a s_a|t_b u_b) = \sum_{i,j,k,\ell} T_{ri}^{a}\, T_{sj}^{a}\, (i_a j_a|k_b \ell_b)\, T_{tk}^{b}\, T_{u\ell}^{b}$$

(v) SCF programs

Closed shell SCF MO programs$^{(6,7)}$ involving either the eigenvalue technique or steepest descent procedure have been used. The eigenvalue technique has been modified by the near diagonalisation of the Hartree-Fock Hamiltonian $\underline{H}$ by the eigenvectors $\underline{U}$ obtained in the previous cycle according to

$$\overline{\underline{H}} = \underline{U}^{\dagger} \underline{H} \underline{U}$$

The diagonalisation process is then entered with the near-diagonal $\overline{\underline{H}}$ and initial eigenvectors $\underline{U}$, so diagonalisation is very quick. Also, as the process approaches self-consistency $\overline{\underline{H}}$ becomes more nearly diagonal, so that successive iterations take less and less time.

Closed shell SCGF programs have been used, the method lending itself to calculations on large molecules with a minimum of computational effort. A conventional SCF MO calculation for a system with, say, 50 basis orbitals requires a fairly large computer and (even assuming reasonable convergence of the process) is expensive in computing time. The SCGF calculation, on the other hand, requires only the diagonalisation of one small matrix (in the present case 3×3) for each electron pair, and is a rapidly convergent process. Moreover, besides being relatively small the SCGF computing time is roughly linear in the number of distinct electron groups, while that for an SCF MO calculation is at least cubic in the number of orbitals used. The calculations reported in this work were in fact performed using an IBM 1620 computer, the computing time for the two types of calculation being in the ratio 40:1 for the larger molecules.

Program Testing

The two-electron transformation program can be tested systematically by using various transformation matrices and integral values. The following tests have been made:

(a) All integrals equal to one, transformation matrix is the unit matrix. Obviously all transformed integrals must be one.

(b) All integrals equal to one, all elements of transformation matrix equal to one

$$
\begin{aligned}
(rs|tu) &= \sum_{i,j,k,\ell}^{n} T_{ri}T_{sj}\,(ij|k\ell)\,T_{tk}T_{u\ell} \\
&= \sum_{i,j,k,\ell}^{n} (1) \\
&= n^4
\end{aligned}
$$

Various other tests of the same nature were used. First the elements of the transformation matrix were varied systematically, all integrals having a constant value. Then the integral values were varied, all elements of the transformation matrix having the same value. Finally both the elements of the transformation matrix and the values of the integrals were varied. All these results are easily checked by hand calculation. The tests were completed by recalculating the two-electron integrals for water over an orthogonalised hybrid basis(3).

The one-electron transformation was tested in a similar manner.

Integral programs, however, cannot be tested in such a systematic manner. It has been seen that the integrals (overlap, one-electron Hamiltonian and two-electron coulomb) are calculated for one pair of centres at a time and so the problem is in fact a diatomic problem. The diatomic parts of the various programs have been tested by comparison with the integrals obtained from J. Miller and J.C. Browne's diatomic package(8). Thus the heavy centre-hydrogen parts have been tested using CH, and the heavy centre-heavy centre parts using N_2 and CO. The full one-electron Hamiltonian program including three-centre nuclear attraction integrals was then tested on water and methane and compared with the calculations of Klessinger and McWeeny(3, 9), who have used Barnett-Coulson programs(10).

The various parts of the transformation matrix formation were tested separately. Thus the Schmidt orthogonalisation and the hybridisation matrices can easily be checked by hand. The formation of $\underline{S}^{-\frac{1}{2}}$ was checked by forming the matrix product

$$\underline{S}^{-\frac{1}{2}}\,\underline{S}\,\underline{S}^{-\frac{1}{2}} = 1$$

The programs were then tested by recalculating the transformation matrices used by Klessinger and McWeeny in their water and methane calculations(3, 9).

The least accurate part of the calculation, the three-centre program, gave results agreeing at worst to three decimal places with the test data. This was with a network of (10×10×10) quadrature points over the elliptical coordinate system. The results of the transformation programs, the one-centre and two-centre integral programs and the programs calculating transformation matrices were in agreement to the full number of significant figures (most of the test data was quoted to six decimal places).

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CHAPTER FIVE

PRELIMINARY CALCULATIONS

The approximations discussed in Chapter 3, neglect of inner-shell electrons (i a,b) and neglect of certain two-electron integrals (ii a,b), were investigated using the SCF MO and SCGF methods. The effect of using approximate integrals was then examined. Finally a scheme for the approximation of two-electron integrals over an orthogonalised hybrid basis is proposed. The preliminary calculations have been performed on the water and methane molecules, for which exact integrals were available, over a minimal AO basis, from previous work. These basic integrals have been transformed to an orthogonal hybrid basis.

(1) Exact Integrals

For these calculations a minimal basis of Slater orbitals was employed, the values of the exponents being

carbon	$\zeta(1s) = 5.7$	$\zeta(2s) = \zeta(2p) = 1.625$
oxygen	$\zeta(1s) = 7.7$	$\zeta(2s) = \zeta(2p) = 2.275$
hydrogen	$\zeta(1s) = 1.0$	

For water the bond length was taken to be 1.8103 a.u.

(experimental value) and the bond angle to be 105°. For methane the bond length used was 2.067419 a.u. (experimental value) and the configuration tetrahedral. The construction of the orthonormal basis follows section (iii) of Chapter 4. All valence orbitals were Schmidt orthogonalised against the oxygen 1s orbital. The oxygen s and p orbitals were then hybridised, the bond orbitals set up to point along the bonds and the lone pair hybrids determined by the orthogonalisation requirements. Finally all orbitals were symmetrically orthogonalised.

(a) Water

The results of the calculation are conveniently expressed in terms of the spinless one-electron density matrix P whose elements completely determine the electron density, orbital and overlap populations etc.

The SCF MO total energy and density matrix were obtained for the exact calculation, in close agreement with those of McWeeny and Ohno(1) (Table 1).

The CNDO approximation in which only $(\phi_i\phi_i|\phi_j\phi_j)$ integrals are included led, in the SCF MO calculation, to a reversal of bond polarity, as indicated by the orbital populations, the electrons being drawn towards the hydrogen atoms, and an energy 0.86 a.u.

too high (Table 3), but the NDDO approximation which includes $(\phi_i\phi_{i'}|\phi_j\phi_{j'})$ integrals gave more encouraging results, with the correct polarity and an energy only 0.105 a.u. too high. But there is a loss of bond density and of atom charge from the lone pair orbitals (Table 2). The integrals neglected, using an orthonormalised hybrid basis, are mostly very small, but in view of their large number it is not surprising that the total energy may be substantially affected. This in itself is no cause for concern if the aim is to obtain a reasonable wave function with which to discuss other molecular properties.

The above calculations were also performed using the SCGF method. The results for the exact calculation and the calculations involving the CNDO and NDDO approximations are given in Tables 4 - 6. The exact SCGF calculation gives total electronic energy slightly lower than the SCF MO calculation, as expected since the SCGF method introduces some measure of correlation between electrons in the same group. The results are reasonably close to those of the SCF MO method, though the density of charge on the hydrogen atom is consistently lower. The density matrix elements predicted using the NDDO approximation are again reasonably close to the exact results while the CNDO approximation again leads to a reversal of bond polarity.

The exact SCF MO calculation was modified in that the 1s electrons were not included in the SCF calculation and this 'core' was allowed for by replacing the one-electron Hamiltonian by an effective Hamiltonian h^{eff}, where (using k to denote the 1s orbital)

$$h^{eff}_{ij} = h_{ij} + 2(kk|ij) - (ki|kj)$$

This reduction may be used whenever part of an antisymmetrised product function referring to a number of electrons is regarded as fixed(2). It would seem very reasonable from a chemical viewpoint to fix the 1s electrons. This core approximation gives excellent results, very close to the exact calculation, the valence electron energy being poorer by only 0.001 a.u. and the density matrix in close agreement (Table 7). But all the integrals have still to be calculated and the only saving is in a reduced SCF problem. For this reason the approximation of representing the 1s electrons as simply a point charge at the nucleus was examined.

The point charge calculation differs from the exact SCF MO calculation in that the 1s electrons were replaced by a point charge -2e at the nucleus. This means that the nuclear charge on the oxygen atom was put equal to Z-2. The only integrals which differ from those used in the exact calculation are the one-electron integrals through the alteration of Z_{oxygen} in the nuclear attraction operator. The procedure is the same as the exact calculation except that the 1s electrons are not included in the SCF calculation (or at least only indirectly in that the 2s, h_1, h_2 are Schmidt orthogonalised to the 1s).

The resulting SCF density matrix and total electronic energy are given in Table 8. The use of the point charge approximation has quite a large effect, the energy being poorer by 0.75 a.u., but the main features of the charge density (including the direction of bond polarity) are still reproduced. It is necessary in the complete calculation to Schmidt orthogonalise all orbitals to the 1s orbital before symmetrically orthogonalising. This is because a higher total energy is obtained if the 1s orbital is contaminated by valence shell orbitals. This constraint does not necessarily apply when the 1s electrons are not explicitly considered.

It may be that when the 1s is represented by a point charge, the 2s orbital should be orthogonal to a Dirac delta function at the nucleus since the 1s has been shrunk into this. The Slater 2s orbital is of course already orthogonal in this sense.

So the above calculation was repeated without Schmidt orthogonalising 2s, h, h' to a 1s orbital. The resulting SCF density matrix and total electronic energy are given in Table 9. The total energy is seen to be very low, 2.7 a.u. lower than the exact calculation. A comparison of the orbital energies for the SCF MO calculations (Table 10) for the above runs shows that the lowest orbital energy in this calculation is lower than in the other calculations described above. This could be ascribed to a slight tendency of the lower orbital to 'collapse' into a 1s orbital. It can be looked at from an alternative point of view. The atomic orbital energy of the Slater 2s is less than that of the Slater 2p while that of the Schmidt orthogonalised 2s is about the same as the 2p. So we would expect that the lowest orbital energy would be less when the 2s is not Schmidt orthogonalised than when it is.

Comparing the above calculations, using the point charge approximation, with calculations using approximate integrals (all non-coulombic two-electron and three-centre one-electron integrals approximated) (Tables 17 and 18 (section (2)) we see that the point charge approximation produces erors of the same order of magnitude as those produced by approximating integrals by the Gaussian fitting procedure.

(b) Methane

SCF MO and SCGF calculations have been performed using all two-electron integrals over an orthogonalised hybrid basis, and also using the NDDO and CNDO approximations. The SCF MO results are given in Tables 11 -13 and the SCGF results in Tables 14 - 16.

The exact SCGF energy is again slightly lower than the SCF MO energy. As in water the use of the CNDO approximation and exact integrals leads to a reversal of the bond polarity compared with the exact calculation. The results using the NDDO approximation are much closer to the exact results, predicting the correct bond polarity. The conclusions apply equally to both the SCF MO and the SCGF calculations, the CNDO approximation showing similar deficiencies in both cases.

(2) Use of Integral Approximations

On a small computer it is possible to calculate exactly at most all the two-centre integrals of the type $(ii'|jj')$; the rest must be approximated. Even with larger computers a similar point is soon reached as molecular size is increased. Calculations on water and methane have therefore been repeated with both Gaussian and Mulliken-type approximation of the many-centre integrals. The three-centre nuclear attraction integrals have also been approximated, though these have been calculated exactly by numerical integration in later calculations.

(a) Gaussian Approximation

The integrals were approximated by expanding the Slater orbitals in terms of Gaussian orbitals(4) (one Gaussian for each p type and two for each s type Slater orbital). The integrals over the Gaussian orbitals are available from a modification of the MIT Polyatom program (adapted for a small computer).

The results for methane (Table 17) were encouraging as the charge and bond orders do not differ as much from those obtained in the exact SCF calculation as these do from those obtained in the group function calculation(3) (section (1)). The results for water (Table 18) were unfortunately not as good as this, though the differences between this calculation and the exact SCF calculation are not as great as those produced by the use of the point charge approximation (section (1)). However if both the Gaussian approximation and the point charge approximation are used then the results are much worse (Table 19), the bonds being hardly polar. It can be seen that the errors are in this case to some extent additive.

An attempt was made to improve the approximation of the two-electron integrals over the hybrid basis. The procedure used was to rescale the charge clouds

$$(i,j) = (i,j)\,\bar{S}_{ij}$$

where

$$\bar{S}_{ij} = (S_{ij})_{\text{SLATER}} \;/\; (S_{ij})_{\text{GAUSSIAN APPROXIMATION}}$$

It was hoped that this factor, a measure of the error in approximating the overlap density,would partially compensate for the errors involved in the calculation of the two-electron integrals. This procedure did not give substantially better results and in the water calculation had the undesirable effect of producing a larger draining away of charge from the lone pair orbitals.

The calculations have been repeated using the NDDO approximation which includes only $(ii'|jj')$ integrals over the orthogonalised hybrid basis. The changes produced by the use of this approximation are similar to the changes produced by its use in the exact calculation (Tables 20 and 21).

(b) Mulliken Approximation

The integrals were approximated by the Mulliken method(5)

$$(i,j) = \frac{S_{ij}}{2}\,(i^2 + j^2)$$

where

$$S_{ij} = \int i^*(1)\, j(1)\, d\tau_1$$

This method allows any two-electron integral to be approximated by a combination of coulomb integrals which are used in the calculation. For this reason the approximation is relatively simple to use. The integrals were approximated over a hybrid basis.

The Mulliken method involves the approximation of a smaller number of integrals than the Gaussian method but the results are not so good as will be seen below. If the aim is to extend the procedure to larger molecules in a semi-empirical manner then the number of two-electron integrals soon becomes unwieldy unless it is reasonable to neglect many of them. But as concluded previously, the neglect of two-electron integrals is only reasonable if an orthogonal basis is used. For this reason the integrals have been transformed even though this is not a necessity with the systematic use of the Mulliken approximation.

The approximated integrals for water are compared with the exact integrals and the Gaussian approximated integrals, for the hybrid basis in Table 22 and for the orthogonalised hybrid basis (i.e. after transformation of the integrals for non-orthogonal hybrids to symmetrically orthogonalised hybrids) in Table 23.

For the larger integrals, the Mulliken approximation is not as good as the Gaussian approximation, but still gives some estimate of the magnitude. It does not, however, give a reasonable estimate of the smaller integrals.

The results for water and methane are given in Tables 24 and 25. The results for water are far worse than those obtained using the Gaussian approximation. The results for methane, however, are almost as good as the Gaussian results and are very close to the exact SCF results. As in the Gaussian calculation this is presumably due to the very high symmetry of the molecule.

The calculations were repeated using only (aa'|bb') two-electron integrals over the orthogonal hybrid basis. The results were similar to the above calculation for the water molecule (Table 26) but were very different for methane (Table 27). The methane results are now very far from the exact SCF results. This did not happen in the exact calculation or the Gaussian calculation when only (aa'|bb') integrals were used, so it appears that it may be necessary to use all two-electron integrals when using the Mulliken approximation.

As stated above, the calculations were performed by approximating the non-coulombic integrals over a hybrid basis. A calculation was also performed for methane by approximating the non-coulombic integrals over a basis of s and p orbitals and then transforming to an orthogonal hybrid basis. In this case the results were far worse. Even the (aa|bb) two-electron integrals over the orthogonal hybrid basis were nowhere near the exact values as can be seen from the table below.

