A CONFIGURATION INTERACTION STUDY OF THE ELECTRONIC STATES OF THE WATER MOLECULE

by

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ABSTRACT

Not much really quantitative work has been done in determining the electronic structure of polyatomic molecules. The lack of the required integrals over orbits on several centers and use of inadequate representations of the electronic wave functions have resulted in calculations which, while giving some indication of the electronic behavior, do not agree well with experimental data. The purpose of this thesis was to examine in the case of the water molecule the effect of using accurate integral values and a more flexible representation for the wave function than has been used before.

The results point the way to quantitative calculations of molecular electronic behavior by showing that the accurate integrals do give to the energy the proper behavior with change of geometrical parameters and that a well chosen basis set of atomic orbitals can give rise to a many-electron function with a good value of binding energy. Further, the results also indicate that a rather simple approximation, a valence-bond function with some correlation between electrons of opposite spin, may be able to give energy values which are a good compromise between accuracy and ease of computation. This method, which has been compared with the configuration interaction study, can be extended with relative ease to larger molecules.

Thesis Advisor: John C. Slater
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The computations were mostly done on the I. B. M. 709 at the Computation Center of the Massachusetts Institute of Technology.
# TABLE OF CONTENTS

Abstract
Table of Contents
List of Figures and Tables

Chapter I: Introduction to the Problem
1. Previous Studies on the Water Molecule
2. Configuration Interaction and the Present Study

Chapter II: Atomic Basis Orbitals and Molecular Integrals
1. Choice of the Primitive Atomic Orbitals
2. Orthogonalization of the Hydrogen Orbitals
3. Hybridization of the 2s and 2pz Orbitals
4. The Molecular Integrals

Chapter III: The Configurations and Their Interaction Matrix
1. Determinantal Functions
2. Symmetry Functions
3. Matrix Elements of the Hamiltonian with Respect to the Symmetry Functions

Chapter IV: The Extended Valence-Bond Approximation
1. The Total Wave Function
2. The Electronic Energy

Chapter V: Discussion of Results
1. Radial Flexibility in the Atomic Basis Orbitals
2. Energy Level Variation with Molecular Geometry
3. The Extended Valence-Bond Approximation
4. Conclusions and Prospects for the Future

References
Biographical Sketch
List of Figures and Tables

Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1:</td>
<td>Coordinate system for H₂O</td>
<td>25</td>
</tr>
<tr>
<td>5-1:</td>
<td>Variation of Energy with OH Distance</td>
<td>55</td>
</tr>
<tr>
<td>5-2:</td>
<td>Variation of Energy with Interband Angle</td>
<td>56</td>
</tr>
</tbody>
</table>

Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1:</td>
<td>Code for Orbital Assignments</td>
<td>28</td>
</tr>
<tr>
<td>3-2:</td>
<td>Symmetry functions for H₂O, in terms of Determinantal functions</td>
<td>33</td>
</tr>
<tr>
<td>5-1:</td>
<td>Dependence of Ground State Energy of H₂O on the Form of the Oxygen 2s and 2p Orbitals</td>
<td>52</td>
</tr>
<tr>
<td>5-2:</td>
<td>Expansion of Total Wave Function in Symmetry Functions</td>
<td>61</td>
</tr>
</tbody>
</table>
CHAPTER I: INTRODUCTION TO THE PROBLEM

Although an increasing amount of significant quantum theoretical calculation of electronic structure is being carried out for atoms\(^1\) and for diatomic molecules\(^2\), only a beginning has been made towards finding an accurate and manageable method to solve the many-electron problem in the case of polyatomic molecules.\(^3\) Two obstacles have stood in the way of progress in handling these systems, the lack of sufficiently accurate methods for evaluating the three- and four-center electron interaction integrals which occur and the difficulty of choosing an adequate representation for the many-electron wave function.

Fortunately, computer programs are now becoming available which will compute the necessary integrals with whatever accuracy is desired. There remains, then, as the main task of the present study, the investigation of several representations of the electronic wave function with a comparison of the resulting energy eigenvalues and electron distributions. In particular, we wish to compare the relatively simple "extended valence-bond" method\(^4\) with a much more elaborate configuration interaction treatment. The variation of the energy states with changes of nuclear configuration will also be investigated for a small number of different values of OH bond length and of interbond angle.
1. Previous Studies on the Water Molecule

The water molecule has been chosen as the subject of this study because it is one of the simplest triatomic molecules. Further, three rather extensive investigations of the electronic structure of H₂O have been made in recent years. Although it will be our contention that much of this previous work is severely damaged by the use of approximate integrals and rather limited forms for the atomic wave functions, we have used these studies as a starting point from which to make improvements.

Ellison and Shull(5) have studied the electronic ground state by a self-consistent field approach, using linear combinations of Slater-type atomic orbitals to represent the molecular orbitals. Approximate values are used for the three-center integrals and there is a further, systematic error introduced by using the wrong value for one of the overlap integrals in the orthogonalization process.

Besides repeating the calculations of Ellison and Shull without the overlap error, McWeeny and Ohno(6) have also studied the ground state electronic structure by the bond-orbital and the electron-pair approximations. In the bond-orbital approach, which is a special case of the electron-pair method, McWeeny and Ohno investigate the importance of a limited configuration interaction in which electrons are assigned to "anti-bond" orbitals. Granted the errors introduced from the use of approximate integral values and single-term Slater functions to represent the atomic orbitals, McWeeny and Ohno find that the
configuration interaction extension of the bond-orbital method is the most accurate of the methods they used, although they point out that there is no advantage to such an approach over a configuration interaction based on atomic, rather than bond, orbitals. They also found that the electron-pair approximation, which is the method we call "extended valence-bond", provides a good compromise between accuracy and simplicity.

Although the studies of Ellison and Shull and of McWeeny and Ohno produced rather good values for the dissociation energy of H₂O, more than 75% of the experimental value, we shall see that this is a fortuitous consequence of the approximate integrals. Another, less happy, result of using these integral values is the lack of an energy minimum as the interbond angle is varied.

A more elaborate configuration interaction study, with rigorously computed integral values, has been done by Boys and others. Single-term Slater-type orbitals with fixed exponents are used. The dissociation energy is less satisfactory than that of the calculations done with the same orbitals and approximate integrals, which corresponds to our findings. The equilibrium angle and bond length found by Boys' group will be considered later on in this study when we discuss our own results of varying the angle and internuclear separation.
2. Configuration Interaction and the Present Study

The method of superposition or mixing of configurations, when the configurations form a complete set, offers a rigorous method for the exact solution of the non-relativistic Schrödinger equation for a many-electron problem. The total electronic wave function is the solution to the equation

$$ H\psi = E\psi, \quad (1-1) $$

where $H$ is the Hamiltonian operator for a system of $N$ electrons, with magnetic effects and motion of the nuclei neglected, and $E$ is the energy of the state. The wave function, $\psi$, can be expanded in a series of product functions constructed from a complete set of single-electron spin-orbitals, $\phi_{i}$:

$$ \psi = \sum_{q} B_{q} \phi_{q}^{1}(\vec{r}_{1})\phi_{q}^{2}(\vec{r}_{2}) \ldots \phi_{q}^{N}(\vec{r}_{N}) \quad (1-2) $$

where all possible assignments of electrons to orbitals are included. The expansion can be simplified if we take advantage of the symmetries of the problem in question. First, because we are dealing with electrons, the total wave function must be antisymmetric under interchange of any two particles. Therefore we use determinantal functions, antisymmetrized products, of the $N$ electron orbitals rather than simple products:

$$ D_{j}(\vec{r}_{1}, \vec{r}_{2}, \ldots, \vec{r}_{N}) = \sum_{p} (-1)^{p} P \phi_{1}^{j}(\vec{r}_{1})\phi_{2}^{j}(\vec{r}_{2}) \ldots \phi_{N}^{j}(\vec{r}_{N}), \quad (1-3) $$
where the summation is over all permutations of electrons among the orbitals. Each determinant is defined by the configuration or selection of N orbitals from which it is constructed. States of definite space and spin symmetry $\alpha$ can now be formed from the determinantal functions by making appropriate linear combinations:

$$S_1^\alpha(\mathbf{r}_1^\alpha, \mathbf{r}_2^\alpha, \ldots, \mathbf{r}_N^\alpha) = \sum_j c_{ij}^\alpha D_j(\mathbf{r}_1^\alpha, \mathbf{r}_2^\alpha, \ldots, \mathbf{r}_N^\alpha). \quad (1-4)$$

The coefficients $c_{ij}^\alpha$ must be determined from the symmetry of the Hamiltonian operator. Their derivation for the case of the water molecule is outlined in Chapter III.

In terms of these product functions of definite symmetry, $S_1^\alpha$, the total wave function of symmetry $\alpha$ can be written:

$$\psi^\alpha(\mathbf{r}_1^\alpha, \mathbf{r}_2^\alpha, \ldots, \mathbf{r}_N^\alpha) = \sum_i U_i^\alpha S_1^\alpha(\mathbf{r}_1^\alpha, \mathbf{r}_2^\alpha, \ldots, \mathbf{r}_N^\alpha). \quad (1-5)$$

The coefficients $U_i^\alpha$ are determined by a variation procedure to minimize the expectation value of the energy computed from the function $\psi^\alpha$. This variation of the $U_i^\alpha$ leads to a secular equation, the solution of which requires the diagonalization of the Hamiltonian matrix with respect to the functions $S_1^\alpha$; i.e., the matrix with the elements

$$(S_1^\alpha | H | S_1^\alpha) - E^\alpha \delta_{ij}. \quad (1-6)$$

where $(S_1^\alpha | H | S_1^\alpha) = \int S_1^\alpha H S_1^\alpha dV_1 dV_2 \ldots dV_N$. The $S_i^\alpha$, constructed from an orthonormal set of single-particle functions, have overlaps

$$\int S_1^\alpha S_j^\alpha dV_1 \ldots dV_N = \delta_{ij}. \quad \text{The roots of the matrix of Eq. (1-6) are}$$
are the eigenvalues for the symmetry $a$ and the linear combinations of $S^a_1$ which diagonalize the energy are the corresponding eigenfunctions for these states.

A complete configuration interaction such as has been outlined here, starting with any complete set of orthonormal, one-electron spin-orbitals, would yield the exact solution to the N-electron problem specified by the Hamiltonian operator. For practical reasons, however, we must always restrict ourselves to a limited one-electron basis of a small number of orbitals. Since such a truncation of the one-electron basis set and, consequently, of the number of possible configurations is necessary, it is very important to choose these one-electron functions with some degree of physical insight to obtain as rapid a convergence of the expansion in configurations as possible. Much of the description of electronic behavior, which might have been handled by including more basis orbitals, must be taken care of by greater flexibility in the few functions used. One of the points to be investigated in this present study is the improvement in the total energy which results from some simple variations in the form of the basis functions. These variations, which are discussed in Chapter II, will not increase the number of basis functions beyond the K and L shell orbitals of oxygen and the K shell orbitals of the hydrogens, but they will allow these functions to more adequately represent the molecular electronic structure than would the single-term Slater functions with fixed screening parameters used by the previous investigators.
Once the one-electron basis set has been chosen and the determinantal functions $D_j$ constructed from the various allowed assignments of electrons to these orbitals, the coefficients $c_{ij}$ which yield the linear combinations of determinants according to Eq. (1-4) must be found. Using these coefficients, the elements of the Hamiltonian matrix of Eq. (1-6) can be written

\[
(S_i^a \mid H \mid S_j^a) = \sum_k \sum_f c_{ik}^a c_{jf}^a (D_k \mid H \mid D_f). \tag{1-7}
\]

Application of the rules for expressing matrix elements between determinantal functions in terms of integrals over the orbitals of which these functions are constructed, as will be shown in more detail in Chapter III, reduces the elements of the right side of Eq. (1-7) to simple sums over molecular integrals:

\[
(D_k \mid H \mid D_f) = \sum_i R_{ik}^{\ell} \phi_i^k | \phi_1^\ell \rangle + \sum_{ij} G_{ij}^{k\ell} [ (\phi_i^k | \phi_j \rangle - (\phi_j | \phi_i^k \rangle) - (\phi_i^k | \phi_j \rangle) + (\phi_j | \phi_i^k \rangle)], \tag{1-8}
\]

where

\[
(\phi_i^k \mid \phi_1^\ell) = \int \phi_i^k(r_1) \phi_1^\ell(r_1) \, dV_1
\]

and

\[
(\phi_i^k \phi_j^l | \phi_j^k \phi_1^l) = \int \phi_i^k(r_1) \phi_j^l(r_1) g_{12} \phi_j^k(r_2) \phi_1^l(r_2) \, dV_1 \, dV_2
\]

The operators, $f_i$ and $g_{ij}$, are the one-and two-electron terms in the Hamiltonian, i.e., $H = \sum_i f_i + \sum_{ij} g_{ij}$. The superscripts on the orbitals refer to the configuration or determinant to which they belong.
The coefficients, $F$, and $G$, as will be shown in Chapter III, are 0 or $\pm 1$.

