A QUANTUM-MECHANICAL DISCUSSION OF THE BIFLUORIDE ION

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Abstract

The variation method for obtaining approximate solutions to the Schrödinger equation is examined. It is demonstrated that one-electron orbitals can be employed in the construction of a convergent variation function. As special cases of the one-electron approach, the valence bond and molecular orbital methods are discussed and compared.

Variation functions containing only a few terms are known to lead to incorrect results. The reasons for this failure are discussed. A semi-theoretical approach, which corrects some of the failings, is developed and tested on HF. Results in good agreement with experimental determinations of the energy and dipole moment are obtained. Application of the method to FHF^- leads to a value of 36.5 kcal. for the energy of the reaction

$$F^- + HF \rightarrow FHF^-$$

Calculation of the FHF^- wave function shows that the completely ionic structure ($F^- H^+ F^-$) makes the largest contribution.

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INTRODUCTION

The hydrogen bond was first recognised in 1912[1]. Since then, experimental studies [2] have provided extensive evidence of its function in determining the properties of inorganic and organic substances. More recently the effect of hydrogen bonds on the structural relations of biologically significant substances has been examined [3].

In spite of the recognized importance of the hydrogen bond, no one has given a detailed discussion of the forces involved in its formation. Since the bifluoride ion (FHF^-) is the simplest hydrogen bonded species, it appears best suited for a theoretical attack. This thesis is an attempt to develop a

semi-theoretical method applicable to highly ionic systems and to apply this method to a treatment of the bifluoride ion. It is hoped that the results contribute to a better understanding of the hydrogen bond and provide an illustration of the power of quantum-mechanical methods in chemistry.

Chapter 1 - METHODOLOGY

Section I - The variation procedure

Quantum chemistry has as its primary concern the solution of the eigenvalue problem posed by the time-independent Schrödinger equation for an isolated molecular system

$$H_T \Psi_N (\underline{r}_i, \underline{r}_\ell) = E_N \Psi (\underline{r}_i, \underline{r}_\ell) \tag{1-1}$$

Here H_T is the complete Hamiltonian operator,

$$H_T = -\sum_{i=1}^{2s} \frac{1}{2} \nabla_i^2 - \sum_{\ell=1}^{t} \frac{1}{2m_\ell} \nabla_\ell^2 - \sum_{i=1}^{2s} \sum_{\ell=1}^{t} \frac{Z_\ell}{r_{i\ell}} + \sum_{i,i'>i}^{2s} \frac{1}{r_{ii'}} + \sum_{\ell,\ell'>\ell}^{t} \frac{Z_\ell Z_{\ell'}}{r_{\ell\ell'}} \tag{1-2}$$

$i = 1, 2 \cdots 2s$ electrons
$\ell = 1, 2 \cdots t$ nuclei

expressed in Hartree units[4] *, and Ψ_N, E_N are its N^{th} eigenfunction and eigenvalue, respectively. Implicit in the writing of (1-2) is the neglect of certain energy terms (e.g. spin-orbital coupling) which usually make only a negligible contribution; their effect on atomic systems

*Hartree units are defined as follows: unit of mass - the electronic mass, $m_o = .9107 \times 10^{-27}$ grams; unit of length - the Bohr radius, $a_o = .529$A; unit of charge - the electronic charge, $e = 4.80 \times 10^{-10}$ e.s.u.; unit of action - $\hbar = 1.05 \times 10^{-27}$ erg. sec., unit of energy - twice the ionization energy of the hydrogen atom, $\frac{e^2}{a_o} = 27.19$ electron volts.

is discussed in Condon and Shortley[5]. By application of the adiabatic approximation[6] to (1-1) a separation of nuclear and electronic motion is achieved[7] and the set of equations

$$H \Psi_n (\underline{r}_i, \underline{r}_e) = E_n (\underline{r}_e) \Psi_n (\underline{r}_i, \underline{r}_e) \tag{1-3}$$

$$H_{nuc} \Psi_N (\underline{r}_e) = E_N \Psi_N (\underline{r}_e) \tag{1-4}$$

results. Here

$$H = -\sum_i \tfrac{1}{2} \nabla_i^2 - \sum_{i,e} \frac{Z_e}{r_{ie}} + \sum_{i,i'>i} \frac{1}{r_{ii'}} + \sum_{e,e'>e} \frac{Z_e Z_{e'}}{r_{ee'}} \tag{1-5}$$

and

$$H_{nuc} = -\sum_e \frac{1}{2m_e} \nabla_e^2 + E_n (\underline{r}_e) \tag{1-6}$$

Studies of the vibrational and rotational spectra of molecules are concerned with equation (1-4). This chapter is restricted to a discussion of equation (1-3), which describes the electronic wave functions and energy levels of molecular systems with stationary nuclei.