Integral	Exact Value (over orthogonal hybrid basis)	Mulliken Approximation	
		hybrid basis	s & p basis
$h_1h_1h_1h_1$	0.6943	0.7155	0.9121
$h_2h_2h_1h_1$	0.2432	0.2491	0.1706
$b_1b_1h_1h_1$	0.4791	0.5377	0.8328
$b_1b_1h_2h_2$	0.3441	0.3346	0.2023
$b_1b_1b_1b_1$	0.7726	0.8501	1.1915
$b_2b_2b_1b_1$	0.6825	0.5842	0.4176
$k\ k\ h_1h_1$	0.3986	0.3855	0.3855
$k\ k\ b_1b_1$	0.9101	0.8820	0.8820

(3) Semi-Empirical Adjustment of Integrals

The use of the Gaussian approximation takes a prohibitively long time for large molecules (unless a large computer is available), as it involves the calculation of a large number of integrals over the Gaussian basis, this being larger than the minimal basis set, followed by a large two-electron transformation. Even the Mulliken approximation, which involves the approximation of a smaller number of integrals and a smaller two-electron transformation, soon becomes unwieldy. It would not be feasible therefore to do calculations on larger molecules using these approximations. For this reason an attempt was made to produce a simpler scheme for approximating two-electron integrals over an orthogonalised hybrid basis directly. Also in π-electron theory the semi-empirical estimation of the two-electron integrals has played a larger part in its success.

In order to study the effect of estimating the two-electron integrals directly, other approximations have been excluded. Thus the one-electron Hamiltonian over the orthogonalised hybrid basis has been calculated exactly, the inner shell electrons have been included explicitly and not implicitly by the use of the core approximation or point charge procedure. The core approximation has been seen to be very accurate (section (1)). But since many of the terms in it were approximated or neglected completely a study of whether this approximation can be used to reduce the problem without making substantial differences to the results was left until later.

It can be seen from the results given in section (1) that the use of exact two-electron integrals over an orthogonalised hybrid basis together with the CNDO scheme does not reproduce the electron density pattern of the full calculation at all well. In both methane and water the bond polarities, indicated by the difference of populations of the hydrogen and bonding hybrid orbitals, are the opposite of those obtained from the full calculation. The results using exact two-electron integrals over an orthogonalised hybrid basis but with the NDDO approximation are much more encouraging. The electron density is much closer to that of the full non-empirical calculations and the bond polarities agree rather well, in both direction and magnitude, with those from the full calculations. Results for formaldehyde using exact integrals given in Chapter 6 (Tables 8, 10 and 11) also suggest that the CNDO is not really satisfactory. Thus in the SCF MO calculations the use of the CNDO approximation produces a very large bond order between the two hydrogen atoms (0.464) and a π group very highly polarised towards the carbon atom. The use of the NDDO approximation does not produce this large bond order between the hydrogen atoms or the very highly polarised π group.

The above results appear to show that CNDO is not a good approximation, even when used to simulate the properties of exact integrals over an orthogonal basis. It does not therefore seem to provide a suitable foundation for a satisfactory semi-empirical scheme. It is clear that in the above examples the one-centre exchange integrals play a crucial role in determining the electron distribution in the molecule, even to the extent of determining polarities of bonds. The general conclusion from this series of calculations is that the NDDO scheme is quite accurately valid as a means of simulating the results of calculations employing a basis of symmetrically orthogonalised hybrid orbitals. The use of this scheme appears to yield reliable molecular wave functions in the examples given above.

The integrals that are retained are in one-one correspondence with those for which closed expressions are available in the non-orthogonal case, namely those which represent the coulomb interaction between monocentric charge distributions. Unfortunately, however, they are related through the equation

$$(\bar{i}\ \bar{i}'|\bar{j}\ \bar{j}') = \sum_{r,s,t,u} T_{ri}{}^{*}\ T_{sj}{}^{*}\ (rs|tu)\ T_{tk}\ T_{u\ell}$$

to the full set of integrals over the non-orthogonal basis and not just to the integrals representing coulomb interactions between monocentric charge distributions. To make progress towards a semi-empirical theory it is therefore necessary to have a simple prescription for obtaining good approximate values of the NDDO integrals. To this end the exact integrals over the non-orthogonal and orthogonal hybrid bases were compared for the water and methane molecules (Table 28). A definite pattern was seen to emerge; the general effect of orthogonalisation can be summed up as follows:

(a) One-centre integrals of the form $(i^A i^A|j^A j^A)$ (where i^A is an orbital on centre A) are increased by 9 - 14% except where $i^A = k, \pi, \ell$ and $j^A = k, \pi$ or ℓ (where k, π, ℓ are used to denote 1s, π and lone pair orbitals respectively). One-centre integrals of the form $(i^A j^A|k^A \ell^A)$ are also increased, though the percentage increases are more variable. These integrals, however, are not so important as those of the

$(i^A i^A | j^A j^A)$ type, having smaller values.

(b) Two-centre integrals of the form $(i^A i^A | j^B j^B)$ are decreased by 9 - 14% when A and B are near neighbours, except when $i^A = k$, π or ℓ and $j^B = k$, π or ℓ. Two-centre integrals of the form $(i^A j^A | k^B \ell^B)$ are also decreased but again are not so important as they have relatively small values.

(c) Integrals which are not of the $(i^A j^A | k^B \ell^B)$ form assume negligible values.

These conclusions can be understood easily in a qualitative manner. At first sight, it might appear that the orthogonalised orbitals are less well localised than the free atom AO's since they contain parts from orbitals on all the centres. Thus to first order in overlap:

$$\bar{i} \simeq i - \tfrac{1}{2} \sum_{j(\neq i)} j\, S_{ji}$$

and $\bar{i}$ therefore contains in general a negative cusp on neighbouring nuclei. McWeeny$^{(6)}$ has pointed out however that the cusps occupy a very small part of space and that the main effect of orthogonalisation is to compress each AO more tightly about its nucleus by "cancelling out" its outer parts and then renormalising.

This increase in concentration of charge explains the increase in value of the repulsion between two charge clouds both on the same centre i.e. the increase in integrals of the form $(i^A j^A | k^A \ell^A)$. It also explains the decrease in the mutual repulsion between two monocentric charge clouds on different centres i.e. the decrease in integrals of the form $(i^A j^A | k^B \ell^B)$.

So the general effect of symmetric orthogonalisation can be simulated by increasing the $(i^A i^A | j^A j^A)$ integrals and decreasing the $(i^A i^A | j^B j^B)$ integrals by approximately 12% and estimating all other $(i^A j^A | k^B \ell^B)$ integrals by their non-orthogonal values. Though this will lead to errors of up to 5% in the larger of the estimated integrals it is hoped that this will be accurate enough to predict the change of properties in a series of molecules.

As a first test of the method calculations were performed on methane using the exact one-electron Hamiltonian and estimating the two-electron integrals by the procedure described above. The results are given in Tables 29 (SCF MO) and 30 (SCGF) and comparison with the exact results (Tables 11 and 14) shows that the predicted density matrix is quite close to that predicted by the exact calculations. The atom densities are in fact closer to the exact results than are the atom densities predicted by the use of exact integrals and the NDDO approximation. This is of course just chance, since the results should really be compared with those of the calculation using exact integrals and the NDDO approximation. The calculation was repeated exactly as above but the smaller two-electron integrals of the $(i^A j^A|k^B \ell^B)$ type were estimated by their non-orthogonal values increased or reduced by 12%. The results were very close to those of the above calculation and so the calculatins described in the next chapter were done using the simpler procedure.

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CHAPTER FIVE

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TABLE 1

WATER. Exact integrals over orthonormal hybrid basis, full calculation. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{l}_1$	$\bar{l}_2$	k
0.884	-0.024	0.992	-0.003	-0.026	-0.026	-0.007
	0.884	-0.003	0.992	-0.026	-0.026	-0.007
		1.116	0.025	0.024	0.024	0.006
			1.116	0.024	0.024	0.006
$E = -84.84$ a.u.				2.000	-0.001	0.000
$N_H = 0.884$					2.000	0.000
$N_O = 8.232$						2.000

TABLE 2

WATER. Exact integrals over orthonormal hybrid basis and NDDO approximation. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{l}_1$	$\bar{l}_2$	k
0.893	-0.172	0.948	-0.050	0.172	0.172	-0.008
	0.893	-0.050	0.948	0.172	0.172	-0.008
		1.154	0.218	-0.120	-0.120	0.005
			1.154	-0.120	-0.120	0.005
$E = -84.74$ a.u.				1.954	-0.046	0.002
$N_H = 0.893$					1.954	0.002
$N_O = 8.308$						2.000

TABLE 3

WATER. Exact integrals over orthonormal hybrid basis and CNDO approximation. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\ell}_1$	$\bar{\ell}_2$	k
1.095	-0.308	0.914	-0.001	0.172	0.172	0.010
	1.095	-0.001	0.914	0.172	0.172	0.010
		0.954	0.358	-0.170	-0.170	-0.008
			0.954	-0.170	-0.170	-0.008
E = -83.98 au				1.950	0.050	-0.003
N_H = 1.095					1.950	-0.003
N_O = 7.908						2.000

TABLE 4

WATER. Exact integrals over orthonormal hybrid basis full calculation. SCCF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\ell}_1$	$\bar{\ell}_2$	k
0.850	0.000	0.972	0.000	0.000	0.000	0.000
	0.850	0.000	0.972	0.000	0.000	0.000
		1.150	0.000	0.000	0.000	0.000
			1.150	0.000	0.000	0.000
E = -84.88 a.u.				2.000	0.000	0.000
N_H = 0.850					2.000	0.000
N_O = 8.300						2.000

TABLE 5

WATER. Exact integrals over orthonormal hybrid basis and NDDO approximation. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{l}_1$	$\bar{l}_2$	k
0.881	0.000	0.971	0.000	0.000	0.000	0.000
	0.881	0.000	0.971	0.000	0.000	0.000
		1.119	0.000	0.000	0.000	0.000
			1.119	0.000	0.000	0.000
E = -84.69 a.u.				2.000	0.000	0.000
N_H = 0.881					2.000	0.000
N_O = 8.238						2.000

TABLE 6

WATER. Exact integrals over orthonormal hybrid basis and CNDO approximation. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{l}_1$	$\bar{l}_2$	k
1.040	0.000	0.976	0.000	0.000	0.000	0.000
	1.040	0.000	0.976	0.000	0.000	0.000
		0.960	0.000	0.000	0.000	0.000
			0.960	0.000	0.000	0.000
E = -83.93 a.u.				2.000	0.000	0.000
N_H = 1.040					2.000	0.000
N_O = 7.920						2.000

TABLE 7

WATER. Exact integrals over orthonormal hybrid basis and core approximation. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\ell}_1$	$\bar{\ell}_2$
0.884	-0.024	0.992	-0.004	-0.028	-0.028
	0.884	-0.004	0.992	-0.028	-0.028
		1.117	0.025	0.025	0.025
			1.117	0.025	0.025
				1.999	-0.001
					1.999

$E = -84.83$ a.u.

$N_H = 0.884$

$N_O = 6.234$

TABLE 8

WATER. Exact integrals over orthonormal hybrid basis and point charge approximation. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\ell}_1$	$\bar{\ell}_2$
0.955	0.004	0.983	-0.016	0.126	0.126
	0.955	-0.016	0.983	0.126	0.126
		1.076	0.026	-0.117	-0.117
			1.076	-0.117	-0.117
				1.999	-0.030
					1.999

$E = -84.09$ a.u.

$N_H = 0.955$

$N_O = 6.152$

TABLE 9

WATER. Exact integrals over orthonormal hybrid basis and point charge approximation. (No Schmidt orthogonalisation to 1s orbital.) SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{l}_1$	$\bar{l}_2$
0.945	0.074	0.938	-0.054	-0.133	-0.133
	0.945	-0.054	0.938	-0.133	-0.133
		1.165	0.037	0.210	0.210
			1.165	0.210	0.210
				1.889	-0.111
					1.889

$E = -87.01$ a.u.

$N_H = 0.945$

$N_O = 6.108$

TABLE 10

ORBITAL ENERGIES (OF THE SCF MO CALCULATIONS)

Exact Calculation	Effective Hamiltonian	Point Charge Approx.		(aa'|bb') Integrals only
		Schmidt Orth.	No Schmidt Orth.	
-20.501				-20.377
-1.298	-1.301	-1.805	-2.440	-1.511
-0.635	-0.636	-0.644	-0.629	-0.452
-0.470	-0.469	-0.423	-0.529	-0.438
-0.420	-0.420	-0.408	-0.435	-0.421
0.391	0.391	0.506	0.316	0.356
0.605	0.606	0.631	0.605	0.629

TABLE 11

METHANE. Exact integrals over orthonormal hybrid basis complete calculation. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{t}_1$	$\bar{t}_2$	$\bar{t}_3$	$\bar{t}_4$	$\bar{k}$
0.915	0.024	0.024	0.024	0.996	0.001	0.001	0.001	-0.008
	0.915	0.024	0.024	0.001	0.996	0.001	0.001	-0.008
		0.915	0.024	0.001	0.001	0.996	0.001	-0.008
			0.915	0.001	0.001	0.001	0.996	-0.008
				1.085	-0.024	-0.024	-0.024	0.008
					1.085	-0.024	-0.024	0.008
						1.085	-0.024	0.008
							1.085	0.008
								2.000

$E = -53.45$ a.u.

$N_H = 0.915$

$N_C = 6.340$

TABLE 12

METHANE. Exact integrals over orthonormal hybrid basis and NDDO approximation. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{t}_1$	$\bar{t}_2$	$\bar{t}_3$	$\bar{t}_4$	$\bar{k}$
0.975	-0.035	-0.035	-0.035	0.998	-0.002	-0.002	-0.002	-0.008
	0.975	-0.035	-0.035	-0.002	0.998	-0.002	-0.002	-0.008
		0.975	-0.035	-0.002	-0.002	0.998	-0.002	-0.008
			0.975	-0.002	-0.002	-0.002	0.998	-0.008
				1.025	0.035	0.035	0.035	0.007
					1.025	0.035	0.035	0.007
						1.025	0.035	0.007
							1.025	0.007
								1.999

$E = -52.71$ a.u.

$N_H = 0.975$

$N_C = 6.100$

TABLE 13

METHANE. Exact integrals over orthonormal hybrid basis and CNDO approximation. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{t}_1$	$\bar{t}_2$	$\bar{t}_3$	$\bar{t}_4$	$\bar{k}$
1.101	-0.065	-0.065	-0.065	0.988	0.002	0.002	0.002	0.013
	1.101	-0.065	-0.065	0.002	0.988	0.002	0.002	0.013
		1.101	-0.065	0.002	0.002	0.988	0.002	0.013
			1.101	0.002	0.002	0.002	0.988	0.013
				0.899	0.065	0.065	0.065	0.002
					0.899	0.065	0.065	0.002
						0.899	0.065	0.002
							0.899	0.002
								2.000

$E = -52.38$ a.u.

$N_H = 1.101$

$N_C = 5.798$

TABLE 14

METHANE. Exact integrals over orthonormal hybrid basis, complete calculation. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{t}_1$	$\bar{t}_2$	$\bar{t}_3$	$\bar{t}_4$	$\bar{k}$
0.921	0.000	0.000	0.000	0.983	0.000	0.000	0.000	0.000
	0.921	0.000	0.000	0.000	0.983	0.000	0.000	0.000
		0.921	0.000	0.000	0.000	0.983	0.000	0.000
			0.921	0.000	0.000	0.000	0.983	0.000
				0.921	0.000	0.000	0.000	0.000
					1.079	0.000	0.000	0.000
						1.079	0.000	0.000
							1.079	0.000
								2.000

$E = -53.48$ a.u.

$N_H = 0.921$

$N_C = 6.316$

TABLE 15

METHANE. Exact integrals over orthonormal hybrid basis and NDDO approximation. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{t}_1$	$\bar{t}_2$	$\bar{t}_3$	$\bar{t}_4$	$\bar{k}$
0.954	0	0	0	0.972	0	0	0	0
	0.954	0	0	0	0.972	0	0	0
		0.954	0	0	0	0.972	0	0
			0.954	0	0	0	0.972	0
				1.046	0	0	0	0
					1.046	0	0	0
						1.046	0	0
							1.046	0
								2.000

$E = -52.76$ a.u.

$N_H = 0.954$

$N_C = 6.184$

TABLE 16

METHANE. Exact integrals over orthonormal hybrid basis and CNDO approximation. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{t}_1$	$\bar{t}_2$	$\bar{t}_3$	$\bar{t}_4$	$\bar{k}$
1.056	0	0	0	0.972	0	0	0	0
	1.056	0	0	0	0.972	0	0	0
		1.056	0	0	0	0.972	0	0
			1.056	0	0	0	0.972	0
				0.944	0	0	0	0
					0.944	0	0	0
						0.944	0	0
							0.944	0
								2.000

$E = -52.41$ a.u.