Essentially, if one is to build up the Hamiltonian matrix of Eq. (1-6), one needs the integrals of Eq. (1-8), namely the one- and two-electron integrals in terms of the spin-orbitals of the basis set from which the determinantal functions are constructed. Actually, it has been found to be convenient to provide the computer with the necessary molecular integrals in terms of a more primitive, non-orthogonal basis and to have them converted to the appropriate orthogonal basis within the machine by a preliminary section of the program. Then, using the rules for reducing matrix elements between determinants and the set of coefficients $c_{ij}^a$, the program builds up the Hamiltonian matrix of Eq. (1-6) for each symmetry $a$ and diagonalizes. This is carried out for several angles and several oxygen-hydrogen separations. By the mixing of configurations, some of the correlation between electrons will be represented, but the limited basis does not allow a completely satisfying representation of this correlation.

By way of comparison a calculation of the electronic structure of the ground state only has also been made by the simpler method of the "extended valence-bond" or "modified electron-pair" approximation mentioned above. This method, found by the previous researchers to be the next best to configuration interaction, does handle some electron correlation within bonds. In calculations on more complicated molecules, configuration interaction of the scope used here would be practically impossible, while the modified electron-pair approximation could be manageable. Thus, in this case in which both can be done, it is
advantageous to compare their results.

In much of the work on the configuration interaction approximation, use was made of an unpublished memorandum of John C. Slater. In the Chapters that follow, when reference is made to Slater with no indication of a published work, it will be to this memorandum that the reference is made.
CHAPTER II: ATOMIC BASIS ORBITALS AND MOLECULAR INTEGRALS

Having considered in outline the process by which the Hamiltonian matrix elements in terms of the many-electron symmetry functions are reduced to sums of integrals over atomic single-particle functions, let us now follow the steps through in more detail and in the order in which the computer programs proceed, namely, from the integrals over atomic orbitals to the Hamiltonian matrix. In the present chapter, our attention will be focused on the choice of the primitive atomic orbitals and the transformations of these into a suitably orthogonalized and hybridized basis set, from which the determinantal many-electron functions will be constructed. The corresponding transformations of the molecular integrals in terms of the primitive basis to integrals in terms of the new basis will also be discussed.

1. Choice of the Primitive Atomic Orbitals

As was mentioned in the introduction, the choice of the form of the atomic orbitals is very important in a limited configuration interaction. Other calculations, particularly that of Karo and Allen(1) for the hydrogen fluoride molecule, have shown the importance of using atomic orbitals with a better radial dependence than that given by the use of single-term Slater-type functions. They found that atomic Hartree-Fock functions for F\(^-\) gave a considerably better result than the Slater-type functions with a single exponential. One would hope to get an even better result for the energy than that found by using atomic Hartree-Fock orbitals if one constructed an analytic function which approached the atomic
Hartree-Fock function for large internuclear separations but which could adjust to the molecular environment at closer internuclear distances. This approach has been explored in the present work with results which confirm our suspicions as to the importance of the form of the atomic orbitals.

In order to allow comparison with the results of McWeeny and Ohno, we first used the same primitive atomic basis set that they and the Ellison and Shull before them had used. This consists of single-term Slater-type orbitals with the screening constants chosen to give the best atomic energy. In our calculations, the integrals over these orbitals were not approximated but computed accurately. Further, the configuration interaction calculation for the ground state involves eighteen configurations and would have been thought to be far superior to any used by McWeeny and Ohno. Nevertheless, the results of our calculation with these orbitals are not as satisfactory when compared with experimental values for the dissociation energy and total molecular energy as those of Ohno and McWeeny. It seems that the estimated integrals gave a better result than would actually be justified by the orbitals and methods used. Thus, we decided to investigate the effect of using a more adequate representation of the radial dependence of the L shell orbitals on the oxygen.

As a first step, the simplest improvement on the single-term atomic orbitals seemed to be to add one or two more terms as needed to give a reasonably satisfactory fit to the atomic Hartree-
Fock functions since these were to be the limiting form of our functions in the case of large internuclear separation. It was found that two terms were adequate for the 2s orbital, while three were needed for the 2p orbitals. These terms correspond roughly to the core, peak, and tail of the function, with the core part of the 2s being handled by its orthogonalization to the 1s. The forms of the 2s functions, with the screening constants found to give the best fit for the atomic case, are as follows:

\[ 2s = r \sum_{i=1}^{2} B_i \left( \frac{k_1^5}{3\pi} \right) e^{-k_i r}, \quad (2-1) \]

where \( k_1 \) is the best single-term value, 2.275, and \( k_2 = .78 \). The coefficients \( B_i \) are free to vary, one of them being chosen so as to keep the function normalized. For the 2pz function, for example, we have

\[ 2pz = r \cos \theta \sum_{i=1}^{3} A_i \left( \frac{k_1^5}{\pi} \right) e^{-k_i r}, \quad (2-2) \]

where \( k_1 \) and \( k_2 \) are the same as for the 2s function and \( k_3 = 6.59 \). The \( A_i \) are to be varied, one of them being determined by the requirement of normality. In the case the \( A_1 \) and \( B_1 \) are unity and the other coefficients vanish, we return to the functions used by McWeeny and Ohno. Another set of coefficients give the best fit possible to the atomic Hartree-Fock orbitals. Variations from these coefficients which allow the atomic charge density to move out radially give a considerable improvement in the molecular energy. A test of our
success in representing the atomic functions of the separated oxygen is the resulting atomic energy value of -74.737 a.u. as compared with Watson's value of -74.809 a.u. The value of the atomic energy in the case of atomic oxygen energy with the Hartree-Fock functions of Hartree, Hartree and Swirles (3) is -74.789 a.u.

The other atomic orbitals, the 1s functions on oxygen and the hydrogens, are given simply as follows, the same ones used in the two previous calculations:

\[
1s = 0 = (k_o^3/\pi)^{1/2} e^{-k_o r}, \text{ where } k_o = 7.7, \\
h_1 = (k_H^3/\pi)^{1/2} e^{-k_H r_1}, \\
\text{and } h_2 = (k_H^3/\pi)^{1/2} e^{-k_H r_2}, \text{ where } k_H = 1.0
\]  

(2-3)

It was felt that the 1s electrons on oxygen are probably very little affected by the presence of the hydrogens in the molecule. Some of the error arising from the use of this simple orbital for the 1s is no doubt cancelled out in computing the binding energy of the molecule, since the same 1s function is used for the atomic energy calculation for the separated oxygen. The use of hydrogen functions with a fixed screening constant of the same value as for atomic hydrogen is much less justifiable. Some variation of this parameter should be allowed for, but, with the present form of the computer programs for molecular integrals and for the configuration interaction calculation, this was not able to be done in a significant way. Further, within the scope of the present number of configurations some polarization of these
hydrogens could be allowed for by the floating orbital technique.\(^{(4)}\)

With adaptations of the present programs, this polarization and the variation of screening constant could be introduced, with the simultaneous variation of the oxygen functions. This seems to be the next step to be taken in improving the present calculations.

The primitive atomic functions which we have just discussed can be written conveniently as a row vector:

\[
a = (x^0y^0z^0h_1^0h_2^0o^0s^0)
\]

(2-4)

where the superscript \(^0\) indicates that these are the primitive functions and where the \(s\) is the 2s function of Eq. (2-1) which has been orthogonalized to the oxygen \(1s\), and \(x\), \(y\), and \(z\) are the 2p orbitals:

\[
s^0 = (2s - OS^0)/\sqrt{(1 - (OS)^2)^{1/2}}
\]

(2-5)

where \(OS\) is the overlap integral of the 2s of Eq. (2-1) and the 1s function, \(o^0\). The \(z\)-axis bisects the angle between the bonds and the positive \(x\)-axis points towards the first hydrogen (see Fig. 2-1).

2. Orthogonalization of the Hydrogen Orbitals

To form an orthogonal atomic basis set, we choose to orthogonalize the two hydrogen orbitals to one another and to the oxygen orbitals, leaving these undisturbed. If we were allowing a mixing of all the possible product, many-electron functions, all possible fillings of the atomic orbitals, it would not matter how the
orthogonalization was carried out. In the present calculations, however, the oxygen 1s orbital will always be kept doubly occupied and there will be some restriction on the occupancies of the 2s orbital, while all occupancies of the hydrogen orbitals will be allowed. Thus, it is best to orthogonalize the hydrogen orbitals to the others.

This orthogonalization process is easier to follow if we first make linear combinations of the two hydrogen orbitals: \((h_1^0 - h_2^0)\) and \((h_1^0 + h_2^0)\). The difference function is orthogonal to all but the \(2p_x\), while the sum function must be made orthogonal to the 1s, 2s, and the \(2p_z\). Thus, we can form two linear combinations, the first of which is an antisymmetric function in \(x\), the other symmetric:

\[
\begin{align*}
\text{antisymmetric:} & \quad h_1^0 - h_2^0 - 2 HP \sin \theta x^0 \\
\text{symmetric:} & \quad h_1^0 + h_2^0 - 2 HO o^0 - 2 HS s^0 - 2 HP \cos \theta z^0,
\end{align*}
\]

where \(HO\) is the overlap between \(o^0\) and one of the \(h^s\), \(HS\) the same with the \(s^0\), and \(HP\) between a \(2p\) orbital and an \(h\) function located on its axis. It is easy to verify that these two combinations are orthogonal to all the oxygen functions and to each other. It remains to form orbitals more localized on the hydrogens. This is done by normalizing each of the above functions and then taking their sum and difference.

The resulting transformation is

\[
\begin{align*}
h_{1,2} &= \frac{(h_1^0 + h_2^0)/2 - 2 HO o^0 - 2 HS s^0 - 2 HP \cos \theta z^0}{(1 + HH - 2(HO)^2 - 2(HS)^2 - 2(HP)^2 \cos^2 \theta)^{-1/2}} \\
&\quad \frac{(h_1^0 - h_2^0)/2 - 2 HP \sin \theta x^0}{(1 - HH - 2(HP)^2 \sin^2 \theta)^{1/2}}.
\end{align*}
\] (2-6)
where the minus sign goes with the $h_2$, the positive sign with $h_1$.

Except for the orbitals $s^0$ and $z^0$ which will undergo a further transformation, the other orbitals are in the form in which they will be used to construct the determinantal functions. Therefore, the superscripts on these later orbitals are now dropped.