Direct solution of the many-body problem presented by equation (1-3) with $2s,t > 1$ is feasible only if a separation of variables can be effected. Since the presence of

electronic interaction terms $\left(\frac{1}{r_{ii'}}\right)$ in the potential energy operator makes such a separation impossible, approximate methods of solution have to be employed. Of these, the most powerful are applications of the variation principle. In general form[9] it states that the functions, which result in extremals, E_n, for the integral*

$$E_n = \int \psi_n H \psi_n d\tau \qquad (1\text{-}7)$$

subject to certain boundary conditions and to the equalities

$$\int \psi_n \psi_n d\tau = 1 \qquad (1\text{-}8)$$

and

$$\int \psi_n \psi_i d\tau = 0 \qquad i = 1, 2 \cdots n-1 \qquad (1\text{-}9)$$

are the eigenfunctions of the Schrödinger equation; the E_n obtained by this procedure are the corresponding eigenvalues. (In equation (1-7) through (1-8) and subsequently $d\tau$ indicates an integration over all the electron

* The wave functions are assumed real throughout to simplify notation. For complex ψ_n each integral would have to be replaced by one including the complex conjugate; e.g., (1-7) would become

$$E_n = \int \psi_n^* H \psi_n d\tau$$

coordinates appearing in ψ_n, and the integral sign without specified limits designates integration over all space.) Actually the ψ_n desired in the many-electron problem are not those yielding absolute minima for E_n subject to (1-8) and (1-9). The Pauli condition[10] that ψ_n be antisymmetric, in general, raises the allowed energy eigenvalues above those obtained from equations (1-7) - (1-9) and has to be introduced as an additional restriction.

By arbitrarily varying ψ_n until E_n is extremized, the correct wave functions and energies for a molecular system can, in principle, be obtained. In practice, the time required for the evaluation of the integral (1-7) drastically restricts the variations to which the approximation function can be subjected. Consequently, the wave function finally obtained in a calculation is often a poor approximation to the true one. The great utility of the variation method arises from the fact that even with poor wave functions good energy values can result, since in the region of the extremum the integral (1-7) is insensitive to the form of the function used. This statement unfortunately applies to the energy alone; other molecular properties, such as the dipole moment, may be far from correct in calculations which yield nearly perfect values for the energy.

The difficulty in carrying out arbitrary variations in ψ_n suggests the introduction of an alternative procedure.

By use of a complete normal set of functions, $g_m(r_i, r_e)$, the variation problem of equation (1-7) can be reduced to an algebraic one. The process of finding extremals for the integral*

$$E_o = \int \Psi_o H \Psi_o \, d\tau \tag{1-10}$$

and, therefore, that of determining the eigenfunctions and eigenvalues of the Schrödinger equation is equivalent[11] to solving the infinite set of linear homogeneous equations

$$\sum_{m=1}^{\infty} a_m [H_{em} - E S_{em}] = 0 \qquad l = 1, 2 \cdots \tag{1-11}$$

Here the a_m are the expansion coefficients of Ψ_o expressed in terms of the g_m, i.e.,

$$\Psi_o = \sum_{m=1}^{\infty} a_m g_m(r_i, r_e) \tag{1-12}$$

$$H_{em} = \int g_e H g_m \, d\tau \tag{1-13}$$

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* Only the ground state, E_o, Ψ_o, is discussed. For excited states ($n > 0$) arguments closely related to those present below are applicable if a restriction of the form of equation (1-9) is included.

and

$$S_{\ell m} = \int g_\ell \, g_m \, d\tau \tag{1-4}$$

For computations, a function $\upsilon_0^{\,K}$

$$\upsilon_0^{\,K} = \sum_{m=1}^{K} a_m^{K} \, g_m \tag{1-15}$$

and the corresponding finite set of linear homogeneous equations

$$\sum_{m=1}^{K} a_m^{K} \left[H_{\ell m} - E^{K} S_{\ell m} \right] = 0 \qquad \ell = 1, 2 \cdots K \tag{1-16}$$

are considered, the assumption being made that

$$\lim_{K \to \infty} \upsilon_0^{\,K} = \psi_0 \tag{1-17}$$

Use of a minimal sequence

$$\upsilon_0^{\,1}, \upsilon_0^{\,2} \cdots \upsilon_0^{\,K} \cdots \tag{1-18}$$

for the solution of variational problems was suggested by Ritz[12]. A necessary condition for the existence of solutions to equations (1-16) is that the E^k satisfy the equation [13]

$$|H_{em} - E^{K} S_{em}| = 0 \qquad (1\text{-}19)$$

If the U_0^K satisfy (1-17), the corresponding E_0^K converge to E_0 monotonically from above, i.e.,

$$E_0^1 > E_0^2 \cdots E_0^K > \cdots > E_0 \qquad (1\text{-}20)$$

By including a sufficient number of terms in U_0^K (equation (1-15)) any accuracy can, in principle, be attained. A limit on the usefulness of the method arises, however, from the lack of an analytic criterion for determining the error at each stage of approximation. Only by comparison with experimental data can the validity of a result be determined. As the various molecular properties depend to different degrees on the form of the wave function, it is difficult to make reliable predictions with the variation procedure.