$N_H = 1.056$

$N_C = 5.776$

TABLE 17

METHANE. Gaussian approximation of integrals. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{b}_1$	$\bar{b}_2$	$\bar{b}_3$	$\bar{b}_4$	$\bar{k}$
0.902	0.085	0.085	0.085	0.984	0.001	0.001	0.001	0.000
	0.902	0.085	0.085	0.001	0.984	0.001	0.001	0.000
		0.902	0.085	0.001	0.001	0.984	0.001	0.000
			0.902	0.001	0.001	0.001	0.984	0.000
				1.098	-.085	-.085	-.085	0.000
					1.098	-.085	-.085	0.000
						1.098	-.085	0.000
							1.098	0.000
								2.000

$E = -53.70$ a.u.

$N_H = 0.902$

$N_C = 6.392$

TABLE 18

WATER. Gaussian approximation of integrals. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{l}_1$	$\bar{l}_2$	$\bar{k}$
0.931	-0.034	0.986	-0.009	-0.106	-0.106	0
	0.931	-0.009	0.986	-0.106	-0.106	0
		1.091	-0.012	0.100	0.100	0
			1.091	0.100	0.100	0
				1.978	-0.021	0
					1.978	0
						2.000

$E = -85.44$ a.u.
$N_H = 0.931$
$N_C = 8.138$

TABLE 19

WATER. Gaussian and point charge approximations. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{l}_1$	$\bar{l}_2$
1.009	0.076	0.984	-0.014	00.115	0.115
	1.009	-0.014	0.984	0.115	0.115
		1.020	-0.047	-0.122	-0.122
			1.020	-0.122	-0.122
				1.971	-0.029
					1.971

$E = -84.69$ a.u.

$N_H = 1.009$

$N_O = 5.982$

TABLE 20

METHANE. Gaussian and NDDO approximations. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{b}_1$	$\bar{b}_2$	$\bar{b}_3$	$\bar{b}_4$	$\bar{k}$
0.927	-0.025	-0.025	-0.025	0.996	-0.003	-0.003	-0.003	-0.009
	0.927	-0.025	-0.025	-0.003	0.996	-0.003	-0.003	-0.009
		0.927	-0.025	-0.003	-0.003	0.996	-0.003	-0.009
			0.927	-0.003	-0.003	-0.003	0.996	-0.009
				1.074	0.025	0.025	0.025	0.008
					1.074	0.025	0.025	0.008
						1.074	0.025	0.008
							1.074	0.008
								2.000

$E = -52.62$ a.u.

$N_H = 0.927$

$N_C = 6.296$

TABLE 21

WATER. Gaussian and NDDO approximations. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{l}_1$	$\bar{l}_2$	$\bar{k}$
0.899	-0.133	0.942	-0.049	0.150	0.150	-0.007
	0.899	-0.049	0.942	0.150	0.150	-0.007
		1.135	0.267	-0.100	-0.100	0.005
			1.135	-0.100	-0.100	0.005
				1.966	-0.034	0.002
					1.966	0.002
						2.000

$E = -84.22$ a.u.

$N_H = 0.899$

$N_O = 8.202$

TABLE 22

WATER NON-COULOMB INTEGRALS OVER HYBRID BASIS

Integral	Exact Value	Gaussian Approx. & % Error		Mulliken Approx. & % Error	
$h_2h_1h_1h_1$	.1757	.1717	- 2	.1791	2
$h_2h_1h_2h_1$	.0685	.0661	- 3½	.0671	- 2
$b_1h_1h_1h_1$	.3617	.3267	-10	.3288	-12
$b_1h_1h_2h_1$	.1117	.1016	- 9	.1012	- 9
$b_1h_1h_2h_2$	.2111	.1961	- 7	.2108	0
$b_1h_1b_1h_1$	.2502	.2217	-11	.2035	-18½
$b_1h_2h_1h_1$	.1064	.1076	1	.0694	-35
$b_1h_2h_2h_1$	.0373	.0382	3	.0281	-25
$b_1h_2h_2h_2$	.0702	.0763	9	.0807	15
$b_1h_2b_1h_1$	.0814	.0795	- 2	.0477	-40
$b_1h_2b_1h_2$	.0354	.0367	3½	.0141	-60
$b_1b_1h_2h_1$	.2122	.2113	- 1½	.1950	- 9
$b_1b_1b_1h_1$	.4545	.4396	- 4	.4237	- 6½
$b_1b_1b_1h_2$	.1465	.1539	5	.1071	-17
$b_2h_1b_1h_1$	.0485	.0484	0	.0496	2
$b_2h_1b_1h_2$	.0210	.0225	8	.0129	-40
$b_2h_1b_1b_1$	.1055	.1112	5	.1028	2½
$b_2h_2b_1h_1$	.1428	.1250	-12	.1465	1
$b_2h_2b_1b_1$	.3252	.3070	- 6	.3310	2
$b_2b_1h_2h_1$	.0148	.0156	5	.0097	-35
$b_2b_1b_1h_1$	.0265	.0260	- 2	.0150	-45

TABLE 22 (CONTD.)

Integral	Exact Value	Gaussian Approx. & % Error		Mulliken Approx. & % Error	
$b_2b_1b_1h_2$	.0281	.0294	5	.0042	-85
$\ell_1h_1h_1h_1$	.0838	.0913	9	.0959	14
$\ell_1h_1h_2h_1$	.0295	.0312	5½	.0310	5
$\ell_1h_1h_2h_2$	.0661	.0715	7½	.0695	5
$\ell_1h_1b_1h_1$	.0580	.0579	0	.0589	2
$\ell_1h_1b_1h_2$	.0144	.0164	14	.0144	0
$\ell_1h_1b_1b_1$	.1260	.1331	5½	.1221	- 3
$\ell_1h_1b_2h_1$	.0083	.0105	25	.0154	85
$\ell_1h_1b_2h_2$	.0439	.0439	0	.0483	11
$\ell_1h_1b_2b_1$	-.0121	-.0127	5	-.0008	-97
$\ell_1h_1b_2b_2$	.1107	.1170	5	.1092	- 1
$\ell_1h_1\ell_1h_1$	.0384	.0404	6	.0203	-47
$\ell_1h_2\ell_1h_1$	.0390	.0358	- 8	.0179	-55
$\ell_1b_1h_2h_1$	.0014	.0011	-20	.0019	50
$\ell_1b_1b_1h_1$	.0316	.0311	- 1	.0179	-45
$\ell_1b_1b_1h_2$	.0152	.0156	3	.0011	-95
$\ell_1b_1b_2h_1$	-.0121	-.0128	5	.0003	
$\ell_1b_1b_2h_2$	-.0224	-.0231	3	-.0130	-42
$\ell_1b_1\ell_1h_1$	.0236	.0248	5	.0047	-75
$\ell_1b_1\ell_1h_2$	.0066	.0066	0½	.0000	-100
$\ell_1\ell_1h_2h_1$	.1826	.1800	- 1½	.1651	- 10
$\ell_1\ell_1b_1h_1$	.3171	.2986	- 6	.3263	3
$\ell_1\ell_1b_1h_2$	.0865	.0912	6	.0907	5

TABLE 22 (CONTD.)

Integral	Exact Value	Gaussian Approx. & % Error		Mulliken Approx. & % Error	
$\ell_1\ell_1\ell_1h_1$	.1678	.1764	6	.1293	-25
$\ell_2h_1\ell_1h_1$	.0099	.0125	25	.0183	83
$\ell_2h_1\ell_1h_2$	.0038	.0113	200	.0159	300
$\ell_2h_1\ell_1b_1$	-.0145	-.0152	5	-.0009	-90
$\ell_2h_1\ell_1b_2$	-.0203	-.0215	6	-.0056	-75
$\ell_2h_1\ell_1\ell_1$	.1035	.1092	5	.1072	3
$\ell_2b_1\ell_1h_2$	-.0203	-.0215	6	-.0056	-70
$\ell_2\ell_1h_2h_1$	-.0116	-.0129	12	-.0093	20
$\ell_2\ell_1b_1h_1$	-.0264	-.0190	-28	-.0165	-40
$\ell_2\ell_1b_1h_2$	-.0202	-.0215	6½	-.0043	-80
$\ell_2\ell_1\ell_1h_1$	.0080	.0079	2	.0001	-100
$\ell_2\ell_2\ell_1h_1$	.1035	.1092	5	.1072	3
$k\ h_1h_1h_1$	.0318	.0266	-17	.0346	8
$k\ h_1h_2h_1$	.0134	.0112	-16	.0113	-15½
$k\ h_1h_2h_2$	.0307	.0262	-15	.0256	-16
$k\ h_1b_1h_1$	.0257	.0203	-26	.0235	- 8
$k\ h_1b_1h_2$	.0082	.0072	-13	.0059	-30
$k\ h_1b_1b_1$	.0681	.0537	-20	.0525	-22
$k\ h_1b_2h_1$	.0076	.0068	-10	.0062	-17½
$k\ h_1b_2h_2$	.0242	.0196	-20	.0199	-19
$k\ h_1b_2b_1$	.0003	.0005	40	.0008	150
$k\ h_1b_2b_2$	.0655	.0525	-20	.0481	-35
$k\ h_1\ell_1h_1$	.0090	.0082	9½	.0074	-16

TABLE 22 (CONTD.)

Integral	Exact Value	Gaussian Approx. & % Error		Mulliken Approx. & % Error	
$k\ h_1\ell_1h_2$	.0088	.0081	- 9	.0066	-25
$k\ h_1\ell_1b_1$	.0004	.0006	35	.0010	170
$k\ h_1\ell_1\ell_1$	.0652	.0524	-20	.0479	-30
$k\ h_1\ell_2\ell_1$	-.0010	-.0001	-90	-.0007	-30
$k\ h_1k\ h_1$	.0090	.0077	-15	.0060	-35
$k\ h_2k\ h_1$	.0090	.0077	-15	.0057	-35
$k\ b_1h_2h_1$	.0015	.0013	-15	.0013	-13½
$k\ b_1b_1h_1$	.0146	.0073	-50	.0080	-50
$k\ b_1b_1h_2$	.0090	.0042	-55	.0013	-85
$k\ b_1\ell_1h_1$	-.0006	.0002	-60	-.0005	-25
$k\ b_1\ell_1h_2$	-.0033	-.0010	-70	-.0016	-50
$k\ b_1k\ h_1$	-.0042	-.0022	-45	-.0059	40
$k\ b_1k\ h_2$	-.0056	-.0027	-50	-.0063	15
$k\ \ell_1\ell_1h_1$	.0078	.0039	-50	.0015	-85
$k\ k\ b_1h_2$	.1240	.1327	7	.1233	½

TABLE 23

WATER COULOMB INTEGRALS OVER THE ORTHOGONALISED HYBRIDISED BASIS

Integral	Exact Value	Gaussian Approx. & % Error		Mulliken Approx. & % Error	
$h_1h_1h_1h_1$	0.6520	0.6810	$4\frac{1}{2}$	0.6760	4
$b_1b_1b_1b_1$	1.0355	1.0100	$-2\frac{1}{2}$	1.0930	6
$\ell_1\ell_1\ell_1\ell_1$	0.9999	0.9955	$-\frac{1}{2}$	1.0320	3
$h_2h_2h_1h_1$	0.2779	0.2810	1	0.2760	- 1
$b_1b_1h_1h_1$	0.4997	0.4996	0	0.5620	12
$b_1b_1h_2h_2$	0.3980	0.3960	$-\frac{1}{2}$	0.4140	4
$\ell_1\ell_1h_1h_1$	0.3884	0.3850	- 1	0.3900	$\frac{1}{2}$
$\ell_1\ell_1b_1b_1$	0.8001	0.7982	0	0.7960	$-\frac{1}{2}$
$k\ k\ h_1h_1$	0.4353	0.4261	- 2	0.4140	- 5
$k\ k\ b_1b_1$	1.2152	1.2110	0	1.1830	- 3
$k\ k\ \ell_1\ell_1$	1.1364	1.1330	0	1.1360	0
$b_2b_2b_1b_1$	0.8448	0.8420	0	0.8380	- 1
$b_1b_2h_1h_1$	0.0200	0.0180	-10	0.0388	95
$b_1b_2b_1b_1$	0.0339	0.0290	-15	0.0654	95
$b_1b_2b_1b_2$	0.0860	0.0842	- 3	0.1331	55
$\ell_1b_1h_1h_1$	0.0262	0.0252	- 4	0.0411	60
$\ell_1b_1h_2h_2$	-.0165	-.0156	- 5	-.0347	110
$\ell_1b_1b_1b_1$	0.0407	0.0355	-12	0.0647	60
$\ell_1b_1b_1b_2$	0.0009	0.0010	10	0.0020	115

TABLE 23 (CONTD.)

Integral	Exact Value	Gaussian Approx. & % Error		Mulliken Approx. & % Error	
$\ell_1 b_1 b_2 b_2$	-.0211	-.0207	-2	-.0297	30
$\ell_1 b_1 \ell_1 b_1$	0.0788	0.0776	-2	0.1012	32
$\ell_1 b_1 \ell_1 b_2$	-.0123	-.0122	-1	-.0116	7
$\ell_1 \ell_1 b_1 b_2$	-.0340	-.0356	5	-.0420	24
$\ell_1 \ell_1 \ell_1 b_1$	0.0285	0.0260	-8	0.0488	67
$k\ b_1 h_1 h_1$	0.0097	0.0142	45	0.0114	17
$k\ b_1 h_2 h_2$	-.0029	-.0066	130	-.0013	-60
$k\ b_1 b_1 b_1$	0.0199	0.0324	70	0.0372	90
$k\ b_1 b_1 b_2$	0.0085	0.0122	50	0.0146	65
$k\ b_1 b_2 b_2$	-.0117	-.0141	20	-.0036	200
$k\ b_1 \ell_1 b_1$	0.0102	0.0127	25	-.0028	-180
$k\ b_1 \ell_1 b_2$	-.0087	-.0122	50	-.0119	45
$k\ b_1 \ell_1 \ell_1$	-.0148	-.0141	-5	-.0028	90
$k\ b_1 k\ b_1$	0.0354	0.0418	26	0.0459	30

TABLE 24

WATER. Mulliken approximation of integrals. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{l}_1$	$\bar{l}_2$	$\bar{k}$
0.728	-0.016	0.947	-0.020	0.120	0.120	-0.008
	0.728	-0.020	0.947	0.120	0.120	-0.008
		1.294	0.038	-0.084	-0.084	0.006
			1.294	-0.084	-0.084	0.006
				1.978	-0.022	0.001
					1.978	0.001
						2.000

E = -84.22 a.u.

N_H = 0.728

N_O = 8.544

TABLE 25

METHANE. Mulliken approximation of integrals. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{b}_1$	$\bar{b}_2$	$\bar{b}_3$	$\bar{b}_4$	$\bar{k}$
0.894	0.019	0.019	0.019	0.994	0.001	0.001	0.001	-0.020
	0.894	0.019	0.019	0.001	0.994	0.001	0.001	-0.020
		0.894	0.019	0.001	0.001	0.994	0.001	-0.020
			0.894	0.001	0.001	0.001	0.994	-0.020
				1.107	-0.018	-0.018	-0.018	0.019
					1.107	-0.018	-0.018	0.019
						1.107	-0.018	0.019
							1.107	0.019
								2.000

E = -52.59 a.u.

N_H = 0.894

N_C = 6.428

TABLE 26

WATER. Mulliken and NDDO approximations. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{b}_1$	$\bar{b}_2$	$\bar{l}_1$	$\bar{l}_2$	$\bar{k}$
0.690	0.015	0.931	-0.015	0.140	0.140	0.002
	0.690	-0.015	0.931	0.140	0.140	0.002
		1.338	0.014	-0.099	-0.099	-0.002
			1.338	-0.099	-0.099	-0.002
				1.973	-0.029	0.000
					1.973	0.000
						2.000

E = -85.02 a.u.