The molecular integrals in terms of the primitive basis are first transformed to the orthogonal basis and subsequently to a basis in which hybrid orbitals are formed from the $s^0$ and $z^0$ orbitals. Let us look briefly, therefore, at the way in which the integrals are transformed. Symbolically, we may write the orthogonalizing transformation

$$a^\dagger = (xyz^0 h_1 h_2 o s^0) = a V_0$$

where the fourth and fifth columns of $V_0$ are just the coefficients in Eq. (2-6). Following McWeeny and Ohno, we may set up the one- and two-electron integrals in matrix form. Thus, if we write $f_{pq} = \int a_p^{(f)} op a_q dV$ and $f^\dagger_{pq}$ for the corresponding integral in terms of the primed functions, where $(f)^{op}$ is one of the one-electron operators in the Hamiltonian, then the transformation can be simply written $f^\dagger = V_0^\dagger f V_0$. Further, the two-electron integrals may be gathered into a 28 by 28 matrix with the elements $g_{pq,rs} = \int a_p^{(1)} a_q^{(1)} (g_{12})^{op} a_r^{(2)} a_s^{(2)} dV_1 dV_2$, with a similar matrix for the primed orbitals, both with a restriction that $p < q$ and $r < s$. Then, each pair
of functions can be expanded in the form, \[ a_{n}^\dagger(1)a_{n}^\dagger(1) = \sum_{m=1}^{7} \sum_{n=1}^{7} (V_{0})_{mp} a_{m}^\dagger(1) \times (V_{0})_{nq} a_{n}^\dagger(1), \]
which can be reduced to \[ \sum_{m=1}^{7} \sum_{n=1}^{7} V_{mn, pq} a_{m}^\dagger(1) a_{n}^\dagger(1), \]
where \[ V_{mn, pq} = (V_{0})_{mp} (V_{0})_{nq} - (V_{0})_{mq} (V_{0})_{np} \] for \( m \neq n \), and \[ V_{mn, pq} = (V_{0})_{mq} (V_{0})_{mp} \] for \( m = n \). With this notation we can write the transformation of the two-electron integrals very simply as \[ g^\dagger = \sqrt{V_{2}} g \sqrt{V_{2}}. \] In actually programming these transformations for the computer, it is not advantageous to carry through the full matrix multiplications as indicated, since only two orbitals are affected. But this is the clearest way to symbolize the transformation and to indicate how one would carry it out in a more difficult problem.

3. Hybridization of the 2s and 2pz Orbitals

Once an orthogonalized basis set of atomic orbitals has been established, hybrid orbitals appropriate to the problem at hand should be formed. We could choose, as we will in the extended valence-bond approximation, to use the four orbitals

\[ b_{1,2} = (z^{0} \cos \alpha + s^{0} \sin \alpha \pm x)/\sqrt{2} \]

and \[ f_{1,2} = (s^{0} \cos \alpha - z^{0} \sin \alpha \pm y)/\sqrt{2} \]

where the first indices take the upper signs. The \( b \) or bond orbitals, can be made to point in the direction of the hydrogens, which would allow for maximum overlap and presumably minimum energy. Actually, it will be seen that a slightly "bent" bond is favored, that is, the \( b \) orbitals point in towards one another somewhat and not directly along the direction to the hydrogens. The \( f \) orbitals are the lone pair orbitals pointing in the negative z direction, above and below the plane of the molecule.
In the configuration interaction treatment we are using, since all occupancies of the x and y orbitals are allowed, it is entirely equivalent to use a simpler hybridization, as Slater has pointed out. In fact, if all the configurations arising from the $s^0$ being either doubly, singly or not occupied were taken into consideration, there would be no need of hybridization at all. But, since following Slater, we want to reduce the number of configurations involved and since we suspect that the 2s orbital is very nearly doubly occupied, we use the following hybrids, the first of which will be kept doubly occupied in all configurations, the second of which will be allowed all occupancies:

\[ s = s^0 \cos \alpha - z^0 \sin \alpha \]
\[ z = s^0 \sin \alpha + z^0 \cos \alpha \]  \hspace{1cm} (2-7)

The molecular integrals must be transformed to this new basis by an operation similar to the orthogonalizing transformation. The final basis set may be symbolized:

\[ d = (xyz_1h_2os) = a^T V_H \]  \hspace{1cm} (2-8)

where $V_H$ is the matrix which transforms according to Eq. (2-7). The orbitals are now in the proper form for constructing the determinantal functions and the molecular integrals over these orbitals in the proper form for expanding the energy matrix elements in terms of these determinantal functions. Before we turn to the discussion of the determinantal functions, let us consider the actual form of the one-
and two-electron operators, \( f_i \) and \( g_{ij} \), and the types of integrals over these operators which will be required as input to any program for computing the molecular energy.

4. The Molecular Integrals

The Hamiltonian operator for a system of \( N \) electrons in the presence of \( M \) nuclei is

\[
H_{\text{op}} = \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{\mu=1}^{M} \frac{Z_\mu}{r_{i\mu}} + \sum_{1 \leq j = 1}^{N} \frac{1}{r_{ij}} \tag{2-9}
\]

if we neglect magnetic effects and nuclear motion, in the Born-Oppenheimer approximation. \( \nabla_i^2 \) is the Laplacian operating on the coordinates of the \( i \)th electron. \( Z_\mu \) is the charge on the \( \mu \)th nuclei. The sum over \( i \) and \( j \) of the electronic repulsion term, \( 1/r_{ij} \), is taken over all pairs of electrons, once. The units used here are Hartree atomic units, in which length is measured in units of the first Bohr orbit of hydrogen, \( 5.28 \times 10^{-8} \text{ cm.} \), and energy is in units of twice the Rydberg, or \( 27.21 \text{ ev.} \)

In the case of the water molecule, \( N \) is ten, \( M \) is three, \( Z_1 \) is eight, and \( Z_2 \) and \( Z_3 \) are one. The required integrals are all the distinct overlap, one-electron kinetic energy and nuclear attraction, and two-electron repulsion integrals that exist for the primitive atomic orbital basis set \( \mathbf{a} \) of Eq. 2-1. The definitions of these integrals are as follows:

- **Overlap:** \( O(m/n) = \int a_m(\mathbf{r}_i) a_n(\mathbf{r}_j) dV_i \)
- **Kinetic energy:** \( KE(m/n) = -\frac{1}{2} \int a_m(\mathbf{r}_i) \nabla_i^2 a_n(\mathbf{r}_j) dV_i \)
- **Nuclear attraction:** \( NF(P/mn) = \int a_m(\mathbf{r}_i)(1/r_{ip}) a_n(\mathbf{r}_j) dV_i \)
- **Electron repulsion:** \( (mn/pq) = \int \int a_m(\mathbf{r}_i) a_n(\mathbf{r}_j) (1/r_{ij}) a_p(\mathbf{r}_j) a_q(\mathbf{r}_j) dV_i dV_j \)
FIG. 2-1: COORDINATE SYSTEM FOR THE WATER MOLECULE
(Y-AXIS OUT OF THE PAGE)
(1) PRIMED, OH-SYSTEM
(2) UNPRIMED, H₂O-SYSTEM
The integral over the $g_{ij}$ operator is simply the electron repulsion integral. The integral of the one-electron operator, which from Eq. 2-9 is

$$f_i = -\frac{1}{2} \nabla_i^2 - \frac{8}{r_i} - \frac{1}{r_i H_1} - \frac{1}{r_i H_2},$$

is constructed from the above one-electron integrals:

$$(m/n) f_{mn} = \int a_m (\vec{r}_i) a_n (\vec{r}_i) dV_i =$$

$$K_E(m/n) - 8 N_F(O/mn) - N_F(H_1/mn) - N_F(H_2/mn) \quad (2-11)$$

The number of integrals to be computed is considerably reduced if the two-center integrals involving oxygen orbitals are computed in a rotated frame, with the z-axis along the OH line. The integrals in the $H_2O$ system are gotten from these by a simple transformation based on the rotation of coordinates (see Fig. 2-1).

The two-center integrals, as well as the one-center integrals, were computed with the SHARE distributed program DIATOM which was written by F. J. Corbató and A. C. Switendick. The three-center nuclear attraction integrals and all the two-electron integrals were computed by packages of programs based on the Barnett and Coulson method of expanding all orbitals about one center. (6)
CHAPTER III: THE CONFIGURATIONS AND THEIR INTERACTION MATRIX

Thus far, we have established the orthonormal set of atomic orbitals from which the many-electron function will be constructed and transformed to this atomic basis the molecular integrals required to evaluate matrix elements with respect to the many-electron function. Now we will consider the determinantal functions which arise from the different possible assignments of electrons to the atomic orbitals and the linear combinations of definite symmetry which are constructed from these determinants.

1. Determinantal Functions

As has been mentioned in the previous chapter, the 1s orbital and the 2s-like hybrid of oxygen will always be kept doubly occupied. This means that there are six of the ten electrons left to be assigned to the other orbitals. A further simplification arises from the fact that we choose to work with states of total magnetic quantum number, $M_S$, equal to zero, which means three electrons will have spin up and three, spin down. Since there are five space functions left, $x$, $y$, $z$, $h_1$, and $h_2$, there are five spin-orbitals with $m_s = \frac{1}{2}$ and five with $m_s = -\frac{1}{2}$. It is now easy to see that, assigning three electrons of spin up to five spin-orbitals, and three of spin down to the other five, the resulting number of configurations will be $(5!/2!3!) \times (5!/2!3!) = 100$. Following Slater, we will designate these configurations by two-digit numbers running from 00 to 99, where the first digit indicates to which orbitals the spin-up electrons are assigned and the second to which the spin-down electrons are assigned. The assignments are listed in Table 3-1. Thus, for example, by (19)
we indicate the determinantal function formed from the spin-orbitals
\((x^+y^+h_1^+o^+s^+z^-h_2^-o^-s^-)\), in the order indicated. The basis ordering
of spin-orbitals in the determinantal functions will be as shown here,
the + spins coming before the - spins, and the spatial orbitals
arranged according to the order in Table 3-1. Interchanging any
two of the symbols will change the sign of the function, since it is
a determinant.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<td>xyz</td>
<td>0</td>
<td>yzh_1</td>
<td>3</td>
<td>xzh_2</td>
</tr>
<tr>
<td>xyh_1</td>
<td>1</td>
<td>yzh_2</td>
<td>4</td>
<td>xh_1 h_2</td>
</tr>
<tr>
<td>xyh_2</td>
<td>2</td>
<td>xzh_1</td>
<td>5</td>
<td>yh_1 h_2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>zh_1 h_2</td>
</tr>
</tbody>
</table>

The one hundred determinantal functions which arise from the
assignments of electrons we have allowed are not states of definite
spin and space symmetry. If linear combinations of these determinants
are constructed which do have a definite symmetry, the Hamiltonian
matrix will factor into several submatrices since the states of different
symmetries will not mix. Let us next consider how these symmetry
states may be constructed.

2. Symmetry Functions

There are two space operations which leave the Hamiltonian
invariant, \(R_x\), the reflection of \(x\) into \(-x\), and \(R_y\), the reflection of
\(y\) into \(-y\). We assume, for the present problem that both oxygen-
hydrogen distances are the same and that the \(z\)-axis bisects the hydrogen-
hydrogen angle. The effect of these operations on the determinantal
functions is to transform them into other determinantal functions. From this behavior, we can easily find those linear combinations of a definite symmetry. For example, if we operate on (19) with $R_x$, $x$ goes into $-x$ and $h_1$ and $h_2$ are interchanged, resulting in the determinant $-(x^+y^+h_2^+z^-h_2^-h_1^-)$, where we omit the o and s orbitals. If we reverse the order of $h_1^-$ and $h_2^-$, with the required change of sign, the determinant is brought back to standard form and we find $R_x(19) = (29)$. In a similar way, we can see that $R_y(19) = -(19)$, since the $y^+$ changes sign. Thus, the linear combinations, $(19) + (29)$ and $(19) - (29)$, both change sign under the operation $R_y$, but only the difference changes sign under $R_x$.

There are four symmetry types under the space operations $R_x$ and $R_y$. If the sign changes under neither operation, the type will be called $\Gamma_1$, if under both, $\Gamma_2$, if only under $R_x$, $\Gamma_3$, and if only under $R_y$, $\Gamma_4$. For this simple case of the water molecule, it is reasonably straightforward to find the combinations of determinants which behave according to these four symmetries.