Section II - The use of one-electron function

Since the Hamiltonian operator (1-2) contains electronic interaction terms, the correct wave function must have a functional dependence on electron-electron distances. The set $q_m(\underline{r}_i, \underline{r}_e)$ (equation 1-12) is, therefore, expected to converge most rapidly to the true wave function if it reflects this dependence explicitly. Calculation of the

Schrödinger integral (equation 1-7) is generally too time-consuming if functions including polynomials in $r_{ii'}$ are used. Only in the case of H_2[14] has such an approach been possible. For more complicated molecules the exclusion of $r_{ii'}$ terms from the $g_m(r_i, r_e)$ is necessary. Such a restriction on the form of the $g_m(r_i, r_e)$ might be expected to limit the accuracy attainable by their use.*

It can, however, be demonstrated[16] that given a complete set of functions of one variable, $h_\ell(r)$ defined over the domain $a \leq r \leq b$, a complete set for p variables $(r_1, r_2 \cdots r_p)$, each defined over domain $a \leq r_1, r_2 \cdots r_p \leq b$, can be formed by taking all possible products of the functions $h_{\ell_1}(r_1), h_{\ell_2}(r_2) \cdots h_{\ell_p}(r_p)$. A function $f(r_1, r_2, \cdots r_p)$ can thus be expressed in terms of the infinite series

$$f(r_1, r_2 \cdots r_p) = \sum_{\ell_1, \ell_2 \cdots \ell_p}^{\infty} a_{\ell_1 \ell_2 \cdots \ell_p} h_{\ell_1}(r_1) h_{\ell_2}(r_2) \cdots h_{\ell_p}(r_p) \qquad (1\text{-}21)$$

where the $a_{\ell_1 \ell_2 \cdots \ell_p}$ are the appropriate coefficients. If the expansion (1-21) is assumed to hold for infinite domains# the use of sets of one-electron product functions

* This misconception can be illustrated by quoting Lennard-Jones[15]: "A good approximation can be obtained to the wave function by expressing it in terms of functions of the coordinates of individual electrons. This means that... the assumed form of wave function can never be exact...."

Proof of completeness theorems have been carried out for finite domains. The difficulties arising in attempts at generalization to infinite domains are presented in Kemble[17].

of the form (1-21) in constructing minimal sequences (see equation 1-17) for molecular calculations is justified.

In each of the one-electron functions, $\Phi_{\ell_i}(\underline{r}_i)$, the electron i, ($i=1,2\cdots 2s$) is specified in terms of its position coordinates (x_i, y_i, z_i) and its spin coordinate (λ_i). By the Pauli principle the wave function is antisymmetric with respect to exchange of electrons in this 4s dimensional configuration space. A corresponding antisymmetry has to be introduced into the variation function

$$\Psi_0 = \lim_{K\to\infty} \sum_{\ell_i=1}^{K} a_{\ell_1\ell_2\cdots\ell_{2s}}\, \underline{\Phi}_{\ell_1}(\underline{r}_1)\, \underline{\Phi}_{\ell_2}(\underline{r}_2)\cdots \underline{\Phi}_{\ell_{2s}}(\underline{r}_{2s}) \qquad (1\text{-}22)$$

Since spin-orbital terms in the Hamiltonian operator have been neglected, each of the one-electron functions can be written as a product of two functions

$$\underline{\Phi}_{\ell}(\underline{r}_i) = \phi_{\ell}(\underline{r}_i)\, \eta(\lambda_i) \qquad (1\text{-}23)$$

where the $\eta(\lambda_i)$ are eigenfunctions of the z - component of the electron spin. Substitution of (1-23) into (1-22) yields

$$\Psi_0 = \lim_{K\to\infty} \sum_{\ell_i}^{K} a_{\ell_1\ell_2\cdots\ell_{2s}}\, \phi_{\ell_1}(\underline{r}_1)\eta(\lambda_1) \cdots\cdots \phi_{\ell_{2s}}(\underline{r}_{2s})\eta(\lambda_{2s}) \qquad (1\text{-}24)$$