N_H = 0.690

N_O = 8.622

TABLE 27

METHANE. Mulliken and NDDO approximations. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{b}_1$	$\bar{b}_2$	$\bar{b}_3$	$\bar{b}_4$	$\bar{k}$
0.592	0.078	0.078	0.078	0.901	0.027	0.027	0.027	0.038
	0.592	0.078	0.078	0.027	0.901	0.027	0.027	0.038
		0.592	0.078	0.027	0.027	0.901	0.027	0.038
			0.592	0.027	0.027	0.027	0.901	0.038
				1.409	-0.077	-0.077	-0.077	-0.032
					1.409	-0.077	-0.077	-0.032
						1.409	-0.077	-0.032
							1.409	-0.032
								1.995

E = -53.94 a.u.

N_H = 0.592

N_C = 7.631

TABLE 28

COULOMB INTEGRALS OVER HYBRID BASIS

Integral	Non-Orth H_2O	Orth H_2O	Non-Orth CH_4	Orth CH_4	% Diff.	
					H_2O	CH_4
$h_1h_1h_1h_1$	0.6250	0.6523	0.6250	0.6943	4½	12
$h_2h_2h_1h_1$	0.3313	0.2779	0.2891	0.2432	-16	-16
$b_1b_1h_1h_1$	0.5912	0.4997	0.5464	0.4791	-15	-12
$b_1b_1h_2h_2$	0.4483	0.3980	0.3765	0.3441	-11	- 9
$b_1b_1b_1b_1$	0.9760	1.0355	0.7063	0.7726	6	9
$b_2b_1h_1h_1$	0.0260	0.0200	0.0232	0.0283	-25	22
$b_2b_1b_1b_1$	0.0295	0.0339	0.0209	0.0282	14	36
$b_2b_1b_2b_1$	0.0735	0.0860	0.0515	0.0702	17	37
$b_2b_2b_1b_1$	0.7756	0.8848	0.5463	0.6285	9	15
$\ell_1b_1h_1h_1$	0.0309	0.0262			-16	
$\ell_1b_1h_2h_2$	-.0210	-.0165			-23	
$\ell_1b_1b_1b_1$	0.0350	0.0407			16	
$\ell_1b_1b_2b_1$	-.0008	0.0009				
$\ell_1b_1b_2b_2$	-.0275	-.0211			-24	
$\ell_1b_1\ell_1b_1$	0.0731	0.0788			8	
$\ell_1b_2\ell_1b_1$	-.0122	-.0123			0	
$\ell_1\ell_1h_1h_1$	0.4407	0.3884			-12	
$\ell_1\ell_1b_1b_1$	0.7657	0.8001			4½	
$\ell_1\ell_1b_2b_1$	-.0343	-.0340			- 1	
$\ell_1\ell_1\ell_1\ell_1$	0.9969	0.9999			0	

TABLE 28 (CONTD.)

Integral	Non-Orth H_2O	Orth H_2O	Non-Orth CH_4	Orth CH_4	% Diff.	
					H_2O	CH_4
$\ell_2\ell_1h_1h_1$	-.0246	-.0185			-24	
$\ell_2\ell_1b_1b_1$	-.0319	-.0298			- 7	
$\ell_2\ell_1b_2b_1$	-.0383	-.0414			8	
$\ell_2\ell_1b_2b_2$	-.0391	-.0298			-24	
$\ell_2\ell_1\ell_2b_1$	-.0146	-.0159			9	
$\ell_2\ell_1\ell_1\ell_1$	0.0265	0.0255			-4	
$\ell_2\ell_1\ell_2\ell_1$	0.0680	0.0655			- 4	
$\ell_2\ell_2\ell_1\ell_1$	0.7511	0.7485			0	
$\ell_2\ell_2\ell_2\ell_1$	0.0265	0.0255			- 4	
$k\ b_1h_1h_1$	0.0097	0.0082	0.0102	0.0088	-15	-14
$k\ b_1h_2h_2$	-.0029	-.0025	-.0039	-.0033	-14	-15
$k\ b_1b_1b_1$	0.0199	0.0220	0.0138	0.0153	10	11
$k\ b_1b_2b_1$	0.0085	0.0104	0.0052	0.0071	21	38
$k\ b_1b_2b_2$	-.0117	-.0144	-.0096	-.0137	25	40
$k\ b_1\ell_1b_1$	0.0109	0.0117			5	
$k\ b_1\ell_1b_2$	-.0087	-.0104			22	
$k\ b_1\ell_1\ell_1$	-.0148	-.0165			11	
$k\ b_1\ell_2\ell_1$	-.0104	-.0117			12	
$k\ b_1k\ b_1$	0.0355	0.0440	0.0247	0.0358	24	44
$k\ b_2k\ b_1$	0.0018	0.0129	0.0074	0.0126	28	40
$k\ \ell_1h_1h_1$	-.0035	-.0025			-28	

TABLE 28 (CONTD.)

Integral	Non-Orth H_2O	Orth H_2O	Non-Orth CH_4	Orth CH_4	% Diff.	
					H_2O	CH_4
$k\ \ell_1 b_1 b_1$	-.0139	-.0160			16	
$k\ \ell_1 b_2 b_1$	-.0087	-.0101			11	
$k\ \ell_1 \ell_1 b_1$	0.0054	0.0053			- 2	
$k\ \ell_1 \ell_1 \ell_1$	0.0201	0.0197			-1½	
$k\ \ell_1 \ell_2 \ell_1$	0.0064	0.0056			-13	
$k\ \ell_1 k\ b_1$	0.0108	0.0144			35	
$k\ \ell_1 k\ \ell_1$	0.0393	0.0415			5	
$k\ \ell_2 k\ \ell_1$	0.0064	0.0151				
$k\ k\ h_1 h_1$	0.5099	0.4353	0.4589	0.3986	-15	-13
$k\ k\ b_1 b_1$	1.1304	1.2152	0.8081	0.9101	7	13
$k\ k\ b_2 b_1$	0.0009	0.0139	0.0006	0.0166		
$k\ k\ \ell_1 b_2$	0.0006	0.0188				
$k\ k\ \ell_1 \ell_1$	1.1307	1.1364			½	
$k\ k\ \ell_2 \ell_1$	0.0021	0.0078				
$k\ k\ k\ b_1$	-.2040	-.2335	-.1583	-.1976	15	26
$k\ k\ k\ \ell_1$	-.2440	-.2594			10	
$k\ k\ k\ k$	4.8125	4.8125	3.5625	3.5625	0	0
$b_3 b_1 b_2 b_1$			-.0056	-.0061		9
$b_3 b_1 b_2 b_2$			-.0248	-.0242		-2½
$b_3 b_2 h_1 h_1$			-.0240	-.0300		25

TABLE 29

METHANE. Integrals as described in text. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{t}_1$	$\bar{t}_2$	$\bar{t}_3$	$\bar{t}_4$	$\bar{k}$
0.942	-0.049	-0.049	-0.049	00.998	-0.005	-0.005	-0.005	-0.003
	0.942	-0.049	-0.049	-0.005	0.998	-0.005	-0.005	-0.003
		0.942	-0.049	-0.005	-0.005	0.998	-0.005	-0.003
			0.942	-0.005	-0.005	-0.005	0.998	-0.003
				1.058	0.049	0.049	0.049	0.002
					1.058	0.049	0.049	0.002
						1.058	0.049	0.002
							1.058	0.002
								2.000

$E = -52.79$ a.u.

$N_H = 0.942$

$N_C = 6.232$

TABLE 30

METHANE. Integrals as described in text. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{t}_1$	$\bar{t}_2$	$\bar{t}_3$	$\bar{t}_4$	$\bar{k}$
0.917	0.000	0.000	0.000	0.968	0.000	0.000	0.000	0.000
	0.917	0.000	0.000	0.000	0.968	0.000	0.000	0.000
		0.917	0.000	0.000	0.000	0.968	0.000	0.000
			0.917	0.000	0.000	0.000	0.968	0.000
				1.083	0.000	0.000	0.000	0.000
					1.083	0.000	0.000	0.000
						1.083	0.000	0.000
							1.083	0.000
								2.000

$E = -52.84$ a.u.

$N_H = 0.917$

$N_C = 6.334$

CHAPTER SIX[†]

FINAL CALCULATIONS

At the end of the last chapter an empirical scheme was proposed for the estimation of the larger two-electron integrals over an orthogonal hybrid basis. The integrals were estimated by a procedure based on the study of the effects of symmetric orthogonalisation on integrals over a non-orthogonal hybrid basis, for the water and methane molecules. The method proposed for the approximation of the integrals over an orthogonal basis from the integrals over a non-orthogonal hybrid basis was:

(a) The NDDO approximation is used, that is only integrals of the form $(\bar{i}^A\bar{j}^A|\bar{k}^B\bar{\ell}^B)$ are given non-zero values. Table 23 gives some comparisons of integral values of the non-coulombic type over a hybrid and an orthogonal hybrid basis, for the water molecule. Comparison with Table 28 of Chapter 5 shows that the largest of these integrals over an orthogonal basis are much smaller than the largest of the integrals of the form $(\bar{i}_A\bar{j}_A|\bar{k}_B\bar{\ell}_B)$ for $i \neq j$ and/or $k \neq \ell$

[†] This Chapter closely follows the presentation given in a joint paper by Cook, Hollis and McWeeny (submitted for publication in Molecular Physics) but also presents new and independent calculations on other molecules.

(b) $(\bar{i}^A\bar{i}^A|\bar{j}^B\bar{j}^B)$ is obtained from the corresponding integral over the non-orthogonal bases $(i^Ai^A|j^Bj^B)$ by increasing it by 12% if A=B and decreasing by 12% if A≠B and A and B are near neighbours. However, if $\bar{i}^A = k, \pi$ or ℓ and $\bar{j}^A = k, \pi$ or ℓ (where k, π, ℓ denote 1s, pi and lone pair orbitals respectively) then $(\bar{i}^A\bar{i}^A|\bar{j}^B\bar{j}^B)$ takes its non-orthogonal value.

(c) All other integrals of the form $(\bar{i}^A\bar{j}^A|\bar{k}^B\bar{\ell}^B)$ take the value of the corresponding integral over the non-orthogonal basis $(i^Aj^A|k^B\ell^B)$.

Two-electron integrals estimated in the above manner and exact one-electron integrals over the orthogonal hybrid basis were used in the last chapter to perform SCF MO and SCGF calculations on methane. The results were very good for methane and so the scheme was examined for a larger system.

The two-electron integrals over the orthogonal hybrid basis were calculated for ethylene, using the Mulliken approximation for the estimation of the many-centre two-electron integrals over non-orthogonal hybrids (the one- and two-centre integrals were calculated exactly), followed by transformation to an orthogonal basis. Although the integrals over the orthogonal basis are not accurate, it has been seen in Chapter 5 that the larger integrals of the form $(\bar{i}^A\bar{i}^A|\bar{j}^A\bar{j}^A)$ are reasonably close to the exact values. So these integrals can probably be used to give a general idea of the effect of orthogonalisation.

The two-electron integrals over the non-orthogonal hybrid basis are given in Table 1; only integrals of the $(i^A i^A | j^A j^A)$ type are given (it has been pointed out in Chapter 5 that the effect of scaling the smaller non-orthogonal integrals, in the methane calculation, was small). It can be seen from Table 1 that the effect of orthogonalisation, in this molecule, is remarkably similar to the effect in the water and methane molecules.

Results

The procedure outlined above, for the approximation of integrals, was next used to perform calculations on the hydrocarbons, ethylene, acetylene and ethane and on two systems containing a heteroatom, formaldehyde and hydrogen cyanide.

Ethylene

A calculation has been performed on ethylene using the following coordinate system (in a.u.): C-C = 2.55116 a.u.

	x	y	z
C1	-1.27558	0	0
C2	1.27558	0	0
H1	-2.286595	1.75113	0
H2	-2.286595	-1.75113	0
H3	2.286595	1.75113	0
H4	2.286595	-1.75113	0

Moskowitz and Harrison(1) have given very extensive results for ethylene using various Gaussian basis sets; up to forty basis orbitals have been used. These very accurate calculations are useful for purposes of comparison. The approximate results are compared below with the calculation using the largest Gaussian basis set (40 orbitals).

The electronic structure of ethylene can be described as resulting from double occupation of eight MO's belonging to the irreducible representation of the group D_{2h}. The symmetry of the MO's for ethylene is shown in the table below. The ground state configuration $({}^1A_g)$ of ethylene is

$$({}^1a_g)^2\ ({}^1b_{\ u})^2\ ({}^2a_g)^2\ ({}^2b_{3u})^2\ ({}^1b_{2u})^2\ ({}^3a_g)^2\ ({}^1b_{1g})^2\ ({}^1b_{1u})^2$$

The orbitals b_{1u} b_{2g} are pi bonding and antibonding orbitals. The other MO's describe the σ-core.

In the table below the SCF MO orbital and electronic energies are given:

M.O.	Gaussian	Approximate
^1a_g	-11.2539	-10.994
$^1b_{3u}$	-11.2526	-10.993
^2a_g	-1.0584	-1.017
$^2b_{3u}$	-0.8067	-0.934
$^1b_{2u}$	-0.6104	-0.375
^3a_g	-0.5829	-0.356
$^1b_{1g}$	-0.5174	-0.355
$^1b_{1u}$	-0.3814	-0.173
$^1b_{2g}$	0.1518	0.282
Electronic Energies	-111.2024	-110.567

It can be seen that the order of the energy levels is the same as the accurate calculation except that the ^3a_g and $^1b_{2u}$ orbitals are in a different order. They are however almost degenerate in the approximate calculation. By Koopman's theorem the ionisation potential (IP) is given by minus the energy of the highest occupied orbital. The experimental IP is 0.386. The Gaussian calculation gives a very good estimate of this quantity - 0.381 a.u. - but the approximate calculation gives a very poor one - 0.173 a.u. This result is disappointing, since in this case the NDDO approximation does not give results close to those of exact calculations. A similar discrepancy is seen, for formaldehyde, later, though it should be noted that in this case the use of the CNDO approximation gives extremely bad results. These results are probably due to the cumulative effect of neglecting so many small integrals giving poor absolute energy values. This is less likely to affect the spacing of the levels (i.e. the relative values): thus the higher levels exact and approximate are almost brought into coincidence if the energy zero for the latter is shifted by about 0.15 a.u. The discrepancies for bonding and anti-bonding partners are opposite in magnitude; this could be due to a poor β value (resulting from neglect of integrals in defining the SCF Hamiltonian). All the Gaussian calculations show well-defined σ-π separations, as does the approximate calculation. The Gaussian calculation using 40 orbitals predicts a separation of 0.136 a.u. and the approximation calculation 0.181 a.u.

The predicted charge densities, the gross atomic populations (N) and the overlap populations (n) are given in the table below:

	Gaussian	Approximate (SCFMO)	Approximate (SCGF)
N(C)	6.330	6.407	6.368
N(H)	0.835	0.796	0.816
$n(C_\sigma - C_\sigma)$	0.943	0.893	0.990
n(C-H)	0.839	0.948	0.960

It can be seen that the charges are reasonably close to those predicted by the calculation using a very large set of Gaussian orbitals. The complete density matrices for the SCF MO and the SCGF calculations are given in Tables 2 and 3.