Next, let us consider the behavior of these determinantal functions, or the space-symmetric combinations, under the total spin operator $S^2$. All of the determinants are already $M_S = 0$ states for the operator $S_z$. For such functions, as Slater shows, the $S^2$ operator has a diagonal matrix element equal to one half the number of orbitals in the determinantal function with unpaired spins. The non-diagonal matrix elements of this operator are unity to each
of the determinants which can be formed from the original one by interchanging the spins of a pair of unpaired orbitals with opposite spin. As an example of this rule, let us consider $S^2(18) = S^2(x^+y^+h_1^+y^-h_1^-h_2^-)$. The unpaired orbitals here are $x^+$ and $h_2^-$. Hence the diagonal matrix element is unity. There is a non-diagonal matrix element of unity to the determinant $(x^-y^+h_1^+y^-h_1^-h_2^+) = -(y^+h_1^+h_2^+x^-y^-h_1^-) = -(81)$. Thus, $S^2(18) = (18) - (81)$. Similarly, $S^2(81) = (81) - (18)$. From these two expressions, it follows that $S^2[(18) + (81)] = 0$ and that $S^2[(18) - (81)] = 2[(18) - (81)]$, that is that the sum is a singlet and the difference a triplet. The situation is similar for each of the determinantal functions having only two unpaired electrons.

For the case of four unpaired electrons, for example, let us consider $(23) = (x^+y^+h_2^+y^-z^-h_1^-)$, in which the four electrons in $x^+$, $h_1^-$, $z^-$, and $h_2^+$ are unpaired. The diagonal matrix component is now two and there are non-diagonal matrix elements of unity to four other determinantal functions:

$(x^-y^+h_2^+y^-z^-h_1^-) = -(41), \ (x^-y^+h_2^+y^-z^-h_1^-) = (80), \ (x^+y^+h_2^-y^-z^+h_1^-) = (08), \ \text{and} \ (x^+y^+h_2^-y^-z^+h_1^-) = -(14)$. Hence the effect of $S^2$ on $(23)$ is

$$S^2(23) = 2(23) - (41) + (80) + (08) - (14).$$

In the same manner, we find that $S^2(32) = 2(32) - (41) + (80) + (08) - (14)$, which leads us directly to the triplet function, since $S^2[(23) - (32)] = 2[(23) - (32)]$. In the case of only one unpaired set of electrons,
we also found that the difference of the determinantal function and the functions with indices reversed was a triplet. This turns out to be the case for all the determinantal functions. But the singlets and quintets for the case of four unpaired electrons are more difficult.

From the branching diagram for four electrons in different space orbitals, we know that we should look for one quintet, three triplets, and two singlets from (23), (32) and the determinants that have non-diagonal matrix components with them. The triplets are (23) - (32), (08) - (80), and (14) - (41). One can make three linearly independent combinations of these triplets, two of them \( \Gamma_1 \) and one \( \Gamma_3 \). The quintet and singlets will involve the three sums (23) + (32), (08) + (80), and (14) + (41), since they must be orthogonal to the triplets. From the above behavior of (23) under the spin operator and the corresponding results for the other determinants, we can write

\[
S^2[(23) + (32)] = 2\left[ [(23) + (32)] + [(08) + (80)] - [(14) + (41)] \right],
\]

\[
S^2[(08) + (80)] = 2\left[ [(08) + (80)] + [(23) + (32)] - [(14) + (41)] \right],
\]

and \[
S^2[(14) + (41)] = 2\left[ [(14) + (41)] - [(23) + (32)] - [(08) + (80)] \right].
\]

Adding these three equations, we find the quintet:

\[
S^2[(23) + (32) - (14) - (41) + (08) + (80)] = 6[(23) + (32) - (14) - (41) + (08) + (80)].
\]

Two singlets, orthogonal to each other and to the states of other multiplicities can be found by inspecting the above equation for the sums of the pairs of determinants. Thus, we have
\[ S^2[(14) + (41) + (23) + (32)] = 0, \]

and,

\[ S^2[2(08) + 2(80) + (41) + (14) - (23) - (32)] = 0. \]

Turning to the results of applying the space operators to each of the determinants, one would find that the above states of definite multiplicity are also states of definite space symmetry. They are \( ^5\Gamma_1, \, ^3\Gamma_3, \, ^3\Gamma_1, \, ^3\Gamma_1, \, ^1\Gamma_1, \) and \(^1\Gamma_3.\)

From the above two examples, one can see how to proceed in the construction of the symmetry functions. Slater, in his memorandum on setting up the configuration interaction treatment of the water molecule, has listed the results of this procedure. These are reproduced in Table 3-2. The functions are normalized and the functions of the same symmetry have been so chosen as to reduce to definite states of the separate atoms. These states are listed in the table just after the name of the symmetry function. Slater has obtained them by removing the hydrogen orbitals from the symmetry functions, after rearranging the determinants to put these orbitals at the end. The oxygen functions thus obtained are compared with oxygen functions expressed in the symmetry appropriate to the water molecule, \( C_{2v}, \) and identified as states of atomic oxygen. One could do the same thing by simply applying the \( S^2 \) and the \( L^2 \) operators to the symmetry functions with the hydrogens removed. As a test of the programs for computing the configuration interaction, we have put in integrals corresponding to the separated atoms, i.e., omitting the oxygen-hydrogen and hydrogen-hydrogen interaction integrals and keeping only one-center integrals, and have
Table 3-2

Symmetry functions for $H_2O$, in terms of determinantal functions

$$\Gamma_1$$

<table>
<thead>
<tr>
<th>$S(00)$, $O^{\pm 1}S$</th>
<th>$H^+H^+$ (00)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S(01)$, $O^2P_h$</td>
<td>$H^+H$ $1/2[(01)+(10)+(02)+(20)]$</td>
</tr>
<tr>
<td>$S(02)$,  &quot;</td>
<td>$1/2[(03)+(30)-(04)-(40)]$</td>
</tr>
<tr>
<td>$S(03)$, $O^3P$</td>
<td>$HH 12^{-1/2}[2(08)+2(80)+(14)+(41)-(23)-(32)]$</td>
</tr>
<tr>
<td>$S(04)$, $O^1D$</td>
<td>$HH 12^{-1/2}[2(12)+2(21)-(34)-(43)-(56)-(65)]$</td>
</tr>
<tr>
<td>$S(05)$,  &quot;</td>
<td>$1/2[(34)+(43)-(56)-(65)]$</td>
</tr>
<tr>
<td>$S(06)$, $O^1S$</td>
<td>$HH 6^{-1/2}[(12)+(21)+(34)+(43)+(56)+(65)]$</td>
</tr>
<tr>
<td>$S(07)$, $O^1D$</td>
<td>$H^+H^- 1/2[(13)+(31)-(24)-(42)]$</td>
</tr>
<tr>
<td>$S(08)$,  &quot;</td>
<td>$12^{-1/2}[2(11)+2(22)-(33)-(44)-(55)-(66)]$</td>
</tr>
<tr>
<td>$S(09)$,  &quot;</td>
<td>$1/2[(33)+(44)-(55)-(66)]$</td>
</tr>
<tr>
<td>$S(10)$, $O^1S$</td>
<td>$H^+H^- 6^{-1/2}[(11)+(22)+(33)+(44)+(55)+(66)]$</td>
</tr>
<tr>
<td>$S(11)$, $O^2D$</td>
<td>$H^- 8^{-1/2}[(18)+(81)+(28)+(82)-(95)-(96)]$</td>
</tr>
<tr>
<td>$S(12)$,  &quot;</td>
<td>$8^{-1/2}[(38)+(83)-(48)-(84)-(57)-(75)+(67)+(76)]$</td>
</tr>
<tr>
<td>$S(13)$, $O^2P$</td>
<td>$H^- 8^{-1/2}[(18)+(81)+(28)+(82)+(95)+(69)+(96)]$</td>
</tr>
<tr>
<td>$S(14)$,  &quot;</td>
<td>$8^{-1/2}[(38)+(83)-(48)-(84)+(57)+(75)-(67)-(76)]$</td>
</tr>
<tr>
<td>$S(15)$, $O^{++}D$</td>
<td>$H^- 2^{-1/2}[(77)-(88)]$</td>
</tr>
<tr>
<td>$S(16)$,  &quot;</td>
<td>$6^{-1/2}[(77)+(88)-(99)]$</td>
</tr>
<tr>
<td>$S(17)$, $O^{++}S$</td>
<td>$H^- 3^{-1/2}[(77)+(88)+(99)]$</td>
</tr>
</tbody>
</table>

$$\Gamma_2$$

| $S(18)$, $O^2P_hH^+$  | $1/2[(05)+(50)-(06)-(60)]$ |
| $S(19)$, $O^3P$       | $HH 12^{-1/2}[2(07)+2(70)+(16)+(61)-(25)-(52)]$ |
| $S(20)$, $O^1D$       | $HH 1/2[(36)+(63)+(45)+(54)]$ |
Table 3-2 (cont)

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<thead>
<tr>
<th>State</th>
<th>Term</th>
<th>Combination</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(21), O^{1}D H^+H^-</td>
<td>1/2</td>
<td>[ (15)+(51)-(26)-(62)]</td>
</tr>
<tr>
<td>S(22),</td>
<td>1/2</td>
<td>[ (35)+(53)+(46)+(64)]</td>
</tr>
<tr>
<td>S(23), O^{+2}D^0 HH^-</td>
<td>8^{-1/2}</td>
<td>[ (37)+(73)-(47)-(74)+(58)+(85)-(68)-(86)]</td>
</tr>
<tr>
<td>S(24),</td>
<td>24^{-1/2}</td>
<td>[ 2(19)+2(91)-2(29)-2(92)-(37)-(73)</td>
</tr>
<tr>
<td>S(25),</td>
<td>8^{-1/2}</td>
<td>[ (17)+(71)+(27)+(72)+(39)+(93)+(49)+(94)]</td>
</tr>
<tr>
<td>S(26), O^{+2}P^0 HH^-</td>
<td>8^{-1/2}</td>
<td>[ (17)+(71)+(27)+(72)-(39)-(93)-(49)-(94)]</td>
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<tr>
<td>S(27), O^{++}1D H^-H^-</td>
<td>2^{-1/2}</td>
<td>[ (78)+(87)]</td>
</tr>
<tr>
<td>S(28), O^{-2}P^0 H^+H</td>
<td>1/2</td>
<td>[ (01)+(10)-(02)-(20)]</td>
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<tr>
<td>S(29),</td>
<td>1/2</td>
<td>[ (03)+(30)+(04)+(04)]</td>
</tr>
<tr>
<td>S(30), O^{1}D HH</td>
<td>1/2</td>
<td>[ (14)+(41)+(23)+(32)]</td>
</tr>
<tr>
<td>S(31), O^{1}D H^+H^-</td>
<td>1/2</td>
<td>[ (13)+(31)+(24)+(42)]</td>
</tr>
<tr>
<td>S(32),</td>
<td>12^{-1/2}</td>
<td>[ 2(11)-2(22)-(33)+(44)-(55)+(66)]</td>
</tr>
<tr>
<td>S(33),</td>
<td>1/2</td>
<td>[ (33)-(44)-(55)+(66)]</td>
</tr>
<tr>
<td>S(34), O^{1}S H^+H^-</td>
<td>6^{-1/2}</td>
<td>[ (11)-(22)+(33)-(44)+(55)-(66)]</td>
</tr>
<tr>
<td>S(35), O^{+2}D^0 HH^-</td>
<td>8^{-1/2}</td>
<td>[ (18)+(81)-(28)-(82)-(59)-(95)+(69)+(96)]</td>
</tr>
<tr>
<td>S(36),</td>
<td>8^{-1/2}</td>
<td>[ (38)+(83)+(48)+(84)-(57)-(75)-(67)-(76)]</td>
</tr>
<tr>
<td>S(37), O^{+2}P^0 HH^-</td>
<td>8^{-1/2}</td>
<td>[ (18)+(81)-(28)-(82)+(59)+(95)-(69)-(96)]</td>
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<tr>
<td>S(38),</td>
<td>8^{-1/2}</td>
<td>[ (38)+(83)+(48)+(84)+(57)+(75)+(67)+(76)]</td>
</tr>
<tr>
<td>S(39), O^{++}1D H^-H^-</td>
<td>2^{-1/2}</td>
<td>[ (79)+(97)]</td>
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\[ ^1\Gamma_4 \]