Since Ψ_0 is already antisymmetric, application to (1-24) of the antisymmetrizer[18]

$$\mathcal{A} = \frac{1}{\sqrt{(2s)!}} \sum_{\text{all } P} (-1)^p P \tag{1-25}$$

where P represents a given permutation and p its parity, results in

$$\Psi_0 = \mathcal{A}\Psi_0 = \frac{1}{\sqrt{(2s)!}} \sum_{\text{all } P} (-1)^p P \lim_{K\to\infty} \sum^{K} a_{\ell_1 \cdots \ell_{2s}} \phi_{\ell_1}(r_1)\eta(\lambda_1) \cdots \phi_{\ell_{2s}}(r_{2s})\eta(\lambda_{2s}) \tag{1-26}$$

or

$$\Psi_0 = \frac{1}{\sqrt{(2s)!}} \lim_{K\to\infty} \sum_{\ell_i}^{K} a_{\ell_1 \cdots \ell_{2s}} \sum_{\text{all } P} (-1)^p P\, \phi_{\ell_1}(r_1)\eta(\lambda_1) \cdots \phi_{\ell_{2s}}(r_{2s})\eta(\lambda_{2s}) \tag{1-27}$$

By the definition of a determinant, (1-27) is equivalent to (1-28)

$$\Psi_0 = \frac{1}{\sqrt{(2s)!}} \lim_{K\to\infty} \sum_{\ell_i}^{K} a_{\ell_1 \cdots \ell_{2s}} \left| \phi_{\ell_1}(r_1)\eta(\lambda_1) \cdots \phi_{\ell_{2s}}(r_{2s})\eta(\lambda_{2s}) \right| \tag{1-28}$$

where $|\quad|$ represents a determinant expressed in terms of its principal diagonal[19]. Use of (1-26) and (1-27) introduces no restriction since the antisymmetric function formed from a simple product function is unique.

By use of the commutation properties[20] of certain operators appearing in molecular problems the number of determin-

ants that have to be considered can be reduced to a fraction of all the non-zero determinants that can be constructed from a complete set of functions. Since any two commuting Hermitian operators have simultaneous eigenfunctions, the variation function has to contain only the determinants which are eigenfunctions of sets of mutually commutable operators. A set of physical significance for molecular problems consists of the Hamiltonian, H, the permutation operators P,* the square of the total spin angular momentum, S^{2}**, the z-component of the total spin angular momentum, S_z ,** and the symmetry operators for the molecule under consideration. Use of the determinantal function (1-28) automatically provides eigenfunctions of the P's and S_z . It is necessary only to choose the spin functions $\eta(\lambda_i)$ in all determinants to yield the same S_z eigenvalue. Usually the ground state in a molecular system corresponds to the eigenvalue zero***

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* In general, two permutation operators do not commute; however, for any antisymmetric function Ψ_0

$$P_1 P_2 \Psi_0 = P_2 P_1 \Psi_0$$

so that the permutation operators may be considered to commute in this case.

**The operators S^2, S_z, commute with the Hamiltonian only if spin-orbital terms have been neglected.

***The oxygen molecule is the most notable exception to this rule.

For excited states other S_z eigenvalues

$$S_3 \Psi_n = \lambda \Psi_n \qquad \lambda > 0 \tag{1-29}$$

are of interest. Restriction of the function (1-28) to a given eigenfunction of S^2 requires the introduction of certain linear combinations of Slater determinants. Rules for the construction of eigenfunctions of the desired multiplicity, usually singlet, have been developed[21]. These rules are not discussed here, as their use is illustrated by application to HF and HF_2^- (see below). Since the Hamiltonian reflects the nuclear configuration of a molecule, the symmetry operators for that molecule commute with the Hamiltonian. For molecules of high symmetry, the set of functions that have to be included can be considerable restricted by the requirement that they yield eigenfunctions of the symmetry operators[22].

Section III - Approximation procedures involving a finite number of functions.

In spite of the reductions outlined in the preceding section, the number of determinants that are required for convergence to the true eigenfunctions of the Hamiltonian is still infinite. Since no formulae exist for the general terms required in (1-11), only a finite number can be included in any calculation. The choice of the functions

$\phi_\rho(r)$ assumes major importance. Two considerations have primacy in the selection. On the one hand, rapidity of convergence is desirable in restricting the number of determinants that must be included; on the other, the ease of calculation with each determinant governs the number that can be included. For atomic problems the first consideration is dominant, since the Schrödinger integral is reasonably simple to calculate regardless of the type of one-electron function. Hydrogen-like[23] or closely related functions (Slater[24] or Hartree - Fock[25]) are used in the hope that they are sufficiently close to the true function to permit rapid convergence. The success achievable with atoms leads to the selection of the same atomic functions for molecular problems. Here they introduce integrals so time-consuming as to drastically restrict the number of determinants that can be considered. It seems, therefore, that more consideration should be given to the second point mentioned above - that of the ease of calculation. By the substitution of error functions for the exponentials commonly employed, the evaluation of molecular integrals is greatly simplified. Before the error functions are used directly for the construction of determinants (1-28) some comparison of their integral behavior with that of exponentials is necessary. In Chapt. III the possibility of approximating by use of error functions the molecular integrals obtained with Slater functions is tested.