Acetylene

A calculation has been performed on acetylene using $R_{CC} = 2.268$ a.u. and $R_{CH} = 2.004$ a.u. A minimal basis calculation using Slater orbitals has been performed by McLean(2) and a Gaussian calculation using 34 basis functions has been performed by Moskowitz(3). The orbital and electronic energies for the approximate SCF MO calculation are compared with those from the exact calculations in the table below:

	Gaussian	Slater	Approximate
$1\sigma_g$	-11.265	-11.400	-11.108
$1\sigma_u$	-11.261	-11.397	-11.106
$2\sigma_g$	-1.042	-1.041	-0.945
$2\sigma_u$	-0.759	-0.776	-0.663
$3\sigma_g$	-0.671	-0.682	-0.613
$1\pi_u$	-0.402	-0.441	-0.267
Electronic	-101.479	-101.283	-101.040

It can be seen that the order of the energy levels for the approximate calculation is the same as in the exact calculations. The experimental ionisation potential is 0.419 a.u. As in ethylene the approximate calculation does not give a good estimate of this. Again the σ-π separation predicted by the approximate calculation, 0.346 a.u., is greater than that predicted by the exact calculations, 0.268 a.u. (Gaussian) and 0.239 a.u. (Slater). The predicted gross atom populations are given in the table below:

	Gaussian	Slater	Approximate (SCFMO)	Approximate (SCGF)
N(H)	0.795	0.775	0.716	0.755
N(C)	6.205	6.225	6.283	6.245

The atom populations predicted by the approximate method are not as close to those predicted by the exact calculation as they are in ethylene, but they are still reasonable. The complete density matrices for the SCF MO and SCGF calculations are given in Tables 4 and 5.

Ethane

A calculation on ethane was performed using $R_{CH} = 2.286592$ and $R_{CC} = 2.910212$ a.u. (1.54 a°). The coordinate system is given in the table below:

Atom	x	y	z
C1	-1.455106	0	0
C2	1.455106	0	0
H1	-2.148013	0	-1.959837
H2	-2.148013	1.697270	0.979918
H3	-2.148013	-1.697270	0.979918
H4	-2.148013	0	1.959837
H5	-2.148013	-1.697270	-0.979918
H6	-2.148013	1.697270	-0.979918

A minimal basis calculation using Slater orbitals has been performed by Pitzer and Lipscomb(4). The orbital and electronic energies for the approximate SCF MO calculation are compared with those for the exact calculations in the table below:

	Exact	Approximate
$1a_{1g}$	-11.346	-11.040
$1a_{2u}$	-11.346	-11.039
$2a_{1g}$	-1.040	-1.240
$2a_{2u}$	-0.859	-1.134
$1a_u$	-0.627	-0.358
$3a_{1g}$	-0.536	-0.357
$1a_g$	-0.515	-0.346
Electronic	-120.923	-120.255

The order of the energy levels for the approximate calculation is the same as in the exact calculation though the absolute energies are not very close. The predicted gross atom populations for the exact calculation and for the approximate calculations are given below:

	Exact	Approximate (SCF MO)	Approximate (SCGF)
N(H)	0.887	0.890	0.874
N(C)	6.339	6.321	6.377

The atom populations predicted by the approximate methods are very close to those predicted by the exact calculation. The complete density matrices for the SCF MO and SCGF calculations are given in Tables 6 and 7.

Formaldehyde

Exact integrals over an AO basis set were available from previous work(5). The following bond distances, bond angles and orbital exponents were used:

$R_{CO} = 2.30$ a.u. $\quad R_{CH} = 2.00$ a.u. $\quad \angle HCH = 120^{\circ}$

$\zeta_{1s_h} = 1.2 \quad \zeta_{1s_c} = 5.7 \quad \zeta_{1s_o} = 7.7$

$\zeta_{2s_c} = \zeta_{2p_c} = 1.625 \qquad \zeta_{2s_o} = \zeta_{2p_o} = 2.275$

The results of exact SCF MO and SCGF calculations are given in Tables 8 and 9. As expected the SCGF calculation again gives a lower total electronic energy than the SCF MO method. As in previous exact calculations on formaldehyde the π-bond is slightly polarised in the C-N direction. SCF MO calculations were also carried out using exact integrals and the NDDO and the CNDO approximations. As pointed out in Chapter 5, the CNDO calculation gives a very large bond order between the two hydrogen atoms and also the π-bond is now extrmely polar in the C-N direction. These drawbacks do not occur in the NDDO calculation, though as in the CNDO calculation there is a reasonably large bond order between the sp_2 orbital on carbon directed towards oxygen and the hydrogen atoms.

As noted earlier in this chapter, the energy of the highest occupied orbital is considerably less when the NDDO approximation is used than in the complete calculation. Table 12 gives the orbital energies for the full calculation and the calculations employing the NDDO and CNDO approximations. It can be seen that the energy of the highest occupied orbital using the CNDO approximation is very poor indeed and is not very good using the NDDO approximation. In fact ϕ_8, the highest occupied orbital, which in the exact calculation consists almost entirely of a lone pair on the oxygen atom, is no longer a lone pair orbital in the approximate calculations.

The two-electron integrals of the form $(i^A i^A | j^B j^B)$ over a non-orthogonal and an orthogonal hybrid basis are given in Table 13. It can be seen that these integrals fit in very well with the scheme proposed for the estimation of two-electron integrals over an orthogonal hybrid basis from the corresponding integrals over the non-orthogonal basis. The results of SCF MO and SCGF calculations using this scheme are given in Tables 14 and 15. For purposes of comparison wave functions have also been calculated using the Pople and Santry approximations(6,7) and the SCF MO NDDO method. Two methods have been used, denoted by Pople and Santry as CNDO/1 and CNDO/2, which differ slightly in the approximations used to estimate the diagonal matrix elements of the one-electron Hamiltonian. The results of these calculations are given in Tables 16 and 17. These approximate calculations were carried out using a hydrogen orbital exponent of 1.2, so that the results could be compared with those of the calculations using exact integrals. The gross atom populations predicted by the exact and approximate calculations are given below:

	N(H)	N(C)	N(O)
Exact calculation SCGF	0.892	6.169	8.047
Exact calculation SCF MO	0.937	6.122	8.014
Exact calculation SCF MO (NDDO)	0.876	6.224	8.020
Exact calculation SCF MO (CNDO)	0.822	6.565	7.792
This work SCGF	0.805	6.089	8.301
This work SCF MO	0.766	6.207	8.221
Pople and Santry CNDO/1	1.057	5.882	8.004
Pople and Santry CNDO/2	1.011	5.791	8.186

It can be seen that the scheme proposed in this work gives a low hydrogen atom population and a high charge on the oxygen atom, while Pople and Santry's method overestimates the hydrogen atom charge and gives a low carbon atom population.

Hydrogen Cyanide

Calculations have been carried out on hydrogen cyanide using the following bond distances and orbital exponents:

$R_{CN} = 2.1872$ a.u. $R_{CH} = 2.0070$ a.u.

$\zeta_{1s_h} = 1.0$

$\zeta_{1s_c} = 5.7 \quad \zeta_{2s_c} = \zeta_{2p_c} = 1.625$

$\zeta_{1s_N} = 6.7 \quad \zeta_{2s_N} = \zeta_{2p_N} = 1.950$

The results of approximate SCF MO and SCGF calculations, estimating the two-electron integrals in the manner described at the start of the chapter, are given in Tables 18 and 19. Results of SCF MO calculations using Pople and Santry's CNDO/1 and CNDO/2 scheme are given in Tables 20 and 21. The gross atom populations predicted by the approximate calculations are given in the table below. The populations predicted by an exact calculation using Slater orbitals and the coordinates and exponents given above (McLean(8)) are also given.

	N(H)	N(C)	N(N)
Exact Calculation	0.761	6.156	7.082
This work (SCF MO)	0.685	6.139	7.176
This work (SCGF)	0.682	6.091	7.227
CNDO/1	0.926	6.099	6.975
CNDO/2	0.982	5.912	7.105

The method proposed in this work overestimates the nitrogen atom population while Pople and Santry's method gives a very high charge on the hydrogen atom.

Discussion

As expected, the total electronic energy of all the calculations is quite close to that reported for the full calculation. The charges on the hydrogen atoms calculated using the approximate method described at the start of this chapter are given in the table below. For comparison the charges calculated by exact minimal basis SCF MO calculations, by Pople and Segal's SCF MO CNDO/1 method, and by Hoffman's(9) extended Hückel method are also given.

	CH_4	C_2H_6	C_2H_4	C_2H_2	CH_2O	HCN
Exact calculation (SCF MO)	0.916	0.887	0.835	0.775	0.900*	0.761
This work (SCFMO)	0.942	0.890	0.800	0.716	0.766	0.685
This work (SCGF)	0.920	0.874	0.816	0.755	0.805	0.682
Pople and Segal's CNDO/1	0.965	0.966	0.954	0.893	0.958	0.847
Extended Hückel	0.867	0.881	0.887	0.843		

* See reference 10

For the hydro carbons CH_4, C_2H_6, C_2H_4 C_2H_4 it is found that the C-H bond polarities are all $\overleftarrow{\text{C-H}}$ and that the magnitude of the polarity increases along the series, the hydrogen atom becoming progressively less shielded by electrons. While this is known to be the correct trend for the last three members of the series, less is known about the relative polarities of the CH bonds in methane and ethane. The full non-empirical calculation indicates that the ethane bond is the more polar, and this result is reproduced by the present calculations. The results of Pople and Santry and Segal predict the opposite trend. The only physical evidence available suggests that the ethane bond is in fact the more polar, the ethane proton resonance occurring at lower field than in methane(11). This fact indicates, assuming that anisotropy effects for methane and ethane are small, that the protons in ethane are less shielded by electrons than those in methane.

The results of the Hückel calculations are not in agreement with the exact minimal basis results or with experimental evidence Thus the Hückel results would predict that ethylene would lose a proton less readily than ethane and methane which is certainly contrary to experimental evidence. It also predicts that the hydrogen atom charge in methane is less than that in ethane, contrary to the evidence of NMR spectra given above.

In hydrogen cyanide the present method gives an atom population on hydrogen close to exact result, but in formaldehyde the predicted charge on hydrogen is much lower than in the exact calculation.

Comparison of SCF MO and SCGF methods

From the results given above it can be seen that the electronic energies and electron distributions in polyatomic molecules, as predicted by the SCF MO and SCGF calculations, are usually in close agreement. In this section the two methods are compared in detail.

When the molecule contains one or more π bonds the SCGF method predicts a much lower π bond order than the SCF MO calculation. At first sight this difference is surprising. It should be remembered, however, that when the bond order is defined formally as an off-diagonal density matrix element (and not as a *ratio* between the values of some index for the given bond and for that in ethylene) there is no reason for close agreement. For ethylene the π-bond order (density matrix element) is unity in an MO calculation based on orthogonal AO's; with non-orthogonal AO's an MO treatment gives $(1+S)^{-1}$ while Heitler-London theory gives $S(1+S)^{-1}$. In the SCGF calculation full configuration interaction is admitted for each electron pair and the optimum bond order is closer to the Heitler-London value; although the present calculation employs orthogonal orbitals a similar result is obtained, the Heitler-London value being lower than the MO value by a factor close to the overlap integral for the non-orthogonal AO's. So for the SCGF method the ratio P_{rs}/P_{cc} (ethylene), which is essentially a fractional double-bond character, should be compared with the π bond order in the SCF MO calculation. The low π bond index in the SCGF calculations thus merely reflects the relatively low overlap integral for π type AO's.

A noteworthy feature of the SCGF calculation is the simple form of the density matrix, whose non-zero elements refer only to real chemical bonds. With a realistic choice of hybrids, the wave function, besides being of considerable accuracy, conforms closely to the description adopted in qualitative valence theory, each bond being associated with a strongly over-lapping pair of orbitals. The MO density matrix, on the other hand, contains many small off-diagonal elements connecting orbitals on different atoms: physical meaning has sometimes been attributed to these elements (e.g. in the interpretation of NMR coupling constants), but in fact they are only very indirectly related to the energy and it is possible that their values are often completely spurious. The so-called "long-range bond orders" between non-bonded atoms must occur in any MO calculation in order that the matrix R ($=\frac{1}{2}P$)

may be idempotent, and are thus related to the orthogonality requirement for MO's; their values fluctuate widely in SCF calculations (cf Tables 8 - 11), without appreciable effect on the energy, and their physical significance appears to be dubious. It is of course true that the SCGF calculation will lead to good results only with well-chosen hybrids and that for some molecules (e.g. those with "bent" bonds) this choice may not be obvious. This matter has been investigated in recent work(12), but for the molecules discussed here the prescription for setting up orthonormal hybrids is reasoanbly satisfactory.

Perhaps the most important advantage of the SCGF method, for present purposes, is its particular suitability for semi-empirical development: for the only one-electron matrix elements required are the diagonal elements and those that link bonded pairs of atoms. Thus, in ethane, only two distinct β's are needed, as compared with 22 in the SCF MO calculation. This may not reduce the calculation of the one-electron Hamiltonian very much in non-empirical work, but is clearly an important factor when such quantities are to be adopted as empirically fitted parameters. In this connection, Table 22 is of considerable interst. It shows, for example, that the approximation of making β's (by implication over orthogonal orbitals) proportional to overlap integrals (over corresponding non-orthogonal orbitals), which is commonly used in semi-empirical work, has little justification; thus $< \sigma_{c_1}|h|h_1 >$ has almost the same value as $< b_1|h|h_1 >$ while the corresponding overlap integrals differ by a factor of almost five.

Finally, it should be noted that the SCGF method lends itself to calculations on large molecules, with a minimum of computational effort. A conventional SCF MO calculation for a system with, say, 50 basis orbitals, requires a fairly large computer and (even assuming reasonable convergence of the process) is expensive in computing time. The SCGF calculation, on the other hand, requires only the diagonalisation of one small matrix (in the present case 3x3) for each electron pair, and is a rapidly convergent process. Moreover, besides being relatively small, the SCGF computing time is roughly linear in the number of distinct electron groups, while that for an SCF MO calculation is at least cubic in the number of orbitals used. The calculations reported in this work were in fact performed using an IBM 1620 computer, the computing times for the two types of calculation being in the ratio 40:1 for the larger molecules.

Conclusions

The main conclusions that emerge from this research are as follows:

1) By using a suitable set of orthonormalised hybrid orbitals it is permissible to neglect all two-electron integrals except the one- and two-centre coulomb integrals and the one-centre exchange integrals. The neglected integrals correspond formally to those which are discarded, without justification, when defined over non-orthogonal AO's in the NDDO scheme; their values are in fact so small that their neglect does not significantly affect the results of complete many-electron calculations. Those integrals which are not neglected must be estimated rather accurately: the invariance requirement of Pople, Santry and Segal, discussed in Chapter 2, which would force equality upon various groups of integrals, is too restrictive for this purpose and must be rejected.

2) The one-electron integrals over the orthonormalised hybrids must be calculated fairly accurately in order to reproduce the results of complete non-empirical calculations; it is not possible, for example, to neglect three-centre

potential energy integrals over the non-orthogonal AO's prior to orthogonalisation.

3) The results of SCF MO and SCGF calculations are in fairly close agreement for the molecules considered so far, the SCGF results being slightly the better at least for the ground states. The SCGF method has considerable computational advantages and leads to a somewhat simpler description of the electron distribution, emphasising the localised-bond picture and being applicable without difficulty (in its semi-empirical form) to much larger molecules.

4) In the molecules so far considered, satisfactory results are obtained by using hybrids that point along the bonds. In cases where there is no intuitively obvious choice of hybrid orbitals (as in "strained" molecules where it is not always possible to find mutually orthogonal hybrids of this kind unless the bonds are regarded as bent) there is an important optimisation problem, namely to find the optimum set of hybrids with which to construct an SCGF wave function.

The methods developed in this work are now being applied to a variety of larger molecules, including strained systems for which the problem of optimising the hybrids is receiving attention(12).

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TABLE 1

ETHYLENE - COULOMB INTEGRALS OVER HYBRID BASIS

TWO-CENTRE INTEGRALS

Integral	Non-Orthogonal	Orthogonal	% Diff.
$h_2h_2h_1h_1$	.280	.229	-18
$\sigma_1\sigma_1h_1h_1$	.367	.332	-10
$\sigma_1\sigma_1h_3h_3$	.306	.256	-17
$b_1b_1h_1h_1$	.559	.518	- 7
$b_1b_1h_2h_2$	.367	.327	-11
$b_1b_1h_3h_3$	.241	.234	- 3
$b_1b_1h_4h_4$	.214	.190	-11
$\pi_1\pi_1h_1h_1$	.406	.370	- 9
$\pi_1\pi_1h_3h_3$	.242	.221	- 9
$k_1k_1h_1h_1$	.467	.386	-17
$k_1k_1h_3h_3$	.251	.229	- 8
$\sigma_2\sigma_2\sigma_1\sigma_1$	.643	.637	- 1
$\sigma_2\sigma_2b_1b_1$	.411	.389	- 6
$\sigma_2\sigma_2\pi_1\pi_1$	.457	.433	- 6
$\sigma_2\sigma_2k_1k_1$	.545	.477	-13
$b_3b_3b_1b_1$	.289	.305	8
$b_3b_3b_2b_2$	.269	.258	- 4
$\pi_2\pi_2b_1b_1$	.303	.302	0
$\pi_2\pi_2\pi_1\pi_1$	.342	.330	- 3
$k_2k_2b_1b_1$	.322	.323	0

TABLE 1 (CONTD.)