<table>
<thead>
<tr>
<th>State</th>
<th>Type</th>
<th>Multiplet</th>
<th>Expression</th>
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<tbody>
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<td>S(40), O^- ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>2P0^+H^+H</td>
<td>( \frac{1}{2} \left[ (05)+(50)+(06)+(60) \right] )</td>
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</tr>
<tr>
<td>S(41), O ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>3P ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( 12^{-\frac{1}{2}} \left[ 2(09)+2(90)-(36)-(63)+(45)+(54) \right] )</td>
<td></td>
</tr>
<tr>
<td>S(42), O ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>1D ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \frac{1}{2} \left[ (16)+(61)+(25)+(52) \right] )</td>
<td></td>
</tr>
<tr>
<td>S(43), O ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>1D ( \cdot ) ( \cdot ) ( \cdot ) ( - )</td>
<td>( \frac{1}{2} \left[ (15)+(51)+(26)+(62) \right] )</td>
<td></td>
</tr>
<tr>
<td>S(44), O^- ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( \frac{1}{2} \left[ (35)+(53)-(46)-(64) \right] )</td>
<td></td>
</tr>
<tr>
<td>S(45), O^+ ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>2D0^+ HH^-</td>
<td>( 8^{-\frac{1}{2}} \left[ (37)+(73)+(47)+(74)+(58)+(85)+(68)+(86) \right] )</td>
<td></td>
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<tr>
<td>S(46), O^- ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 24^{-\frac{1}{2}} \left[ 2(19)+2(91)+2(29)+2(92)-(37)-(73) \right] )</td>
<td></td>
</tr>
<tr>
<td>S(47), O^- ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( - (47)-(74)+(58)+(85)+(68)+(86) )</td>
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</tr>
<tr>
<td>S(48), O^+ ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>2P0^+ HH^-</td>
<td>( 8^{-\frac{1}{2}} \left[ (17)+(71)-(27)-(72)+(39)+(93)-(49)-(94) \right] )</td>
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<td>S(49), O^+ ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 8^{-\frac{1}{2}} \left[ (17)+(71)-(27)-(72)-(39)-(93)+(49)+(94) \right] )</td>
<td></td>
</tr>
<tr>
<td>( \frac{2}{3} \Gamma_1 )</td>
<td>( \frac{1}{2} \left[ (01)-(10)+(02)-(20) \right] )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(50), O^- ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 1/2 \left[ (03)-(30)-(04)+(40) \right] )</td>
<td></td>
</tr>
<tr>
<td>S(51), O^- ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 2^{-\frac{1}{2}} \left[ (08)-(80) \right] )</td>
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<tr>
<td>S(52), O ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 2^{-\frac{1}{2}} \left[ (08)-(80) \right] )</td>
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<tr>
<td>S(53), O ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 2^{-\frac{1}{2}} \left[ (14)-(41)-(23)+(32) \right] )</td>
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<tr>
<td>S(54), O ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 1/2 \left[ (13)-(31)-(24)+(42) \right] )</td>
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<tr>
<td>S(55), O^+ ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 8^{-\frac{1}{2}} \left[ (18)-(81)+(28)-(82)-(59)-(95)-(69)+(96) \right] )</td>
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</tr>
<tr>
<td>S(56), O^+ ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 8^{-\frac{1}{2}} \left[ (38)-(83)-(48)+(84)-(57)+(75)+(67)-(76) \right] )</td>
<td></td>
</tr>
<tr>
<td>S(57), O^+ ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 8^{-\frac{1}{2}} \left[ (18)-(81)+(28)-(82)+(59)-(95)+(69)-(96) \right] )</td>
<td></td>
</tr>
<tr>
<td>S(58), O^+ ( \cdot ) ( \cdot ) ( \cdot ) ( \cdot )</td>
<td>( \cdot )</td>
<td>( 8^{-\frac{1}{2}} \left[ (38)-(83)-(48)+(84)-(57)-(75)-(67)+(76) \right] )</td>
<td></td>
</tr>
</tbody>
</table>
\[ ^3\Gamma_2 \]

| \( S(59), \; O^- \; ^2P^0 \; H^+H \) | \( 1/2 \left[ (05)-(50)-(06)+(60) \right] \)
| \( S(60), \; O \; ^3P \; HH \) | \( 1/2 \left[ (36)-(63)+(45)-(54) \right] \)
| \( S(61), \; " \) | \( 2^{-1/2} \left[ (07) - (70) \right] \)
| \( S(62), \; O \; ^1D \; HH \) | \( 1/2 \left[ (16)-(61)-(25)+(52) \right] \)
| \( S(63), \; O \; ^3P \; H^+H^- \) | \( 1/2 \left[ (15)-(51)-(26)+(62) \right] \)
| \( S(64), \; " \) | \( 1/2 \left[ (35)-(53)+(46)-(64) \right] \)
| \( S(65), \; O^+ \; ^4S^0 \; HH^- \) | \( 12^{-1/2} \left[ (19)-(91)-(29)+(92)+(37)-(73) - (47)+(74)-(58)+(85)+(68)-(86) \right] \)
| \( S(66), \; O^+ \; ^2D^0 \; HH^- \) | \( 8^{-1/2} \left[ (37)-(73)-(47)+(74)+(58)-(85)-(68)+(86) \right] \)
| \( S(67), \; " \) | \( 24^{-1/2} \left[ (219)-2(91)-2(29)+2(92)-(37)+(73) + (47)-(74)+(58)-(85)-(68)+(86) \right] \)
| \( S(68), \; " \) | \( 8^{-1/2} \left[ (17)-(71)+(27)-(72)+(39)-(93)+(49)-(94) \right] \)
| \( S(69), \; O^+ \; ^2P^0 \; HH^- \) | \( 8^{-1/2} \left[ (17)-(71)-(27)-(72)-(39)+(93)-(49)+(94) \right] \)
| \( S(70), \; O^{++} \; ^3P \; H^-H^- \) | \( 2^{-1/2} \left[ (78)-(87) \right] \)

\[ ^3\Gamma_3 \]

| \( S(71), \; O^- \; ^2P^0H^+H \) | \( 1/2 \left[ (01)-(10)-(02)+(20) \right] \)
| \( S(72), \; " \) | \( 1/2 \left[ (03)-(30)+(04)-(40) \right] \)
| \( S(73), \; O \; ^3P \; HH \) | \( 1/2 \left[ (14)-(41)+(23)-(32) \right] \)
| \( S(74), \; O \; ^1D \; HH \) | \( 12^{-1/2} \left[ 2(12)-2(21)-(34)+(43)-(56)+6(5) \right] \)
| \( S(75), \; " \) | \( 1/2 \left[ (34)-(43)-(56)+(65) \right] \)
| \( S(76), \; O \; ^1S \; HH \) | \( 6^{-1/2} \left[ (12)-(21)+(34)-(43)+(56)-(65) \right] \)
| \( S(77), \; O \; ^3P \; H^+H^- \) | \( 1/2 \left[ (13)-(31)+(24)-(42) \right] \)
| \( S(78), \; O^+ \; ^2D^0 \; HH^- \) | \( 8^{-1/2} \left[ (18)-(81)-(28)+(82)-(59)+(95)+(69)-(96) \right] \)
$S(79), \ O^+ {^2D^0} \text{HH}^-$

$S(80), \ O^+ {^2P^0} \text{HH}^-$

$S(81), \ "$

$S(82), \ O^{++} {^3P} \text{H}^- \text{H}^-$

$^3\Gamma_4$

$S(83), \ O^- {^2P^0} \text{H}^+ \text{H}$

$S(84), \ O {^3P} \text{HH}$

$S(85), \ "$

$S(86), \ O {^1D} \text{HH}$

$S(87), \ O {^3P} \text{H}^+ \text{H}^-$

$S(88), \ "$

$S(89), \ O^+ {^4S^0} \text{HH}^-$

$S(90), \ O^+ {^2D^0} \text{HH}^-$

$S(91), \ "$

$S(92), \ "$

$S(93), \ O^+ {^2P^0} \text{HH}^-$

$S(94), \ O^{++} {^3P} \text{H}^- \text{H}^-$

$^5\Gamma_1$

$S(95), \ O {^3P} \text{HH}$

$6^{-1/2} [(08)+(80)-(14)-(41)+(23)+(32)]$
\begin{align*}
^{5}\Gamma_2 \\
S(96), \ O^3P \ &HH \\
S(97), \ O^+ \ 4S^0 \ &HH^- & 6^{-1/2} \left[ \left( 07 \right)+\left( 70 \right)-(16)-(61)+(25)+(52) \right] \\
&\phantom{6^{-1/2} \left[ \left( 07 \right)+\left( 70 \right)-(16)-(61)+(25)+(52) \right]} \hfill 12^{-1/2} \left[ \left( 19 \right)+\left( 91 \right)-(29)-(92)+(37)+(73) \right] \\
&\phantom{6^{-1/2} \left[ \left( 07 \right)+\left( 70 \right)-(16)-(61)+(25)+(52) \right]} \hfill -(47)-(74)-(58)-(85)+(68)+(86) \right] \\
\end{align*}

\begin{align*}
^{5}\Gamma_4 \\
S(98), \ O^3P \ &HH \\
S(99), \ O^+ \ 4S^0 \ &HH^- & 6^{-1/2} \left[ \left( 09 \right)+(90)+(36)+(63)-(45)-(54) \right] \\
&\phantom{6^{-1/2} \left[ \left( 09 \right)+(90)+(36)+(63)-(45)-(54) \right]} \hfill 12^{-1/2} \left[ \left( 19 \right)+(91)+(29)+(92)+(37)+(73) \right] \\
&\phantom{6^{-1/2} \left[ \left( 09 \right)+(90)+(36)+(63)-(45)-(54) \right]} \hfill +(47)+(74)-(58)-(85)+(68)-(86) \right] \\
\end{align*}
found that the symmetry functions do go to the proper levels in this limit.

3. Matrix Elements of the Hamiltonian with respect to the Symmetry Functions

Once the expressions for the symmetry functions have been found, the Hamiltonian matrix in terms of the determinantal functions can be transformed simply into the symmetry basis, in which it factors. Calling the coefficients of the expansions in Table 3-2 \( c_{jk}^a \), we may indicate this transformation as

\[
H_{mn}^a = \int S_m^a \text{Hop} S_n^a \, dV_{10} = \frac{100}{\sum_{k=1}^{100} \sum_{\ell=1}^{100} c_{mk}^a c_{n\ell}^a H_{k\ell}^0},
\]

where \( H_{k\ell}^0 = \int D_k \text{Hop} D_\ell \, dV_{10} \). The \( S_m^a \) is the \( m \)th state of symmetry \( a \), \( D_k \) is the \( k \)th of the determinantal functions, or, in the previous notation, \( D_k \) is the determinant (\( k-1 \)), and the integrations are over all ten electrons. In actual computation, the summations are not carried out over all the determinantal functions, but only those few involved in a given symmetry function. The \( H_{k\ell}^0 \) are given by the general formulas for the matrix elements of one- and two-electron operators between determinantal functions.\( ^{(2)} \) These formulas are now to be discussed.

For the one-electron operators, \( \sum f_i \), the diagonal matrix component is \( \Sigma (m/m) \), where \( (m/m) = \int u_m^i (r_i^m) f_i^i u_m^i (r_i^m) \, dV_i \), where \( u_m^i \) is the \( m \)th spin-orbital and the sum is over all the ten spin-orbitals occupied in the determinant in question. The integral is over the space of any electron, including a summation over spin.
The non-diagonal matrix element of the one-electron operators vanishes unless the two determinants differ in only one of their spin-orbitals. Thus, if $u_m$ in one determinantal function is replaced by $u_{m^i}$ in the other, both having the same spin and the order of identical orbitals being the same in both, the non-diagonal matrix element is $(m/m^i) = \int u_m(r_i) f_i u_{m^i}(r_i^i) dV_i$. The spins must be the same, since the integrations over the space of an electron are always understood to include a summation over spin. If the two orbitals in which the determinants differ, or those in which they are the same, are not in the same order in the determinants, the change of sign arising from the interchanging of columns necessary to put them in the same sequence must be taken into account.