Once the set of one-electron functions $\phi_\ell(r)$ is chosen certain members of that set have to be selected and combined into the finite sum U^K (equations 1-15 and 1-28). For generating U^K a number of procedures are employed. Amongst these, the commonest is the valence-bond method[21,26]. It selects from a set of atomic functions (see above) the subset corresponding to the inner-shell orbitals plus the valence-shell orbitals of the isolated atoms and combines these into determinantal functions such that the inner-shell orbitals are filled (i.e., appear twice with paired spins in each determinant) and some or all of the valence shell orbitals are involved in forming bonds. A bond exists between pairs of orbitals if sets of determinants antisymmetric with respect to the spin functions of these pairs of orbitals appear in the variation function. For four electrons in four valence-shell orbitals, bonds between one and two and between three and four exist, if

$$\begin{aligned}\Psi = &|\phi_1(r_1)\beta(1)\,\phi_2(r_2)\alpha(2)\,\phi_3(r_3)\beta(3)\,\phi_4(r_4)\alpha(4)| \\ &- |\phi_1(r_1)\alpha(1)\,\phi_2(r_2)\beta(2)\,\phi_3(r_3)\beta(3)\,\phi_4(r_4)\alpha(4)| \\ &- |\phi_1(r_1)\beta(1)\,\phi_2(r_2)\alpha(2)\,\phi_3(r_3)\alpha(3)\,\phi_4(r_4)\beta(4)| \\ &+ |\phi_1(r_1)\alpha(1)\,\phi_2(r_2)\beta(2)\,\phi_3(r_3)\alpha(3)\,\phi_4(r_4)\beta(4)| \qquad (1\text{-}30)\end{aligned}$$

Here $\alpha(i)$, $\beta(i)$ have replaced the $\eta(\lambda_i)$ and correspond to a z-component of the electron spin equal to $\frac{1}{2}\hbar$, $-\frac{1}{2}\hbar$ respectively. In the simple valence bond theory only one electron per valence orbital is permitted. A generalization[27] to include ionic structures is carried out by introducing determinants in which the requisite valence orbitals appear twice.

An approach closely related to the valence bond procedure is the molecular orbital method. It employs as one-electron functions, $\psi_i(r_i)$, not atomic orbitals, but rather linear combinations of atomic orbitals

$$\psi_i(r_i) = \sum_{\ell_i=1}^{m} b_{\ell_i} \phi_{\ell_i}(r_i) \qquad (1\text{-}31)$$

so constructed that

$$\int \psi_i(r_i)\, \psi_{i'}(r_i)\, d\tau = \delta_{ii'} \qquad (1\text{-}32)$$

The choice of atomic orbitals, $\underline{m}$ in number, is usually restricted to the same set as that used in valence bond theory. Their coefficients b_{ℓ_i} cannot be determined by use of a

variation procedure (equation 1-28); an iterative method based on the general variation principle (equation 1-7) has to be employed. To understand this fact and to obtain a direct comparison with valence bond theory, it is useful to examine the determinants constructed with the molecular orbitals (1-31). A typical molecular orbital calculation requires evaluation of the coefficients appearing in determinants of the form

$$D = \frac{1}{\sqrt{(2s)!}} \left| \psi_1(r_1)\beta(1) \cdots \psi_{2s}(r_{2s})\alpha(2s) \right| \tag{1-33}$$

or, in terms of (1-31),

$$D = \frac{1}{\sqrt{(2s)!}} \left| \sum_{\ell_1=1}^{m} b_{\ell_1} \phi_{\ell_1}(r_1)\beta(1) \cdots \sum_{\ell_{2s}=1}^{m} b_{\ell_{2s}} \phi_{\ell_{2s}}(r_{2s})\alpha(2s) \right| \tag{1-34}$$

By use of the distributive law of multiplication, (1-34) can be written as the sum

$$D = \frac{1}{\sqrt{(2s)!}} \sum_{\ell_1,\ell_2\cdots\ell_{2s}}^{m} \left| b_{\ell_1}\phi_{\ell_1}(r_1)\beta(1) \cdots b_{\ell_{2s}}\phi_{\ell_{2s}}(r_{2s})\alpha(2s) \right| \tag{1-35}$$

Since multiplying all the elements of a column of a determinant by a number multiplies the determinant by that number, (1-35) is equivalent to

$$D = \sum_{\ell_1 \cdots \ell_{2S}}^{m} \frac{1}{\sqrt{(2S)!}}\, b_{\ell_1} \cdots b_{\ell_{2S}} \left| \phi_{\ell_1}(r_1)\beta(1) \cdots \phi_{\ell_{2S}}(r_{2S})\alpha(2S) \right| \qquad (1\text{-}36)$$

or

$$D = \frac{1}{\sqrt{(2S)!}} \sum A_{\ell_1 \cdots \ell_{2S}} \left| \phi_{\ell_1}(r_1)\beta(1) \cdots \phi_{\ell_{2S}}(r_{2S})\alpha(2S) \right| \qquad (1\text{-}37)$$