ETHYLENE - COULOMB INTEGRALS OVER HYBRID BASIS

ONE-CENTRE INTEGRALS

Integral	Non-Orthogonal	Orthogonal	% Diff.
$h_1h_1h_1h_1$	.625	.690	10
$\sigma_1\sigma_1\sigma_1\sigma_1$	.717	.847	17
$b_1b_1b_1b_1$	.717	.849	17
$\pi_1\pi_1\pi_1\pi_1$	.636	.647	2
$k_1k_1k_1k_1$	3.562	3.562	0
$b_1b_1\sigma_1\sigma_1$	.527	.594	13
$\pi_1\pi_1\sigma_1\sigma_1$	.572	.627	10
$\pi_1\pi_1b_1b_1$	.572	.625	10
$b_2b_2b_1b_1$	.527	.579	10
$k_1k_1\sigma_1\sigma_1$	.808	.906	12
$k_1k_1b_1b_1$	.808	.896	11
$k_1k_1\pi_1\pi_1$	.807	.816	1

TABLE 2

ETHYLENE - INTEGRALS AS DESCRIBED IN TEXT. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{\sigma}_1$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\pi}_1$	$\bar{k}_1$	$\bar{\sigma}_2$	$\bar{b}_3$	$\bar{b}_4$	$\bar{\pi}_2$	$\bar{k}_2$
0.796	0.013	-0.056	0.064	0.226	0.948	-0.020	0.000	-0.004	0.001	-0.013	0.013	0.000	-0.001
	0.796	0.064	-0.056	0.226	-0.020	0.948	0.000	-0.004	0.001	0.013	-0.013	0.000	-0.001
		0.796	0.013	0.001	-0.013	0.013	0.000	-0.001	0.226	0.948	-0.020	0.000	-0.004
			0.796	0.001	0.013	-0.013	0.000	-0.001	0.226	-0.020	0.948	0.000	-0.004
				1.019	0.041	0.041	0.000	0.005	0.893	-0.219	-0.219	0.000	-0.002
					1.194	-0.023	0.000	0.003	-0.219	0.109	-0.011	0.000	0.002
						1.194	0.000	0.003	-0.219	-0.011	0.109	0.000	0.002
							1.000	0.000	0.000	0.000	0.000	1.000	0.000
								2.000	-0.002	0.002	0.002	0.000	0.000
									1.019	0.041	0.041	0.000	0.005
										1.194	-0.023	0.000	0.003
											1.194	0.000	0.003
												1.000	0.000
													2.000

$E = -110.57$ a.u.

$N_H = 0.796$

$N_C = 6.407$

TABLE 3

ETHYLENE - INTEGRALS AS DESCRIBED IN TEXT. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{\sigma}_1$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\pi}_1$	$\bar{k}_1$	$\bar{\sigma}_2$	$\bar{b}_3$	$\bar{b}_4$	$\bar{\pi}_2$	$\bar{k}_2$
0.816	0.000	0.000	0.000	0.000	0.960	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.816	0.000	0.000	0.000	0.000	0.960	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		0.816	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.960	0.000	0.000	0.000
			0.816	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.960	0.000	0.000
				1.000	0.000	0.000	0.000	0.000	0.990	0.000	0.000	0.000	0.000
					1.184	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
						1.184	0.000	0.000	0.000	0.000	0.000	0.000	0.000
							1.000	0.000	0.000	0.000	0.000	0.655	0.000
								2.000	0.000	0.000	0.000	0.000	0.000
									1.000	0.000	0.000	0.000	0.000
										1.184	0.000	0.000	0.000
											1.184	0.000	0.000
												1.000	0.000
													2.000

$E = -110.42$ a.u.

$N_H = 0.816$

$N_C = 6.368$

TABLE 4

ACETYLENE - INTEGRALS AS DESCRIBED IN TEXT. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{\sigma}_1$	$\bar{b}_1$	$\bar{\pi}_1$	$\bar{\pi}_2$	$\bar{k}_1$	$\bar{\sigma}_2$	$\bar{b}_2$	$\bar{\pi}_3$	$\bar{\pi}_4$	$\bar{k}_2$
0.716	0.057	0.391	0.853	0.000	0.000	-0.005	0.175	-0.062	0.000	0.000	-0.003
	0.716	0.175	-0.062	0.000	0.000	-0.003	0.391	0.853	0.000	0.000	-0.005
		0.904	-0.033	0.000	0.000	0.011	0.833	-0.333	0.000	0.000	-0.007
			1.379	0.000	0.000	0.002	-0.333	0.109	0.000	0.000	0.004
				1.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000
					1.000	0.000	0.000	0.000	0.000	1.000	0.000
						2.000	-0.007	0.004	0.000	0.000	0.000
							0.904	-0.033	0.000	0.000	0.011
								1.379	0.000	0.000	0.001
									1.000	0.000	0.000
										1.000	0.000
											2.000

$E = -101.04$ a.u.

$N_H = 0.716$

$N_C = 6.283$

TABLE 5

ACETYLENE - INTEGRALS AS DESCRIBED IN TEXT. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{\sigma}_1$	$\bar{b}_1$	$\bar{\pi}_1$	$\bar{\pi}_2$	$\bar{k}_1$	$\bar{\sigma}_2$	$\bar{b}_2$	$\bar{\pi}_3$	$\bar{\pi}_4$	$\bar{k}_2$
0.755	0.000	0.000	0.948	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.755	0.000	0.000	0.000	0.000	0.000	0.000	0.948	0.000	0.000	0.000
		1.000	0.000	0.000	0.000	0.000	0.994	0.000	0.000	0.000	0.000
			1.245	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
				1.000	0.000	0.000	0.000	0.000	0.855	0.000	0.000
					1.000	0.000	0.000	0.000	0.000	0.855	0.000
						2.000	0.000	0.000	0.000	0.000	0.000
							1.000	0.000	0.000	0.000	0.000
								1.245	0.000	0.000	0.000
									1.000	0.000	0.000
										1.000	0.000
											2.000

$E = -100.77$ a.u.

$N_H = 0.755$

$N_C = 6.245$

TABLE 6

ETHANE - INTEGRALS AS DESCRIBED IN TEXT. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{h}_5$	$\bar{h}_6$	$\bar{\sigma}_1$	$\bar{b}_1$
0.890	-0.089	-0.089	0.070	-0.001	-0.001	0.220	0.956
	0.890	-0.089	-0.001	0.070	0.001	0.220	-0.040
		0.890	-0.001	-0.001	0.070	0.220	-0.040
			0.890	-0.089	-0.089	0.048	-0.001
				0.890	-0.089	0.048	-0.001
					0.890	0.048	-0.001
						0.979	0.031
							1.114

$E = -120.26$ a.u.

$N_H = 0.890$

$N_C = 6.321$

$\bar{b}_2$	$\bar{b}_3$	$\bar{k}_1$	$\bar{\sigma}_2$	$\bar{b}_4$	$\bar{b}_5$	$\bar{b}_6$	$\bar{k}_2$
-0.040	-0.040	-0.003	0.048	-0.001	-0.001	-0.001	-0.001
0.956	-0.040	-0.003	0.048	-0.001	-0.001	-0.001	-0.001
-0.040	0.956	-0.003	0.048	-0.001	-0.001	-0.001	-0.001
-0.001	-0.001	-0.001	0.220	0.956	-0.040	-0.040	-0.003
-0.001	-0.001	-0.001	0.220	-0.040	0.956	-0.040	-0.003
-0.001	-0.001	-0.001	0.220	-0.040	-0.040	0.956	-0.003
0.020	0.020	0.003	0.840	-0.200	-0.200	-0.200	-0.001
0.094	0.094	0.002	-0.200	-0.001	-0.001	-0.001	0.001
1.114	0.094	0.002	-0.200	-0.001	-0.001	-0.001	0.001
	1.114	0.002	-0.200	-0.001	-0.001	-0.001	0.001
		2.000	-0.001	0.001	0.001	0.001	0.000
			0.979	0.031	0.020	0.020	0.003
				1.114	0.094	0.094	0.002
					1.114	0.094	0.002
						1.114	0.002
							2.000

TABLE 7

ETHANE - INTEGRALS AS DESCRIBED IN TEXT. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{h}_5$	$\bar{h}_6$	$\bar{\sigma}_1$	$\bar{b}_1$	$\bar{b}_2$	$\bar{b}_3$	$\bar{k}_1$	$\bar{\sigma}_2$	$\bar{b}_4$	$\bar{b}_5$	$\bar{b}_6$	$\bar{k}_2$
0.874	0.000	0.000	0.000	0.000	0.000	0.000	0.964	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.874	0.000	0.000	0.000	0.000	0.000	0.000	0.964	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		0.874	0.000	0.000	0.000	0.000	0.000	0.000	0.964	0.000	0.000	0.000	0.000	0.000	0.000
			0.874	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.964	0.000	0.000	0.000
				0.874	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.964	0.000	0.000
					0.874	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.964	0.000
						1.000	0.000	0.000	0.000	0.000	0.973	0.000	0.000	0.000	0.000
							1.126	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
								1.126	0.000	0.000	0.000	0.000	0.000	0.000	0.000
									1.126	0.000	0.000	0.000	0.000	0.000	0.000
										2.000	0.000	0.000	0.000	0.000	0.000
											1.000	0.000	0.000	0.000	0.000
												1.126	0.000	0.000	0.000
													1.126	0.000	0.000
														1.126	0.000
															2.000

$E = -119.85$

$N_H = 0.874$

$N_C = 6.377$

TABLE 8

FORMALDEHYDE - EXACT INTEGRALS OVER AN ORTHONORMAL HYBRID BASIS FULL CALCULATION. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{\sigma}_C$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\pi}_C$	$\bar{k}_C$	$\bar{\sigma}_O$	$\bar{\ell}_{1O}$	$\bar{\ell}_{2O}$	$\bar{\pi}_O$	$\bar{k}_O$
0.937	-0.053	0.035	0.975	0.016	0.000	-0.007	-0.010	-0.127	0.158	0.000	0.000
	0.937	0.035	0.016	0.975	0.000	-0.007	-0.010	0.158	-0.127	0.000	0.000
		0.884	0.019	0.019	0.000	-0.009	0.991	-0.024	-0.024	0.000	-0.009
			1.103	0.012	0.000	0.007	-0.036	0.122	-0.148	0.000	0.000
				1.103	0.000	0.007	-0.036	-0.148	0.122	0.000	0.000
					1.032	0.000	0.000	0.000	0.000	0.999	0.000
						1.999	0.008	0.000	0.000	0.000	0.000
							1.119	0.021	0.021	0.000	0.008
								1.959	0.039	0.000	0.000
									1.959	0.000	0.000
										0.977	0.000
											1.999

$E = -144.89$ a.u.

$N_H = 0.937$

$N_C = 6.122$

$N_O = 8.014$

TABLE 9

FORMALDEHYDE - EXACT INTEGRALS OVER AN ORTHONORMAL HYBRID BASIS
FULL CALCULATION. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{\sigma}_C$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\pi}_C$	$\bar{k}_C$	$\bar{\sigma}_O$	$\bar{\ell}_{10}$	$\bar{\ell}_{20}$	$\bar{\pi}_O$	$\bar{k}_O$
0.892	0.000	0.000	0.987	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.892	0.000	0.000	0.987	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		0.887	0.000	0.000	0.000	0.000	0.986	0.000	0.000	0.000	0.000
			1.108	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
				1.108	0.000	0.000	0.000	0.000	0.000	0.000	0.000
					1.066	0.000	0.000	0.000	0.000	0.878	0.000
						2.000	0.000	0.000	0.000	0.000	0.000
							1.113	0.000	0.000	0.000	0.000
								2.000	0.000	0.000	0.000
									2.000	0.000	0.000
										0.934	0.000
											2.000

$E = -144.92$ a.u.

$N_H = 0.892$

$N_C = 6.169$

$N_O = 8.047$

TABLE 10

FORMALDEHYDE - EXACT INTEGRALS OVER AN ORTHONORMAL HYBRID BASIS AND NDDO APPROXIMATION. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{\sigma}_C$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\pi}_C$	$\bar{k}_C$	$\bar{\sigma}_O$	$\bar{\ell}_{1O}$	$\bar{\ell}_{2O}$	$\bar{\pi}_O$	$\bar{k}_O$
0.876	-0.048	0.270	0.950	-0.043	0.000	-0.007	0.034	-0.011	0.055	0.000	-0.002
	0.876	0.270	-0.043	0.950	0.000	-0.007	0.034	0.055	-0.011	0.000	-0.002
		0.877	0.061	0.061	0.000	0.005	0.892	-0.132	-0.132	0.000	-0.005
			1.117	0.037	0.000	0.005	-0.272	0.046	-0.015	0.000	0.003
				1.117	0.000	0.005	-0.272	-0.015	0.046	0.000	0.003
					1.114	0.000	0.000	0.000	0.000	0.993	0.000
						2.000	0.000	0.000	0.000	0.000	0.000
							1.172	0.109	0.109	0.000	0.005
								1.982	-0.014	0.000	-0.001
									1.982	0.000	-0.001
										0.885	00.000
											2.000

E = -143.89 a.u.

N_H = 0.876

N_C = 6.224

N_O = 8.020

TABLE 11

FORMALDEHYDE - EXACT INTEGRALS OVER AN ORTHONORMAL HYBRID BASIS AND CNDO APPROXIMATION. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{\sigma}_C$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\pi}_C$	$\bar{k}_C$	$\bar{\sigma}_O$	$\bar{\ell}_{1O}$	$\bar{\ell}_{2O}$	$\bar{\pi}_O$	$\bar{k}_O$
0.822	0.464	0.237	0.819	0.053	0.000	0.018	-0.099	0.074	0.085	0.000	0.000
	0.822	0.237	0.053	0.819	0.000	0.018	-0.099	0.085	0.074	0.000	0.000
		0.994	0.069	0.069	0.000	-0.004	0.860	-0.265	-0.265	0.000	0.002
			1.137	-0.505	0.000	-0.025	-0.215	-0.004	-0.009	0.000	-0.001
				1.137	0.000	-0.025	-0.215	-0.009	-0.004	0.000	-0.001
					1.298	0.000	0.000	0.000	0.000	0.955	0.000
						2.000	-0.002	-0.002	-0.002	0.000	0.000
							1.232	0.221	0.221	0.000	-0.002
								1.929	-0.071	0.000	0.000
									1.929	0.000	0.000
										0.702	0.000
											2.000

$E = -143.05$ a.u.