In the case of the two-electron operators, the diagonal matrix component is $\Sigma_{m<n} [(mm/nn) - (mn/mn)]$, where the Coulomb integral is $(mm/nn) = \int u_m(r_i) u_n(r_i^i) f_{ij}^1 u_n(r_j) u_m(r_j^j) dV_i dV_j$, and the exchange integral $(mn/mn) = \int u_m(r_i) u_n(r_i^i) f_{ij}^1 u_n(r_j) u_m(r_j^j) dV_i dV_j$. If $u_m$ and $u_n$ do not have the same spin, the exchange integral vanishes since the summation over spin is implicit in the integration over each electron-space.

For the non-diagonal matrix elements of the two-electron operator, $\Sigma_{i<j} g_{ij}$, two cases can occur. The final determinant may differ from the original in either one or two spin-orbital assignments. If it differs in only one, having $u_m$ replaced by $u_{m^i}$, both appearing in
the same place in the determinants, once they have been rearranged, the non-diagonal matrix element is

\[ \sum_{n \neq m} \left[ \frac{(mm^f/nn)}{(mn/m^f n)} \right] \]

where the first integral vanishes if \( u_m \) and \( u_{m^f} \) do not have the same spins and the second vanishes unless \( u_m \), \( u_{m^f} \), and \( u_n \) all have the same spins. If the two determinants differ in two orbitals, having \( u_m \) and \( u_n \) replaced by \( u_{m^f} \) and \( u_{n^f} \) in the final state, the non-diagonal matrix element is two integrals:

\( \left( \frac{mm^f/nn^f}{nn^f} \right) - \left( \frac{mn/m^f n^f}{mn/m^f n^f} \right) \),

with the usual conditions on the spins if the integrals are not to vanish.

Using these rules for the matrix elements of the determinantal functions and the coefficients of the determinants in the symmetry functions, we have written out explicitly the expressions for the Hamiltonian matrix in the symmetry basis for the states of \( ^1\Gamma_1 \) symmetry. These expressions were used to check the computer programs which calculate the elements of the Hamiltonian matrix for each symmetry from the molecular integrals, the equivalent of a table of \( c_{ij}^a \) coefficients and the rules for the determinantal function matrix elements.
CHAPTER IV: THE EXTENDED VALENCE BOND APPROXIMATION

One of the reasons for undertaking a configuration interaction study of the electronic states of the water molecule has been to compare the results it yields for the ground state with those obtained from a much simpler approximation, an extension of the valence-bond method which could be used for more complicated molecules for which a configuration interaction calculation is not practical. McWeeny and Ohno found that this approach, which they call the modified electron-pair method, gave the best results of all the methods they used, except for configuration interaction. McWeeny and Ohno found that this approach, which they call the modified electron-pair method, gave the best results of all the methods they used, except for configuration interaction. (1) This approximation takes into account some of the correlation between electrons of opposite spin by allowing different orbitals for the two electrons of opposite spin within a bond; the simpler methods do not have the possibility of representing this correlation. The valence-bond wave function which we will set up can be expanded in a series of the same determinantal functions that were used in the configuration interaction calculations. Thus it is possible to compare coefficients of the determinants in the best ground state function from each approximation and discover what sort of configurations in the more complete calculation make it superior to the extension of the valence-bond method.

1. The Total Wave Function

The bond orbitals are to be constructed from the same orthogonalized atomic basis set which was used in the configuration
interaction calculation. It is simple to write the expression for the energy of the ground state if all the orbitals are orthogonal to each other except each pair in a bond. This pair must overlap in order that a single configuration give bonding. Directed orbitals are constructed from the atomic orbitals, as a first step:

\[ b_{1,2} = \frac{z^0 \cos \alpha + s^0 \sin \alpha \pm x}{\sqrt{2}}, \]

and

\[ l_{1,2} = \frac{s^0 \cos \alpha - z^0 \sin \alpha \pm y}{\sqrt{2}}, \]  

(4-1)

where the upper sign goes with the first subscript on the orbital, the lower with the second. The two orbitals \( b_1 \) and \( b_2 \) point in the general direction of the hydrogen nuclei. The two \( l \) orbitals are the lone pair orbitals pointing away from the hydrogens.

The directed orbitals \( b_1 \) and \( b_2 \) and the orthogonalized hydrogen orbitals, \( h_1 \) and \( h_2 \), are combined to form the bond orbitals:

\[ A_4 = \cos \lambda_1 h_1 + \sin \lambda_1 b_1, \]
\[ B_4 = \cos \lambda_2 b_1 + \sin \lambda_2 h_1, \]
\[ A_5 = \cos \lambda_1 h_2 + \sin \lambda_1 b_2, \]
\[ B_5 = \cos \lambda_2 b_2 + \sin \lambda_2 h_2, \]

(4-2a)

where \( \lambda_1 \) and \( \lambda_2 \) are free parameters, to be used in minimizing the energy. The lone pair and 1s orbitals are not transformed, but they will correspond to the following:

\[ A_1 = B_1 = 0 \text{ (oxygen 1s)}, \]
\[ A_2 = B_2 = l_1, \]

and

\[ A_3 = B_3 = l_2. \]

(4-2b)
This set of A and B orbitals has the desired orthogonality properties; namely, the only space-wise non-orthogonal pairs are the two orbitals in the same bond. Thus we have the following overlap integrals:

\[ \int A_i A_j \, dV = \int A_i B_j \, dV = \int B_i B_j \, dV = 0, \quad i \neq j, \]

\[ \int A_i B_i \, dV = 1, \quad i = 1, 2, \text{ or } 3, \]

and

\[ \int A_i B_i \, dV = S = \cos \lambda_1 \sin \lambda_2 + \sin \lambda_1 \cos \lambda_2, \quad i = 4, 5 \quad (4-3) \]

The ground state many-electron wave function constructed from these orbitals must be a sum of determinantal functions such that it possesses \( ^1\Gamma_1 \) symmetry. There are four distinct determinants arising from the possible spin assignments for the electrons in the bonds:

\[ \phi_1 = (A_1^+ B_1^- A_2^+ B_2^- A_3^+ B_3^- A_4^+ B_4^- A_5^+ B_5^-), \]

\[ \phi_2 = (A_1^+ B_1^- A_2^+ B_2^- A_3^+ B_3^- A_4^+ B_4^- A_5^+ B_5^-), \]

\[ \phi_3 = (A_1^+ B_1^- A_2^+ B_2^- A_3^+ B_3^- A_4^+ B_4^- A_5^+ B_5^-), \]

and

\[ \phi_4 = (A_1^+ B_1^- A_2^+ B_2^- A_3^+ B_3^- A_4^+ B_4^- A_5^+ B_5^-). \]

No new functions can be produced by switching spin assignments in the non-bond orbitals since \( A_i \) and \( B_i \) are identical for \( i = 1, 2, \text{ and } 3 \). The combination of these functions with total spin zero is \( \phi_1 - \phi_2 - \phi_3 + \phi_4 \), as can be shown by applying the rules for operating on such functions with the \( S^2 \) operator. (3) The space symmetry of this above linear combination of the four determinants can also be checked and is \( \Gamma_1 \); thus, we have a \( ^1\Gamma_1 \) state, as desired. Making use of the relations of Eq. 4-3, we find for the normalized, extended valence-bond wave function for the electronic ground state of the water molecule:
\[ \psi = \frac{1}{2(1+S^2)} (\phi_1 - \phi_2 - \phi_3 + \phi_4). \]  \hfill (4-5)

It is worthwhile to expand this function in terms of the symmetry functions of Table 3-2. The expansion coefficients can then be compared with the eigenvector components for the configuration interaction ground state. To make such an expansion, we must reconvert the orbitals used in the valence-bond functions into the orthogonalized atomic basis set, that is, transform back to the orbitals \( d \) of Eq. 2-8. Since the lone-pair orbitals are a unitary transformation of the \( y \) and \( s \) orbitals, \( A_2 \) and \( B_2 \) will be replaced by \( s \), and \( A_3 \) and \( B_3 \) by \( y \). Using the relationships

\[
\begin{align*}
A_4 &= \cos \lambda_1 h_1 + (z + x)\sin \lambda_1 /\sqrt{2}, \\
B_4 &= \sin \lambda_2 h_1 + (z + x)\cos \lambda_2 /\sqrt{2}, \\
A_5 &= \cos \lambda_1 h_2 + (z - x)\sin \lambda_1 /\sqrt{2} \\
B_5 &= \sin \lambda_2 h_2 + (z - x)\cos \lambda_2 /\sqrt{2}
\end{align*}
\]

which follow from Eqs. (4-2a), (4-1), and (2-7), we expand the total wave function of Eq. 4-5, sort out the symmetry functions of Table 3-2, and thus determine their coefficients in terms of \( \lambda_1 \) and \( \lambda_2 \). We should observe, however, that this procedure assumes that the hybridizing parameter \( \alpha \) is the same in both cases, the configuration interaction and the valence-bond. In the discussion of results, in Chapter VI, we will see how well this is verified and consider what differences in the two values for \( \alpha \) may mean.
The result of this expansion of the valence-bond wave function is as follows:

\[
= (1 + S^2)^{-1} \left\{ \left[ 2 \sin^2 \lambda_1 \cos^2 \lambda_2 \right] S(00) 
+ \sqrt{2} \left[ \sin^2 \lambda_1 \cos \lambda_2 \sin \lambda_2 + \sin \lambda_1 \cos \lambda_1 \cos^2 \lambda_2 \right] 
\right. \\
\left. \left[ S(01) + S(02) \right] 
+ \frac{1}{4} \left[ \sin \lambda_1 \sin \lambda_2 + \cos \lambda_1 \cos \lambda_2 \right]^2 
\right. \\
\left. \left[ -2\sqrt{3} S(03) + \sqrt{3} S(04) - S(05) \right] 
+ \left[ \sin \lambda_1 \sin \lambda_2 \cos \lambda_1 \cos \lambda_2 
\right. \\
\left. \left[ 2 S(07) + \frac{1}{\sqrt{3}} S(08) + S(09) + \frac{2\sqrt{6}}{3} S(10) \right] 
- \left[ \sin \lambda_2 \cos^2 \lambda_1 \cos \lambda_2 + \sin \lambda_1 \sin^2 \lambda_2 \cos \lambda_1 \right] 
\right. \\
\left. \left[ S(11) + S(12) + S(13) + S(14) \right] 
+ \left[ 2 \cos^2 \lambda_1 \sin^2 \lambda_2 
\right. \\
\left. \left[ - \frac{1}{\sqrt{2}} S(15) + \frac{1}{\sqrt{6}} S(16) + \frac{1}{\sqrt{3}} S(17) \right] \right\}. \tag{4-6}
\]

2. The Electronic Energy

The energy expression in this extension of the valence-bond method can be separated into three parts, each capable of being interpreted as a particular type of interaction.\(^4\) The first group of terms represents the interaction of the electrons within a bond or closed shell:

\[
E_{\text{bonds}} = \sum_i (1 + S_i^2)^{-1} \left[ (A_i/A_i) + 2 S_i (A_i/B_i) + (B_i/B_i) \right. \\
+ (A_iA_i/B_iB_i) + (A_iB_i/A_iB_i) \right] \tag{4-7}
\]

where \( S_i \) are the overlaps of Eq. 4-3, and where the notation for the
integrals is the same as used previously; two-orbital integrals are
over the \( f \) operator, four-orbital integrals over the \( g \) operator. Slater
points out that it is the term \( 2S_i(A_i/B_i) \) which is mainly responsible
for the binding because it includes the interaction between the exchange
charge density and the nuclei.