Equation (1-37), which is obtained from a single molecular orbital determinant, is formally identical to the expression (1-28) with finite $K=m$ and zero S_z eigenvalue. In (1-28) the coefficients $a_{\ell_1 \cdots \ell_{2S}}$ are independent except for the overall normalization requirement (equation 1-8) and certain linear relations of the form (1-30). The $A_{\ell_1 \cdots \ell_{2S}}$ of equation (1-37), however, are related, in addition, by non-linear restrictions of the type

$$\frac{A_{\ell_1'\ell_2' \cdots \ell_{2S}'}}{A_{\ell_1''\ell_2' \cdots \ell_{2S}'}} = \frac{A_{\ell_1'\ell_2'' \cdots \ell_{2S}''}}{A_{\ell_1''\ell_2'' \cdots \ell_{2S}''}} = \frac{b_{\ell_1}'}{b_{\ell_1}''} \qquad (1\text{-}38)$$

For a closed shell ground state[22] the molecular orbital description consists of a single determinant (1-33) in which each orbital $\phi_i(r_i)$ appears twice, once with spin β and once with spin α. The number (N_b) of coefficients, b_{ℓ_i}, to be determined by the iterative procedure is

$$N_b = mxs - s^2 \tag{1-39}$$

since there are mxs coefficients b_i which are related by s^2 orthonormality conditions (equation 1-32). The number N_D of different non-zero determinants appearing in (1-37) from the expansion of (1-33) is

$$N_D = \left\{ \frac{m!}{(m-s)!\,s!} \right\}^2 \tag{1-40}$$

This expression is obtained by considering the orbitals with spin β and spin α independently and by realizing that the number of ways s electrons can be distributed among m orbitals is just

$$\frac{m!}{(m-s)!\,s!} \tag{1-41}$$

Subtraction of (1-39) from (1-40) yields

$$\left\{ \frac{m!}{(m-s)!\,s!} \right\}^2 - (mxs - s^2) \tag{1-42}$$

the number of relations amongst the $A_{\ell_1 \cdots \ell_{2s}}$. It is these relations which complicate the molecular orbital procedure and require introduction of an iterative method of solution.

If for m>s not just a single determinant (1-33), but all possible determinants are constructed and used in the variation function, the results of the molecular orbital procedure

become identical with those of the valence bond method. From $\underline{m}$ atomic orbitals $\underline{m}$ linearly independent molecular orbitals can be formed. Consequently

$$\left\{ \frac{m!}{(m-s)!\,s!} \right\}^2 \qquad (1-43)$$

determinants can be constructed out of the $\underline{m}$ atomic or the $\underline{m}$ molecular orbitals. Selection of the number of singlet functions that can be formed in each case requires more detailed consideration. For $\underline{s}$ electrons and $\underline{m}$ atomic orbitals, $\underline{k}$ of which contain two electrons (appear twice in a determinant), the number of determinants that can be constructed is

$$\frac{m!}{k!\,(2s-2k)!\,(m-2s+k)!} \qquad (1-44)$$

i.e., the $\underline{m}$ orbitals are divided into three groups: $\underline{K}$ containing 2 electrons, $(2s-2K)$ containing 1 electron, and

$$m-(2s-2k)-K=m-2s+K \qquad (1-45)$$

containing no electrons. In the $\underline{K}$ orbitals with 2 electrons the spins are determined by the exclusion principle; each of the $\underline{K}$ orbitals appears once with spin α and once with spin β. The spins of the $(2s-2K)$ singly occupied orbitals can be so arranged that linear combinations of the determin-

ants (1-44) yield

$$\frac{(2s-2k)!}{(s-k)!(s-k+1)!} \tag{1-46}$$

functions of singlet multiplicity[28]. For each value of k there are, therefore,

$$\frac{m!}{k!(s-k)!(s-k+1)!(m-2s+k)!} \tag{1-47}$$

singlet functions. Since

$$s \geq k \geq 2s-m \tag{1-48}$$

the total number (Ns) of independent singlet functions is

$$N_s = \sum_{k=2s-m}^{s} \frac{m!}{k!(s-k)!(s-k+1)!(m-2s+k)!} \tag{1-49}$$

This series sums* to

$$N_s = \left\{ \frac{m!}{(m-s)!\ s!} \right\}^2 \left(\frac{m+1}{(m-s+1)(s+1)} \right) \tag{1-50}$$