$N_H = 0.822$

$N_C = 6.565$

$N_O = 7.792$

TABLE 12

FORMALDEHYDE - ORBITAL ENERGIES OF SCF MO CALCULATIONS

	Complete Calculation	NDDO Calculation	CNDO Calculation
ϕ_1	-20.588	-20.365	-20.377
ϕ_2	-11.338	-11.074	-10.863
ϕ_3	-1.360	-1.177	-1.043
ϕ_4	-0.830	-0.859	-0.571
ϕ_5	-0.674	-0.388	-0.547
ϕ_6	-0.563	-0.231	-0.058
ϕ_7	-0.468	-0.311	-0.089
ϕ_8	-0.384	-0.497	-0.375

TABLE 13

FORMALDEHYDE - COULOMB INTEGRALS OVER HYBRID BASIS ONE-CENTRE INTEGRALS

Integral	Non-Orthogonal	Orthogonal	% Diff.
$h_1h_1h_1h_1$	0.750	0.845	12.66
$\sigma_C\sigma_C\sigma_C\sigma_C$	0.727	0.718	-1.44
$b_1b_1\sigma_C\sigma_C$	0.530	0.613	16.36
$b_1b_1b_1b_1$	0.727	0.778	8.47
$b_2b_2b_1b_1$	0.530	0.625	18.69
$\pi_C\pi_C\sigma_C\sigma_C$	0.575	0.605	5.70
$\pi_C\pi_Cb_1b_1$	0.575	0.620	8.41
$\pi_C\pi_C\pi_C\pi_C$	0.636	0.644	1.26
$k_Ck_C\sigma_C\sigma_C$	0.807	0.883	9.22
$k_Ck_Cb_1b_1$	0.807	0.918	13.60
$k_Ck_C\pi_C\pi_C$	0.807	0.815	0.94
$k_Ck_Ck_Ck_C$	3.5625	3.5625	0.00
$\sigma_O\sigma_O\sigma_O\sigma_O$	1.017	1.114	11.12
$\ell_1\ell_1\sigma_O\sigma_O$	0.742	0.801	8.64
$\ell_1\ell_1\ell_1\ell_1$	1.017	1.012	-0.49
$\ell_2\ell_2\ell_1\ell_1$	0.742	0.736	-0.81
$\pi_O\pi_O\ell_1\ell_1$	0.805	0.811	0.75
$\pi_O\pi_O\pi_O\pi_O$	0.890	0.904	1.48
$k_Ok_O\sigma_O\sigma_O$	1.130	1.288	13.85
$k_Ok_O\ell_1\ell_1$	1.130	1.140	0.77
$k_Ok_O\pi_O\pi_O$	1.130	1.143	1.17
$k_Ok_Ok_Ok_O$	4.8125	4.8125	0.00

TABLE 13 (CONTD.)

FORMALDEHYDE - COULOMB INTEGRALS OVER HYBRID BASIS TWO-CENTRE INTEGRALS

Integral	Non-Orthogonal	Orthogonal	% Diff.
$h_2h_2h_1h_1$	0.286	0.253	-11.84
$\sigma_C\sigma_Ch_1h_1$	0.376	0.371	-1.33
$b_1b_1h_1h_1$	0.599	0.507	-15.29
$b_1b_1h_2h_2$	0.376	0.371	-1.10
$\pi_C\pi_Ch_1h_1$	0.419	0.386	-7.75
$k_Ck_Ch_1h_1$	0.485	0.437	-10.39
$\sigma_O\sigma_Oh_1h_1$	0.310	0.279	-10.04
$\sigma_O\sigma_O\sigma_C\sigma_C$	0.718	0.589	-17.71
$\sigma_O\sigma_Ob_1b_1$	0.423	0.428	1.40
$\sigma_O\sigma_O\pi_C\pi_C$	0.475	0.443	-6.76
$\sigma_O\sigma_Ok_Ck_C$	0.575	0.530	-7.64
$\ell_1\ell_1h_1h_1$	0.262	0.249	-5.27
$\ell_1\ell_1h_2h_2$	0.236	0.225	-4.63
$\ell_1\ell_1\sigma_C\sigma_C$	0.496	0.431	-13.01

TABLE 13 (CONTD.)

FORMALDEHYDE - COULOMB INTEGRALS OVER HYBRID BASIS
TWO-CENTRE INTEGRALS

Integral	Non-Orthogonal	Orthogonal	% Diff.
$\ell_1\ell_1b_1b_1$	0.324	0.339	-4.94
$\ell_1\ell_1b_2b_2$	0.304	0.324	6.88
$\ell_1\ell_1\pi_C\pi_C$	0.345	0.343	-0.35
$\ell_1\ell_1k_Ck_C$	0.374	0.381	2.12
$\pi_O\pi_Oh_1h_1$	0.262	0.246	-6.08
$\pi_O\pi_O\sigma_C\sigma_C$	0.545	0.467	-14.58
$\pi_O\pi_Ob_1b_1$	0.336	0.353	4.92
$\pi_O\pi_O\pi_C\pi_C$	0.380	0.373	-2.11
$\pi_O\pi_Ok_Ck_C$	0.411	0.409	-0.46
$k_Ok_Oh_1h_1$	0.268	0.252	-6.01
$k_Ok_O\sigma_C\sigma_C$	0.614	0.511	-17.05
$k_Ok_Ob_1b_1$	0.348	0.370	6.10
$k_Ok_O\pi_C\pi_C$	0.389	0.385	-1.19
$k_Ok_Ok_Ck_C$	0.435	0.435	0.00

TABLE 14

FORMALDEHYDE - INTEGRALS AS DESCRIBED IN TEXT. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{\sigma}_C$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\pi}_C$	$\bar{k}_C$	$\bar{\sigma}_O$	$\bar{\ell}_{1O}$	$\bar{\ell}_{2O}$	$\bar{\pi}_O$	$\bar{k}_O$
0.736	0.118	0.292	0.893	-0.020	0.000	-0.007	0.147	-0.096	0.048	0.000	-0.002
	0.736	0.292	-0.020	0.893	0.000	-0.007	0.147	0.048	-0.096	0.000	-0.002
		0.757	-0.020	-0.020	0.000	0.010	0.844	-0.164	-0.164	0.000	-0.001
			1.328	-0.068	0.000	0.004	-0.282	0.099	0.003	0.000	0.002
				1.328	0.000	0.004	-0.282	0.003	0.099	0.000	0.002
					0.800	0.000	0.000	0.000	0.000	0.979	0.000
						2.000	-0.004	0.001	0.001	0.000	0.000
							1.194	0.154	0.154	0.000	0.002
								1.963	-0.022	0.000	-0.001
									1.963	0.000	-0.001
										1.201	0.000
											2.000

$E = -144.24$ a.u.

$N_H = 0.736$

$N_C = 6.207$

$N_O = 8.221$

TABLE 15

FORMALDEHYDE - INTEGRALS AS DESCRIBED IN TEXT. SCGF.

$\bar{h}_1$	$\bar{h}_2$	$\bar{\sigma}_C$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\pi}_C$	$\bar{k}_C$	$\bar{\sigma}_O$	$\bar{\ell}_{1O}$	$\bar{\ell}_{2O}$	$\bar{\pi}_O$	$\bar{k}_O$
0.805	0.000	0.000	0.950	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.805	0.000	0.000	0.950	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		0.660	0.000	0.000	0.000	0.000	0.933	0.000	0.000	0.000	0.000
			1.195	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
				1.195	0.000	0.000	0.000	0.000	0.000	0.000	0.000
					1.039	0.000	0.000	0.000	0.000	0.700	0.000
						2.000	0.000	0.000	0.000	0.000	0.000
							1.340	0.000	0.000	0.000	0.000
								2.000	0.000	0.000	0.000
									2.000	0.000	0.000
										0.961	0.000
											2.000

$E = -144.06$ a.u.

$N_H = 0.805$

$N_C = 6.089$

$N_O = 8.301$

TABLE 16

FORMALDEHYDE - USING POPLE AND SEGAL'S APPROXIMATION CNDO/1. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{s}_C$	$\bar{x}_C$	$\bar{y}_C$	$\bar{z}_C$	$\bar{s}_O$	$\bar{x}_O$	$\bar{y}_O$	$\bar{z}_O$
1.057	-0.128	0.578	0.402	0.770	0.000	0.013	-0.044	-0.184	0.000
	1.057	0.578	0.402	-0.770	0.000	0.013	-0.044	0.184	0.000
		1.064	0.056	0.000	0.000	0.273	0.500	0.000	0.000
			0.932	0.000	0.000	-0.460	-0.676	0.000	0.000
				0.898	0.000	0.000	0.000	0.302	0.000
					0.988	0.000	0.000	0.000	1.000
						1.735	-0.416	0.000	0.000
							1.340	0.000	0.000
								1.917	0.000
									1.012

$N_H = 1.057$

$N_C = 3.882$

$N_O = 6.004$

TABLE 17

FORMALDEHYDE - USING POPLE AND SEGAL'S APPROXIMATION CNDO/2. SCF MO.

$\bar{h}_1$	$\bar{h}_2$	$\bar{s}_C$	$\bar{x}_C$	$\bar{y}_C$	$\bar{z}_C$	$\bar{s}_O$	$\bar{x}_O$	$\bar{y}_O$	$\bar{z}_O$
1.011	-0.114	0.580	0.395	0.680	0.000	0.012	-0.037	-0.174	0.000
	1.011	0.580	0.395	-0.680	0.000	0.012	-0.037	0.174	0.000
		1.071	0.084	0.000	0.000	0.278	0.487	0.000	0.000
			0.931	0.000	0.000	-0.468	-0.676	0.000	0.000
				0.944	0.000	0.000	0.000	0.271	0.000
					0.845	0.000	0.000	0.000	0.988
						1.732	-0.409	0.000	0.000
							1.369	0.000	0.000
								1.930	0.000
									1.155

$N_H = 1.011$

$N_C = 3.791$

$N_O = 6.186$

TABLE 18

HYDROGEN CYANIDE - INTEGRALS AS DESCRIBED IN TEXT. SCF MO.

$\bar{h}_1$	$\bar{\sigma}_C$	$\bar{b}_1$	$\bar{\pi}_1$	$\bar{\pi}_2$	k_C	$\bar{\sigma}_N$	$\bar{\ell}_N$	$\bar{\pi}_3$	$\bar{\pi}_4$	k_N
0.685	0.424	0.805	0.000	0.000	-0.006	0.264	-0.055	0.000	0.000	-0.003
	0.794	-0.010	0.000	0.000	0.014	0.790	-0.391	0.000	0.000	-0.002
		1.449	0.000	0.000	0.001	-0.366	0.129	0.000	0.000	0.002
			0.948	0.000	0.000	0.000	0.000	1.000	0.000	0.000
				0.948	0.000	0.000	0.000	0.000	1.000	00.000
					2.000	-0.008	0.004	0.000	0.000	0.000
						1.231	0.346	0.000	0.000	0.003
							1.841	0.000	0.000	-0.001
								1.052	0.000	0.000
									1.052	0.000
										2.000

$E = -116.16$ a.u.

$N_H = 0.685$

$N_C = 6.139$

$N_N = 7.176$

TABLE 19

HYDROGEN CYANIDE - INTEGRALS AS DESCRIBED IN TEXT. SCGF.

$\bar{h}_1$	$\bar{\sigma}_C$	$\bar{b}_1$	$\bar{\pi}_1$	$\bar{\pi}_2$	$\bar{k}_C$	$\bar{\sigma}_N$	$\bar{\ell}_N$	$\bar{\pi}_3$	$\bar{\pi}_4$	$\bar{k}_N$
0.682	0.000	0.931	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.671	0.000	0.000	0.000	0.000	0.941	0.000	0.000	0.000	0.000
		1.318	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
			1.051	0.000	0.000	0.000	0.000	0.850	0.000	0.000
				1.051	0.000	0.000	0.000	0.000	0.850	0.000
					2.000	0.000	0.000	0.000	0.000	0.000
						1.329	0.000	0.000	0.000	0.000
							2.000	0.000	0.000	0.000
								0.949	0.000	0.000
									0.949	0.000
										2.000

$E = -115.825$ a.u.

$N_H = 0.682$

$N_C = 6.091$

$N_N = 7.227$

TABLE 20

HYDROGEN CYANIDE - USING POPLE AND SEGAL'S APPROXIMATIONS CNDO/1. SCF MO.

$\bar{h}$	$\bar{s}_C$	$\bar{x}_C$	$\bar{y}_C$	$\bar{z}_C$	$\bar{s}_N$	$\bar{x}_N$	$\bar{y}_N$	$\bar{z}_N$
0.926	0.698	-0.701	0.000	0.000	0.023	0.122	0.000	0.000
	1.121	-0.041	0.000	0.000	0.361	-0.605	0.000	0.000
		0.962	0.000	0.000	0.468	-0.535	0.000	0.000
			1.008	0.000	0.000	0.000	1.000	0.000
				1.008	0.000	0.000	0.000	1.000
$N_H = 0.926$					1.655	0.469	0.000	0.000
$N_C = 4.099$						1.336	0.000	0.000
$N_N = 4.975$							0.992	0.000
								0.992

TABLE 21

HYDROGEN CYANIDE - USING POPLE AND SEGAL'S APPROXIMATIONS CNDO/2. SCF MO.

$\bar{h}$	$\bar{s}_C$	$\bar{x}_C$	$\bar{y}_C$	$\bar{z}_C$	$\bar{s}_N$	$\bar{x}_N$	$\bar{y}_N$	$\bar{z}_N$
0.982	0.698	-0.704	0.000	0.000	0.033	0.121	0.000	0.000
	1.082	-0.023	0.000	0.000	0.369	-0.607	0.000	0.000
		0.928	0.000	0.000	0.475	-0.522	0.000	0.000
			0.951	0.000	0.000	0.000	0.999	0.000
				0.951	0.000	0.000	0.000	0.999
$N_H = 0.982$					1.649	0.464	0.000	0.000
$N_C = 3.912$						1.358	0.000	0.000
$N_N = 5.105$							1.049	0.000
								1.049

TABLE 22

ETHYLENE - ONE-ELECTRON HAMILTONIAN, ORTHOGONAL HYBRID BASIS

$\bar{h}_1$	$\bar{h}_2$	$\bar{h}_3$	$\bar{h}_4$	$\bar{\sigma}_1$	$\bar{b}_1$	$\bar{b}_2$	$\bar{\pi}_1$	$\bar{k}_1$	$\bar{\sigma}_2$	$\bar{b}_3$	$\bar{b}_4$	$\bar{\pi}_2$	$\bar{k}_2$
-4.691	-0.004	0.021	-0.01	-0.256	-0.278	-0.190	0.000	-0.018	-0.016	-0.009	-0.013	0.000	-0.001
	-4.691	-0.01	0.021	-0.256	-0.190	-0.278	0.000	-0.018	-0.016	-0.013	-0.009	0.000	-0.001
		-4.691	-0.004	0.016	-0.009	-0.013	0.000	0.001	-0.256	-0.278	-0.190	0.000	-0.018
			-4.691	0.016	-0.013	-0.009	0.000	0.001	-0.256	-0.190	-0.278	0.000	-0.018
				-7.897	-0.112	-0.112	0.000	0.107	-0.404	-0.024	-0.024	0.000	-0.005
					-7.326	0.196	0.000	0.181	0.024	-0.031	-0.036	0.000	-0.010
						-7.326	0.000	0.181	0.024	-0.036	-0.031	0.000	-0.010
							-7.036	0.000	0.000	0.000	0.000	-0.046	0.000
								-21.800	0.005	-0.010	-0.010	0.000	0.000
									-7.987	-0.112	-0.112	0.000	0.107
										-7.326	0.196	0.000	0.181
											-7.326	0.000	0.181
												-7.036	0.000
													-21.800

TABLE 23

NON-COULOMBIC INTEGRALS FOR WATER MOLECULE

Integral	Non-Orthogonal Hybrid Basis	Orthogonal Hybrid Basis
$(h_2h_2 \vert h_1h_1)$	.1757	-.0119
$(h_2h_1 \vert h_2h_1)$	.0685	.0029
$(b_1h_1 \vert h_1h_1)$	.3615	.0246
$(b_1h_1 \vert h_2h_1)$	.1118	.0004
$(b_1h_1 \vert h_2h_2)$	.2116	.0063
$(b_1h_1 \vert b_1h_1)$	.2507	.0143
$(b_1h_2 \vert h_1h_1)$	.1069	.0167
$(b_1h_2 \vert h_2h_1)$	.0374	.0007
$(b_1h_2 \vert h_2h_2)$	.0699	-.0081
$(b_1h_2 \vert b_1h_1)$	.0822	.0017
$(b_1h_2 \vert b_1h_2)$	.0359	.0050
$(b_1b_1 \vert h_2h_1)$	.2124	-.0045
$(b_1b_1 \vert b_1h_1)$	.4582	.0228
$(b_1b_1 \vert b_1h_2)$	.1501	.0334
$(b_2h_1 \vert b_1h_1)$	.0490	-.0010
$(b_2h_1 \vert b_1h_2)$	.0212	.0002
$(b_2h_1 \vert b_1b_1)$	.1079	.0181
$(b_2h_2 \vert b_1h_1)$	.1442	.0017
$(b_2h_2 \vert b_1b_1)$	.3283	.0002
$(b_2b_1 \vert h_2h_1)$	.0150	.0020
$(b_2b_1 \vert b_1h_1)$	.0272	.0077
$(b_2b_1 \vert b_1h_2)$	.0285	-.0003
$(b_2b_2 \vert b_1h_1)$	.3283	.0002
$(b_2b_2 \vert b_1h_2)$	.1079	.0181
$(\ell_1h_1 \vert h_1h_1)$	.0837	-.0205
$(\ell_1h_1 \vert h_2h_1)$	.0298	.0003

TABLE 23 (CONTD.)