The next set of terms in the energy expansion is the sum of
the electrostatic interactions between electrons in different bonds
and shells. The charge density of the electrons in a bond, obtained
by integrating the total charge density over the coordinates of all but
two electrons in the \( i \)th bond, is of the form

\[
(1 + S_i^2)^{-1} (A_i^2 + 2S_i A_i B_i + B_i^2). \]

The interaction between these charge distributions is then

\[
E_{\text{coul}} = \sum_{i<j} \left(1 + S_i^2\right)^{-1} \left(1 + S_j^2\right)^{-1} \left\{ (A_i A_j/A_i A_j) + (A_i A_j/B_j B_j) + (B_i B_j/A_i A_j) + (B_i B_j/B_j B_j) + 2 S_i \left[ (A_i B_i/A_i A_j) + (B_i A_i/B_j B_j) \right] + 4 S_i S_j \left[ (A_i B_i/A_i A_j) + (B_i A_i/B_j B_j) \right] \right\}. \] (4-8)

A final group of terms can be recognized as the sum of interactions
between the bond or closed shell exchange densities; \((1 + S_i^2)^{-1}\)

\[
(A_i(r_i) A_i(r_i) + S_i A_i(r_i) B_i(r_i) + S_i A_i(r_i) B_i(r_i) + B_i(r_i) B_i(r_i) + B_i(r_i) B_i(r_i)).
\]

\[
E_{\text{exch}} = \sum_{i<j} (1 + S_i^2)^{-1} \left(1 + S_j^2\right)^{-1} \left\{ (A_i A_j/A_i A_j) + (A_i B_j/A_i B_j) + (B_i A_j/B_j A_j) + (B_i B_j/B_j B_j) + 2 S_i \left[ (A_i A_j/B_i A_j) + (A_i B_j/B_j A_j) \right] + 2 S_j \left[ (A_i A_j/B_i A_j) + (A_i B_j/B_j A_j) \right] + 2 S_i S_j \left[ (A_i A_j/B_i A_j) + (A_i B_j/B_j A_j) \right] \right\}. \] (4-9)
The total energy, then, is

$$E = E_{\text{bonds}} + E_{\text{coul}} - \frac{1}{2} E_{\text{exch}} \quad (4-10)$$

The minus sign comes from the interchange of rows in the determinantal functions, and the factor of one half appears because exchange interactions can take place only if the two spin-orbitals for a given electron have the same spin part. $E_{\text{exch}}$ is expected to be small compared to the $E_{\text{coul}}$ and the $E_{\text{bonds}}$, since the exchange charge densities which are interacting each integrate to zero total charge. This is indeed the case; $E_{\text{exch}}$, as calculated for the water molecule, is a small but significant fraction of the total electronic energy. Certainly, for a quantitative treatment of the problem it cannot be ignored, as will be made clear from the discussion of the results in Chapter V.
CHAPTER V: DISCUSSION OF RESULTS

Following the order of the theoretical considerations of the three previous chapters, we shall present the results of our calculations in this sequence: (1) the effect on the ground state energy of varying the radial dependence of the oxygen L-shell orbitals, (2) the dependence of the ground and excited state energies on the interbond angle and on the oxygen-hydrogen separation, and (3) a comparison of the configuration interaction ground state energy and wave function with the energy and wave function obtained from the extension of the valence-bond approximation.

1. Radial Flexibility in the Atomic Basis Orbitals

In Chapter II, we mentioned that atomic orbitals consisting of a sum of several Slater-type functions had to be used in representing the oxygen 2s and 2p behavior if we were to get satisfactory values for the binding energy. Ideally, for a consistent variation calculation, the coefficients in these expansions should be allowed to adjust freely, along with the variation of the hybridizing parameter \( \alpha \) and the mixing of configurations. Within the scope of the present programs, however, this complete variation was not possible. Further, until the integral programs have been written that will allow a more flexible description of the hydrogen 1s orbitals, it is not too meaningful to attempt a complete variation of the oxygen orbitals. When these integrals, with some 2p character in the hydrogen 1s and a mixing of several 1s-like functions are available, it would seem that the simplest way to find an
adequate basis would be to do a self-consistent field calculation for
the ground state. The resulting functions could be used in either the
configuration interaction or the extended valence-bond approximation,
after some modification of the present programs.

As a pilot study to determine the general effect of varying the
radial dependence of the oxygen L-shell orbitals, the present calculations
have turned out to be very enlightening, in spite of their limitations.
The logic behind the choice of coefficients chosen for the 2s and 2p
expansions is straightforward. First, before it was decided that more
adequate basis functions would be needed, the one-term orbitals used
by Ohno and McWeeny were tried (set I in Table 5-1). Ohno and
McWeeny had gotten a reasonably satisfactory value of the binding
energy with a configuration interaction based on these orbitals and we
hoped to do well also, using better integral values and a larger number
of configurations. As can be seen by a comparison of the results of
set I with the McWeeny and Ohno result in Table 5-1, the improvements
in our calculation gave a poorer value of the total and binding energy.
In both cases the energy of the separated atoms was calculated with the
same wave functions as used in the molecule.

Coefficients were chosen, in the next trial, to fit Hartree-
Fock wave functions for atomic oxygen. As appears in the table, under
set II, the total electronic energy improved by 4.5 ev, although the
binding energy, now calculated using the Hartree-Fock wave functions for
the separated-atoms energy, is poorer than with set I. Within the
molecular environment, however, one would expect the outer shell wave
functions to expand in the general direction of the two hydrogens, so this choice of atomic functions can be improved upon. To test the effect of such an expansion on the energy, the 2p orbital was given more tail and less core contribution, which let the maximum shift out slightly. The 2s was left as in the previous case, both because 2s mixing with the 2pz can be varied through hybridization and because Watson's Hartree-Fock wave functions for O⁻ and O⁺ show much less radial shift for the 2s than for the 2p in comparison to the atomic wave functions. This set is III. The improvement, as can be seen from the table, is again significant, the total energy decreasing by almost 4 ev, with a consequent binding energy of about 80% of the experimental value.

Two more trial sets of coefficients for the 2p function were investigated. Set IV increases the tail of the function at the expense of the height of the maximum, but does not shift it out radially. Set V goes further than the "best" set, III, in accentuating the tail at the expense of the core. Both of these sets of coefficients led to much poorer values of total electronic and of binding energy. Again, as in sets II and III, the functions which we obtained by fitting to the calculated Hartree-Fock atomic functions were used to compute the separated atom energy used in computing the binding energy. This value of the oxygen energy, while not the best Hartree-Fock value, is consistent with the molecular energy computed with the same type of functions. The experimental values for the total electronic and binding energy are listed in Table 5-1 for comparison. The coefficients
are given only to three figures in the table; seven figures were used in the calculations. The experimental values, as well as those of McWeeny and Ohno and Boys et al. are included for comparison.

Table 5-1

Dependence of Ground State Energy of H₂O on the Form of the Oxygen 2s and 2p Orbitals (Interbond angle, 105°; OH separation, 1.8103 a.u.)

<table>
<thead>
<tr>
<th>Coefficients in 2p</th>
<th>Coefficients in 2s</th>
<th>Electronic Energy(ev)</th>
<th>Binding Energy(ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁ A₂ A₃</td>
<td>B₁ B₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>1.0 .0 .0</td>
<td>1.0 .0</td>
<td>-2310.3</td>
</tr>
<tr>
<td></td>
<td>Boys et al. (30 configurations)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Best McWeeny and Ohno value (12 configurations)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>.835 .216 .076</td>
<td>.966 .065</td>
<td>-2314.7</td>
</tr>
<tr>
<td>III</td>
<td>.832 .276 .0</td>
<td>.966 .065</td>
<td>-2318.4</td>
</tr>
<tr>
<td>IV</td>
<td>.743 .325 .107</td>
<td>.966 .065</td>
<td>-2311.8</td>
</tr>
<tr>
<td>V</td>
<td>.736 .4 .0</td>
<td>.966 .065</td>
<td>-2306.8</td>
</tr>
<tr>
<td></td>
<td>Experimental values</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

No such even limited exploration of the effect of variation of coefficients has been carried through for the other geometrical configurations of the molecule, except that calculations using both set II and III were carried through for the configurations, R<sub>OH</sub> = 1.8103 a.u., θ<sub>HH</sub> = 120°, and R<sub>OH</sub> = 3.6206 a.u., θ<sub>HH</sub> = 105°. The lowest values in each of these cases came from the functions fitted to the Hartree-Fock functions, set II. This indicates the necessity for carrying out
a complete variation of all coefficients for each geometrical configuration, producing a different basis set for each. This might be done, as we have suggested, by first doing a self-consistent field calculation to determine the basis functions for use in a configuration interaction or valence-bond calculation.

One of the unsatisfactory features of the present variation procedures, determined by the fact that the configuration interaction programs presume the same radial dependence for all three of the 2p functions, is that the lone-pair orbitals move out in the presence of the hydrogens in the same way as the bonding orbitals do. If we determined the radial form of the 2p's in a self-consistent field calculation, where they can all be different, or allowed for different forms within the configuration interaction programs, both the energy and the wave functions should be improved.

Within the present formulation of the configuration interaction calculation, using the symmetry functions of Table 3-2, we could introduce many more configurations with the $^1\Gamma_1$ and other symmetries by making use of each of the s, x, y, and z functions which are used as terms in the expansions. In other words, one of the results of the present study is that the energy could be improved either by increasing the number of basis orbitals and configurations, through a careful choice of additional contributions needed, or by increasing the quality of the basis orbitals themselves. We favor the latter.
2. Energy Level Variation with Molecular Geometry

The configuration interaction calculation has been carried out for four values of the interbond angle and four values of the OH bond length, keeping always $C_{2v}$ symmetry, with both bonds the same length. One of the first things that one would want to investigate in going beyond the present study is the $H^+ + OH^-$ system. This could be done with some alterations of the programs, which at present presume $C_{2v}$ symmetry.

In Fig. 5-1, the variation of the molecular energy with oxygen-hydrogen separation is shown for a number of states. The angle between the OH lines is fixed at the experimental ground-state value of $105^\circ$. The lowest state of each symmetry type is given, together with some of the higher states in the case of $^1\Gamma_1$ symmetry. Four values of separation were used in these calculations, the experimental value of 1.8103 a.u., two-thirds and twice this value, and infinite separation. These four points do not give the curves in detail, but allow us to consider the general behavior of the energy levels with separation of the atoms. The calculation of the energy levels for infinite separation forms a check on the assignments of Table 3-2 and on the configuration interaction program. Since it was not possible to carry through a complete variation of the form of the atomic basis functions, set II, the approximation to atomic Hartree-Fock functions, was used for infinite separation and for the point two-thirds of the experimental distance. Of course, as we have already discussed, set III, the
FIG. 5-1 VARIATION OF MOLECULAR ENERGY WITH OH DISTANCE (CALCULATED BY CONFIGURATION INTERACTION METHOD)

- LOWEST STATE OF EACH SYMMETRY
- 9 NEXT LOWEST STATES OF $^1\Gamma_1$ SYMMETRY

MOLECULAR ENERGY (ABOVE ATOMIC GROUND STATE, IN E.V.)

OH DISTANCE (IN UNITS OF EQUILIBRIUM VALUE 18103 au)
FIG. 5-2 VARIATION OF MOLECULAR ENERGY WITH INTERBOND ANGLE FOR LOWEST STATE OF EACH SYMMETRY
slightly expanded functions, gives a lower value for the experimental separation. But for twice the experimental separation, the lowest value came from the atomic functions, set II. All the energies for all symmetries are computed with the same atomic basis functions and the hybridization that minimize the ground state energy.

The variation of molecular energy with interbond angle is much more striking, as is seen in Fig. 5-2. The OH distance has been kept fixed at the experimental value of 1.8103 a.u. and the energies of all symmetries were calculated for four angles, 95°, 105°, 120° and 180°. For all these angles, the atomic basis set III was used in the first calculations, but further calculations at 120° with set II gave a lower energy. There is question, therefore, whether the "hump" in the lowest $^1\Sigma_1$ state at 120° is really meaningful. Only the full variation calculation would be able to determine that. It is worthwhile remarking, however, that the lowest states for all symmetries at 120° were shifted by very nearly the same amount by the improved atomic basis set. This makes the very strong behavior of some of the curves in the 120° region less suspicious.