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* Given

$$N_s = m! \sum_{k=2s-m}^{s} \frac{1}{k!(s-k)!(m-2s+k)!(s-k+1)!}$$

make the substitution

$$k' = k-2s+m$$

Then

$$N_s = m! \sum_{K=0}^{m-s} \frac{1}{(K'+2s-m)!\,(m-s-K')!\,K'!\,(m-s-K'+1)!}$$

If

$$(1+x)^{m-s} = \sum_{K'=0}^{m-s} a_{K'}\, x^{K'}$$

$$\frac{1}{K'!\,(m-s-K')!} = \frac{1}{(m-s)!}\, a_{K'}$$

Similarly, if $(1+x)^{s+1} = \sum_{K=0}^{s+1} b_K x^K$

$$\frac{1}{(K'+2s-m)!\,(m-s-K'+1)!} = \frac{1}{(s+1)!}\, b_{K'+2s-m}$$

Since

$$a_{K'} = a_{m-s-K'}$$

$$N_s = \frac{m!}{(m-s)!\,(s+1)!} \sum_{K'=0}^{m-s} a_{m-K'-s}\, b_{K'+2s-m}$$

but, the last summation is just the coefficient of x^s in

$$(1+x)^{m-s}(1+x)^{s+1} = (1+x)^{m+1}$$

Thus

$$N_s = \frac{m!}{(m-s)!\,(s+1)!} \times \frac{(m+1)!}{s!\,(m+1-s)!} = \left\{\frac{m!}{(m-s)!\;s!}\right\}^2 \left\{\frac{m+1}{(m-s+1)(s+1)}\right\}$$

- -

(Ns-1) gives the number of independent coefficients to be determined in the solution of a generalized valence bond treatment on the assumption that symmetry conditions do not provide any additional relations. An identical argument (equations (1-44) - (1-50) holds for molecular orbital theory if m is the number of molecular orbitals and k represents those containing two electrons. The additional m^2 coefficients, b_{ℓ_i}, appearing in molecular orbital theory have no

effect on the result since they are completely determined by the $\underline{m}^2$ orthonormality conditions. Consequently the complete molecular orbital and valence bond theories are identical. Calculation in the presence of the $b_{\ell i}$ is extremely complicated (see above). Only if symmetry considerations permit evaluation of the $b_{\ell i}$ by inspection or by group theoretical methods does the complete molecular orbital treatment approach the relative simplicity of the generalized valence bond method. In case the complete treatment is replaced by one using only those singlet functions which are expected to make an important contribution, the superiority of the valence bond method is particularly evident. Expression of the variation function in the form (1-30) permits the direct utilization of physical reasoning. Structures corresponding to known distributions of chemical bonds can be included, and others may be neglected. For the choice of important ionic structures electronegativity data can easily be employed.

The restrictions placed on the general variation function to reduce it to the valence bond procedure do not in any way affect the applicability of the variation principle. In many cases additional approximations are introduced which do violate the variation principle. Most prominent among these is the use of an approximate Hamiltonian[29]. Inner shell electron terms may be completely neglected in the

Hamiltonian, their existence being accounted for by a change in nuclear charge; or they may be replaced by a coulombic charge distribution, In either case the process has meaning only if the quantity being calculated (e.g. the dissociation energy) is obtained by the subtraction of two or more quantities to which the inner electron terms are common (e.g. isolated atom energy subtracted from total molecular energy). It is also possible to replace some of the required terms in an energy expression by experimental values (see Chap. 2). If such procedures are used there is no longer any guarantee that the resulting value for the molecular energy approaches the true energy as a minimum. In using these approximations great care must, therefore, be employed to ascertain that the violation of the variation principle does not invalidate the results.

CHAPTER 2 - The Matrix Elements

Section I - General Considerations

In the solution of a problem by the variation method in its general or restricted forms (equation 1-28) three steps are necessary. A choice of orbitals has to be made and these orbitals, combined into a suitable variation function (Chapter 1, Sec. II). With this function, the required matrix elements (equation 1-13, 1-14) are constructed and their values computed. Finally, the resultant secular equation (equation 1-28) is solved. In this thesis the first and third steps are performed by standard methods and the illustration provided by the specific examples (Chapter 4) should suffice. The second step, concerned with the evaluation of matrix elements, is, however, treated in a somewhat novel manner; the method used is presented below.

From a variation function composed of a linear combination of Slater determinants, matrix elements of the form

$$M_{ij} = \int \psi^i M \psi^j d\tau \qquad (2\text{-}1)$$

arise. Here M is an operator, the Hamiltonian H or the unit operator 1, and the ψ^i, ψ^j represent Slater determinants. The M_{ij} are composed of integrals independent of the internuclear distances (atomic terms) and integrals

that are functions of the internuclear distances (interaction terms). For simple product functions the separation of the two types of terms is straightforward. One may consider a molecule consisting of nuclei a, b,... q and described by the product function

$$\psi^i = \phi_i(r_{ia}) \cdots \phi_\ell(r_{\ell a})\phi_{\ell+1}(r_{\ell+1\,b}) \cdots \phi_{2s}(r_{i\,2sq}) \qquad (2\text{-}2)$$