NON-COULOMBIC INTEGRALS FOR WATER MOLECULE

Integral	Non-Orthogonal Hybrid Basis	Orthogonal Hybrid Basis
$(\ell_1 h_1 \| h_2 h_2)$	.0669	.0050
$(\ell_1 h_1 \| b_1 h_1)$	.0586	-.0012
$(\ell_1 h_1 \| b_1 h_2)$	.0149	-.0007
$(\ell_1 h_1 \| b_1 b_1)$	.1291	.0075
$(\ell_1 h_1 \| b_2 h_1)$	.0089	.0011
$(\ell_1 h_1 \| b_2 h_2)$	.0451	-.0004
$(\ell_1 h_1 \| b_2 b_1)$	-.0121	-.0071
$(\ell_1 h_1 \| b_2 b_2)$	.1142	.0187
$(\ell_1 h_1 \| \ell_1 h_1)$	.0391	.0045
$(\ell_1 h_2 \| \ell_1 h_1)$	.0399	.0108
$(\ell_1 b_1 \| h_2 h_1)$	.0016	-.0004
$(\ell_1 b_1 \| b_1 h_1)$	.0326	.0069
$(\ell_1 b_1 \| b_1 h_2)$	.0158	.0069
$(\ell_1 b_1 \| b_2 h_1)$	-.0121	-.0061
$(\ell_1 b_1 \| b_2 h_2)$	-.0218	-.0055
$(\ell_1 b_1 \| \ell_1 h_1)$	.0241	-.0022
$(\ell_1 b_1 \| \ell_1 h_2)$	.0072	.0049
$(\ell_1 \ell_1 \| h_2 h_1)$	.1829	-.0026
$(\ell_1 \ell_1 \| b_1 h_1)$	.3204	-.0022
$(\ell_1 \ell_1 \| b_1 h_2)$	.0893	.0228
$(\ell_1 \ell_1 \| \ell_1 h_1)$	.1723	.0310
$(\ell_2 \ell_1 \| h_2 h_1)$	-.0115	-.0007
$(\ell_2 \ell_1 \| b_1 h_1)$	.0261	-.0076
$(\ell_2 \ell_1 \| b_1 h_2)$	-.0210	-.0001
$(\ell_2 \ell_1 \| \ell_1 h_1)$	.0086	.0062
$(\ell_2 \ell_2 \| \ell_1 h_1)$	.1069	.0165

APPENDIX

OUTLINE OF PROGRAM SYSTEM

During the course of the work described in this thesis a considerable body of programs was developed. The scheme of these programs is described below. Details of the function of the programs and of the data required are given and the overall scheme is illustrated in flow diagram form.

The series consists of

(1) Programs to calculate the one-electron Hamiltonian and the two-electron repulsion integrals over a standard orbital basis (p.56). (Note that a program was developed for the coulomb type two-electron integrals and other two-electron integrals were approximated in various ways described in Chapter 5).

(2) A program to calculate the transformation matrix from the standard orbital to an orthogonalised hybrid basis.

(3) A program to transform the one-electron and two-electron integrals over the standard orbital basis to

integrals over the orthogonalised hybrid basis.

(4) SCF programs to obtain the self-consistent wave function using the integrals over the orthogonalised hybrid basis.

The Jacobi diagonalisation routine and the SCFMO programs used were already available. The SCGF program and the three-centre numerical integration programs were developed by colleagues with some help from the author. The other programs described, the one-electron Hamiltonian, the overlap integrals, the two-electron coulomb integrals, the transformation to a standard orbital and hybrid basis, the transformation matrix from a standard orbital to an orthogonalised hybrid basis, and the transformation programs, were developed by the author during the course of the work described in this thesis.

(1) The calculation of the one-electron Hamiltonian integrals over a standard orbital basis

Input Coordinates, orbital exponents and nuclear charge for each centre and the three-centre nuclear attraction integrals for the system.

The one- and two-centre parts of the Hamiltonian are calculated over a sig Slater orbital basis and the three-centre integrals are calculated separately, by numerical integration, and added in to the one- and two-centre parts. The integrals are then transformed to a standard orbital basis or alternatively to a hybrid basis (the hybridisation is specified by data).

(2) The calculation of the coulomb type two-electron integrals over a standard orbital basis

Input Coordinates, orbital exponents and nuclear charge for each centre.

Again the integrals are calculated over a sigma-pi basis and then transformed to a standard orbital basis or alternatively to a hybrid basis (the hybridisation is specified by data). The two-electron transformation required is built into the program.

(3) The calculation of the transformation matrix, $WU\bar{S}^{-\frac{1}{2}}$, between the standard orbital and the orthogonlaised hybrid basis

$\bar{S}$ is the matrix of overlap integrals for the Schmidt orthogonalised hybrid basis, $\underline{W}$ the transformation matrix to a Schmidt orthogonalised basis, and $\underline{U}$ to a hybrid basis. The program consists of the following steps:

(a) The overlap matrix $\underline{S}$ over the standard orbital basis is calculated. Input Coordinates, orbital exponents and nuclear charges for each centre.

(b) Calculation of $\underline{W}$ Input Overlap matrix $\underline{S}$.

(c) Calculation of $\underline{U}$ Input Data specifying hybrids.

(d) Transformation of overlap integrals to a Schmidt orthogonalised hybrid basis $\bar{\underline{S}}$. Input $\underline{S}$, $\underline{W}$ and $\underline{U}$.

(e) Formation of $\bar{\underline{S}}^{-\frac{1}{2}}$ by using Jacobi diagonalisation, the diagonalisation process being terminated when $|\bar{S}_{pq}|_{max} \leqq 10^{-8}$. Input $\bar{\underline{S}}$

(f) Formation of $\underline{WU\bar{S}}^{-\frac{1}{2}}$ Input $\underline{W}$, $\underline{U}$ and $\bar{\underline{S}}^{-\frac{1}{2}}$.

(4) The transformation of the one-electron and two-electron integrals to an orthogonalised hybrid basis

Input One-electron Hamiltonian and two-electron repulsion integrals over a standard orbital basis. Transformation matrix $\underline{WU\bar{S}}^{-\frac{1}{2}}$.

All one-electron integrals over the transformed basis are obtained. For the two-electron integrals, there is a choice of obtaining all integrals over the transformed basis, or of obtaining only those which are non-zero in the CNDO or the NDDO approximations.

(5) Self-Consistent Field Programs

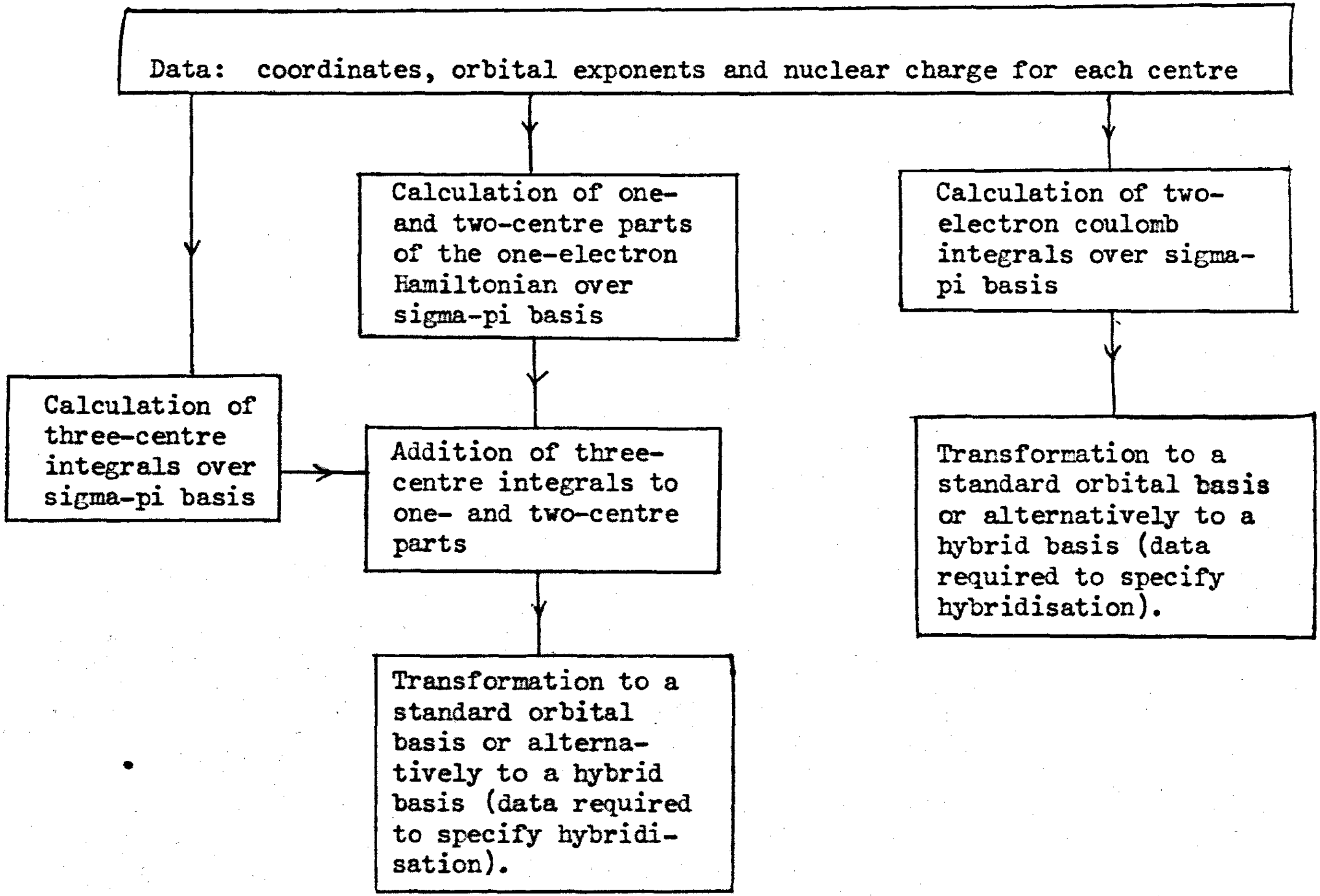
Input The one-electron Hamiltonian and the two-electron repulsion integrals over an orthogonalised basis. An initial matrix

$\underline{R}$ of atom charges and bond orders.

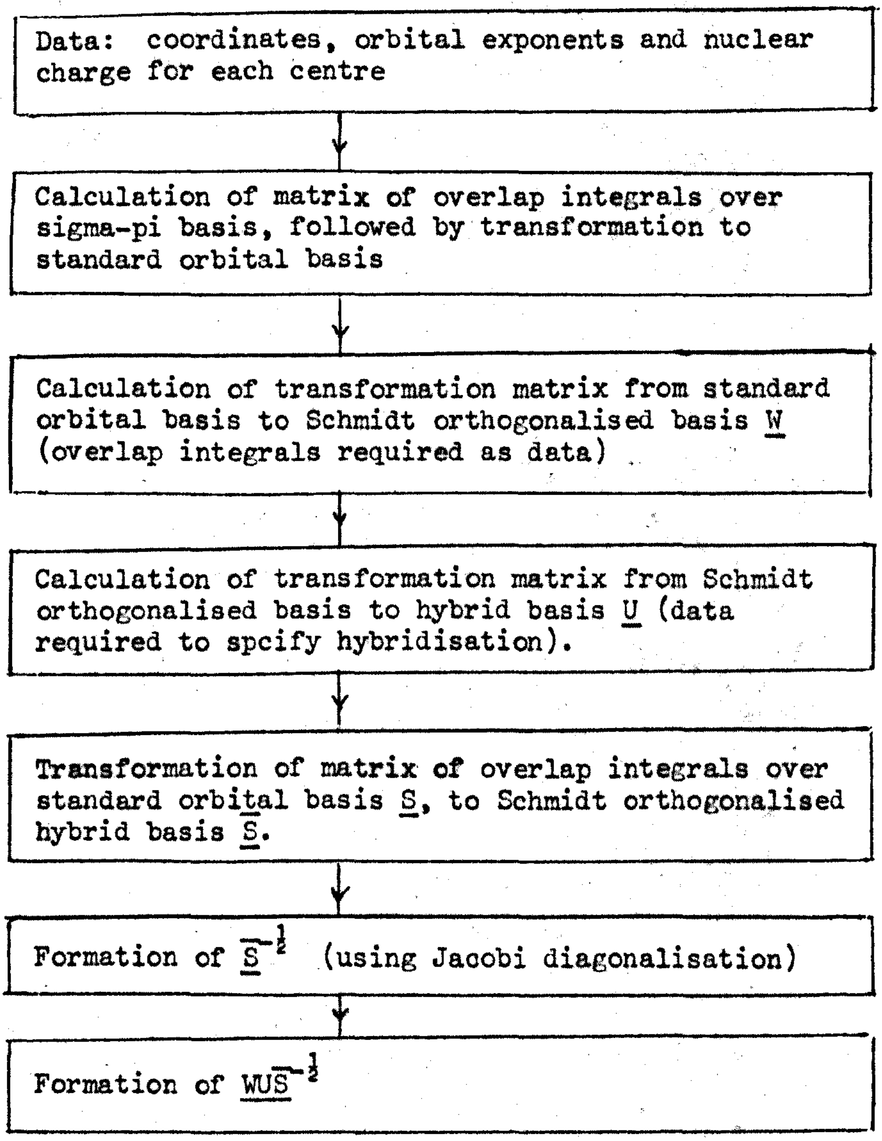
This form of input is required for both the molecular orbital and group function methods. In the case of the group function program, orbitals belonging to each group must also be specified; in addition, since not all the available integrals are required in this approach, a sorting program is first entered to select those needed for the calculation. With these preliminaries completed, the main group function program, described on p.68, is then entered.

The self-consistency procedure is terminated when $\sum_{i,j} |\delta R_{ij}|$ in a cycle $\leq 10^{-4}$ and the self-consistent atom charges, bond orders, orbital and total energies are then given.

I FLOW DIAGRAM ILLUSTRATION CALCULATION OF INTEGRALS OVER A STANDARD ORBITAL BASIS



II FLOW DIAGRAM FOR CALCULATION OF TRANSFORMATION MATRIX $(\underline{WU\bar{S}}^{-\frac{1}{2}})$ FROM STANDARD ORBITAL TO ORTHOGONALISED HYBRID BASIS



Data: coordinates, orbital exponents and nuclear charge for each centre

Calculation of matrix of overlap integrals over sigma-pi basis, followed by transformation to standard orbital basis

Calculation of transformation matrix from standard orbital basis to Schmidt orthogonalised basis $\underline{W}$ (overlap integrals required as data)

Calculation of transformation matrix from Schmidt orthogonalised basis to hybrid basis $\underline{U}$ (data required to spcify hybridisation).

Transformation of matrix of overlap integrals over standard orbital basis $\underline{S}$, to Schmidt orthogonalised hybrid basis $\underline{S}$.

Formation of $\underline{\bar{S}}^{-\frac{1}{2}}$ (using Jacobi diagonalisation)

Formation of $\underline{WU\bar{S}}^{-\frac{1}{2}}$

III FLOW DIAGRAM ILLUSTRATING OVERALL SCHEME OF THE PROGRAMS