While it is certainly satisfying to find that the minimum of energy for the ground state appears to lie near the actual experimentally found values of OH separation and angle, any definitive statement on the prediction of the geometry of the molecule would have to be postponed until a complete variation of the basis set could be made and that for a number of points in the general region of the minimum. For the same
reasons, no attempt will be made to calculate the vibration frequencies from these curves, except to note that rough approximations to the second derivatives of the curves of energy versus angle and versus separation, for the ground state, while of the right order of magnitude are considerably larger than the experimental frequencies would give. This may be an indication that the 95° and 120° points are still too high, but it may mean only that the approximation to the second derivative is bad, and therefore, that the energy points must be computed before such a calculation is attempted. No attempt to correlate the levels found with absorption spectra is meaningful, since the upper states to which dipole transitions are allowed are not bound and since identification of the absorption spectra of water vapor in the ultraviolet seems to indicate that the excited states are those of OH or OH-. (2)

The variation of the hybridizing parameter α never had as great an effect as the variation of the form of the atomic basis set. In the 180° case, the minimum in energy occurred for cos α = 0. For all the other cases, the values of cos α were above .90 and indicated considerable "bending" of the bonds in towards one another. The general conclusion is that, while not being of primary importance, the flexibility introduced by this parameter certainly could not have been dispensed with; the 2s orbital enters into the bond formation, and the charge along the bond shifts into the area between bonds.

3. The Extended Valence-Bond Approximation

In the calculation of McWeeny and Ohno, the extended valence-
bond or modified electron-pair approximation gave a binding energy almost as good as the interaction of twelve bond-orbital configurations, 6.1 as compared to 6.8 ev.\(^{(3)}\). While our results are not quite so pleasing, they also indicate that the extended valence-bond approach is a good compromise between accuracy and ease of use. The ease of use is a little less than McWeeny and Ohno's work would imply, since, once again, we have found that the answer depends very strongly on the wave functions used as an atomic basis. Using the functions of set III which had been so good for the configuration interaction calculations, we found that the valence-bond energy was scarcely enough to bind the molecule. However, with the functions of set II, which are the approximation to the atomic oxygen functions, the binding energy becomes 3.7 ev, an indication that with suitable variation of the basis orbitals a reasonable answer might result. Certainly this binding energy can be increased. The relative contributions to the total electronic energy for this calculation are

\[
\begin{align*}
E_{\text{bonds}} &= -114.737 \text{ a.u.}, \\
E_{\text{coul}} &= 30.624 \text{ a.u.}, \\
E_{\text{exch}} &= -923 \text{ a.u.}
\end{align*}
\]

So it is true that the exchange energy is very small compared to the other contributions.

It was mentioned above that one of the handicaps of the present formulation of the variation of atomic orbital form has been the identification of the radial parts of all three \(p\) functions on the oxygen. Thus, though the expanded functions give a better answer in the configuration interaction case, where all occupancies of the \(x\), \(y\), and \(z\) orbitals are allowed so that some compensation can be made for orbitals
expanding out even in the direction away from the hydrogens, in the valence-bond case the less expanded functions give a better answer. In the valence-bond method, there is no way to compensate for the doubly-occupied lone pair orbitals if they shift out radially with the shift of the bond orbitals. It would seem that an immediate benefit of freeing the formulation from this identification of the radial distribution in the 2p functions will be a better energy from the valence-bond method. The use of good atomic basis functions, adapted to the molecular environment, is much more important in the valence-bond case than in the configuration interaction approximation we have carried through. But both will be improved by a full variation of the atomic basis set.

For comparison with McWeeny and Ohno, we may note that their values of the parameters in Eqs. 4-2a are \( \cos \lambda_1 = .17 \) and \( \cos \lambda_2 = .71 \), while the values of these parameters which minimize the energy in our calculation, with \( \cos \alpha = .97 \), are \( \cos \lambda_1 = .12 \) and \( \cos \lambda_2 = .84 \), indicating less mixing of hydrogen wave functions into the bond orbital, no doubt because of the more extended oxygen functions. In the case of the valence-bond calculation with atomic basis set III, for which the binding energy was negative, the contributions of the hydrogens to the bond orbitals was much less, with \( \cos \lambda_1 = .05 \) and \( \cos \lambda_2 = .92 \).

In Table 5-2, the coefficients for the expansion of the total ground state wave function in terms of the symmetry functions of Table 3-2 are given for the valence-bond approximation and, for comparison, for the configuration interaction with the same basis set II and with the
best basis for that calculation, set III. Only the first five symmetry functions make any sizable contribution and the coefficients of the other terms show no correlation in the three calculations, so only the partial list is given here. The only striking feature seems to be that the $S(02)$ contribution in the valence-bond function, being constrained to equal the $S(01)$ value, is considerably higher than in the configuration interaction on the same basis. If one looks into the orbitals involved in these symmetry functions, one can see that while $S(01)$ occupies the $z$ orbital and the symmetric combination of the two hydrogens, $S(02)$ occupies the $x$ orbital and the antisymmetric combination. In the valence-bond approximation, the $x$ and $z$ orbitals are occupied together, in the $b$ orbitals of Eq. 4-1, but in the configuration interaction all combinations of occupancies are allowed. This suggests that, even after the atomic basis set is varied to provide the suitable radial dependence in the molecular environment, a simple configuration interaction of valence-bond structures might be of advantage.

Table 5-2

Expansion of Total Wave Function in Symmetry Functions

<table>
<thead>
<tr>
<th></th>
<th>Extended Valence-Bond (atomic basis II)</th>
<th>Configuration Interaction (atomic basis III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S(00)$</td>
<td>.768</td>
<td>.664</td>
</tr>
<tr>
<td>$S(01)$</td>
<td>.417</td>
<td>.569</td>
</tr>
<tr>
<td>$S(02)$</td>
<td>.417</td>
<td>-.287</td>
</tr>
<tr>
<td>$S(03)$</td>
<td>-.198</td>
<td>-.025</td>
</tr>
<tr>
<td>$S(04)$</td>
<td>.099</td>
<td>-.323</td>
</tr>
</tbody>
</table>

All other contributions for the valence-bond function are less than .06. The symmetry functions are given in Table 3-2.
4. Conclusions and Prospects for the Future

The present study has gone beyond previous calculations on the electronic structure of the water molecule in the use of accurate values for the three-center integrals, in the variation of the radial behavior of the functions used as an atomic basis set, and in the survey of the dependence of the molecular energy on the geometrical parameters. While McWeeny and Ohno, building on the work of Ellison and Shull, have compared the results from use of various approximate methods of computing energies and wave functions, their work is in need of confirmation since it is based on approximate integral values and single-term Slater atomic orbitals. The work of Boys and associates, while not using approximate integral values, shows, as does our calculation, that poor basis orbitals cannot be easily overcome in a limited configuration interaction. With the use of single-term Slater type orbitals and retaining the 30 most significant configurations out of 96 for the ground state symmetry, these investigators still got a binding energy of only 5.81 ev. The use of accurately calculated values for the integrals led to a minimum of energy near the experimental value, as it did in our case, but, since they do not give the values of energy for the various geometrical parameters, we can not make any detailed comparison.

Thus, in terms of a comparison with previous calculations and within the scope of our own work, the main conclusion we come to is the need for varying the parameters in the atomic basis functions expressed as a sum of Slater-type orbitals. With such a variation, good binding energies can be obtained by the full configuration interaction used in
this study, and, it seems to us, fair binding energies will be obtained by the valence-bond method with correlated bond orbitals. In this latter method, it is even more imperative than in the configuration interaction to have good basis orbitals, either computed by self-consistent field calculation separate from the valence-bond calculation or within the programs for the valence-bond computations. The use of a combination of the bond functions which allow some correlation with the self-consistent basis set should be the best possible approximation which still retains a single-particle point of view.

The next result of these calculations is that a more adequate representation of the hydrogen orbitals is necessary. Although the energy has been considerably lowered in the configuration interaction calculation by allowing the p functions to move out radially toward the hydrogens, this has been at the cost of a distortion of the true electronic density. This is asserted on the basis of the dipole moment calculated for the wave functions that give the best energy. As is apparent in McWeeny and Ohno's results, better energies, particularly through configuration interaction, seem to lead to poorer dipole moments. Repeating the calculation with their integrals, but with more configurations, we found a poorer dipole moment than theirs for 12 configurations. With our integrals, for the best energy, the dipole moment is 1.26 Debyes (experimental, 1.84; McWeeny and Ohno, for best energy, 1.53). Thus, in computing atomic oxygen functions appropriate to the molecular environment, it will be necessary
to express the hydrogen orbitals as a sum of at least three Slater functions, two 1s functions with different exponents and one p function to handle polarization of the orbitals.

Throughout all of this work it became increasingly apparent that the use of physical insight into the problem and into the way one would expect the orbitals to behave as the molecule is formed from the separated atoms can suggest what orbitals are essential to a basis set and how the basis functions should adapt to the environment. The use of configuration interaction with many orbitals in an attempt to produce the effect of a good basis set seems the less satisfactory way of proceeding. With the valence-bond approximation, using correlated orbitals, one retains a physically meaningful picture which is possible of extension to larger molecules. By introducing flexibility within the basis orbitals, rather than by inclusion of higher orbitals, this valence-bond approach can no doubt have a greatly improved result. We have seen in both the configuration interaction and in the valence-bond methods a very marked dependence on the radial dependence of just two of the orbitals. There is great hope for a calculation which allows variation in the radial distribution of each of the four L shell orbitals separately and of both the oxygen and hydrogen 1s orbitals. Considerations of angular correlation and correlation between electrons in different closed shells or bonds should be left aside until a complete investigation has been made of electronic structure of the water molecule by these methods which are a direct
generalization of the work of the present thesis. It is no longer sufficient to base a molecular calculation on single Slater-type functions as orbitals, unless very many more were used than in this work, as the calculations of Boys and associates have shown. Neither can one simply use the atomic Hartree-Fock functions, as several of the better diatomic calculations have done. Even if one is doing a self-consistent field calculation, the importance of including several terms for each orbital is made clear from this study.

Thus, in summary, although this study has been an advance over the earlier ones, it is not a finished piece of work, but rather a suggestion of what are the next steps to be taken for a more fruitful investigation of the electronic structure of molecules.
REFERENCES

CHAPTER I


2 For example, see B. J. Ransil, Rev. Mod. Phys., 32, 239 (1960), and the survey of L. C. Allen and A. M. Karo, Rev. Mod. Phys., 32, 275 (1960).


CHAPTER II


2 R. E. Watson has provided analytic Hartree-Fock wave functions with a five-term expression in Slater functions for the s-like functions and a three-term expression for the p-like. Our expansions were fitted to the charge densities for these functions.
CHAPTER II (cont)

3 D. R. Hartree, W. Hartree, and B. Swirles, Trans. Roy. Soc. (London) A238, 229 (1939); the value given is calculated from their functions by A. J. Freeman, J. Chem. Phys. 28, 230 (1958). Freeman gives the experimental value of the total energy, the sum of energy necessary to strip off the electrons one by one, as -75.112 a.u., computed from the values in C. E. Moore, Atomic Energy Levels, Vol. I, National Bureau of Standards Circular 467, 1949. The Hartree energy unit, a.u., is two Rydbergs or 27.21 e.u.


5 art. cit., p. 371.


CHAPTER III


CHAPTER IV

1 art. cit., p. 373.


3 See the discussion in Chapter III, section 2.

4 J. C. Slater, Quarterly Progress Report, Solid-State and Molecular Theory Group, April 15, 1955, p. 5.

CHAPTER V


CHAPTER V (cont)

3 McWeeny and Ohno, art. cit., p. 373.

4 S. F. Boys, G. B. Cook, C. M. Reeves, and I. Shavitt, art. cit., p. 1208.

5 _art. cit._, Table 4, p. 380.
BIOGRAPHICAL SKETCH

The author was born in Los Angeles, California, on November 14, 1928. He received his elementary schooling in Los Angeles, and was graduated from Inglewood High School in June, 1946. He did his undergraduate physics studies at the California Institute of Technology, receiving the Bachelor of Science degree there in June, 1950. At the University of Notre Dame, in August, 1951, he completed work for the degree of Master of Science. In the same month, the author began preparation for the Roman Catholic priesthood in the Society of Jesus. After two years of novitiate, a period of religious training, and a year of humanities, he entered St. Louis University to study for the Master of Arts degree in philosophy, which he received in 1957. Since that time he has been enrolled as a graduate student in physics at the Massachusetts Institute of Technology. He has been a Research Assistant in the Solid-State and Molecular Theory Group since 1959.