The unit matrix element is written directly as

$$\int \psi^i \psi^{i'} d\tau = 1 \qquad (2\text{-}3)$$

and is independent of internuclear distances. To expand the Hamiltonian matrix element, the Hamiltonian is separated in a manner corresponding to the function (2-2)

$$H_a = \sum_{i=1}^{\ell} -\tfrac{1}{2}\nabla_i^2 + \sum_{i,i'>i} \frac{1}{r_{ii'}} + \sum_{i=1}^{\ell} \frac{-Z_a}{r_{ia}}$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots \qquad (2\text{-}4)$$

$$H_q = \sum_{i=2s-t}^{2s} -\tfrac{1}{2}\nabla_i^2 + \sum_{i,i'>i}^{2s} \frac{1}{r_{ii'}} + \sum_{i=2s-t}^{2s} -\frac{Z_q}{r_{iq}}$$

$$H^I = -\sum_{i=1}^{\ell}\left(\frac{Z_b}{r_{ib}} + \cdots \frac{Z_q}{r_{iq}}\right) \cdots + \sum_{i=1}^{\ell}\sum_{i'=\ell+1}^{2s} \frac{1}{r_{ii'}} \cdots$$

$$+ \frac{Z_a Z_b}{r_{ab}} + \frac{Z_a Z_c}{r_{ac}} \cdots \frac{Z_{q-1} Z_q}{r_{q-1\,q}}$$

Substitution of (2-4) into the Hamiltonian matrix element leads to

$$\int \psi^i H \psi^i d\tau = \int \phi_1(r_{1a}) \cdots \phi_p(r_{ea})\, H_a\, \phi_1(r_{1a}) \cdots \phi_p(r_{ea})\, d\tau$$

$$+ \cdots \int \phi_{2s-t}(r_{2s-t\,q}) \cdots \phi_{2s}(r_{2sq})\, H_q\, \phi_{2s-t}(r_{2s-t\,q}) \cdots \phi_{2s}(r_{2sq}) \times d\tau \qquad (2\text{-}5)$$

$$+ \int \psi^i H^I \psi^i d\tau$$

In (2-5) the desired separation has been accomplished; the last term is an interaction term and all the others are atomic. For the matrix elements

$$\int \psi^i H \psi^j d\tau \qquad i \neq j \qquad (2\text{-}6)$$

a similar procedure can be applied.

The method leading to equation (2-5) becomes inapplicable as soon as antisymmetrized functions are introduced. Since these no longer permit identification of each electron with a particular orbital, the Hamiltonian separation (equation 2-4) loses its meaning. However, by using some

of the properties of the antisymmetrizer $\mathcal{A}$ (equation 1-25), the M_{ij} can still be expressed as a sum of atomic terms, interaction terms, and products of the two (see below, Sec. II). The relative importance of these terms to the total energy of the system can be estimated by a comparison of the dissociation energy of the molecule and the energy of its dissociation products (see table 1). In the case of H_2 and H_2^+ the interaction energy is seen to provide a considerable fraction of the total energy of the molecule. With an increase in the number of electrons, or, better, electrons per nucleus, this fraction rapidly decreases. For a molecule like HF with 5 electrons per nucleus, the atomic energies account for over 99% of the total energy. A 1% error in the calculation of atomic energies can introduce a 100% error in the dissociation energy. Since computed atomic energies are generally in error by more than 1%, completely theoretical treatments for molecular systems appear rather hopeless.

When a number of Slater determinants are used in the variation function, each of the matrix elements H_{ij} includes a different set of atomic terms. For a molecule in which the atomic terms are predominant, the contribution made by the various determinants is governed by the differences amongst these terms. In HF, for example, the relative stability of the valence bond structures

Table I

Molecule	Dissociation Products	D'(a.u.)	A^2(a.u.)	D/A
H_2^+	$H + H^+$	.097	.5	.194
H_2	2H	.164	1.0	.164
HF	H + F	.225	100.30	.0022
H_2O	2H + O	.349	80.96	.0043
O_2	2O	.187	159.92	.0012

' D is the dissociation energy of the molecule

2 A is the total electronic energy of the isolated dissociation products

$$H - F_{\sigma} \, , \; H^{+} F^{-} \qquad (2\text{-}7)$$

(see Chapt. 4) depends on the energy difference between F and F^-. The best calculations[30] show that F^- is unstable with respect to $F + e^-$, though the opposite is true experimentally. Any attempt to evaluate a molecular property strongly dependent on the form of the wave function must fail. In the case of the dipole moment ($H \longrightarrow F$) too small a value is expected.

The above arguments suggest the following procedure as a possible substitute for completely theoretical calculations: separation of the required energies into atomic and interaction terms, evaluation of the atomic terms by use of observed spectroscopic values, calculation of interatomic terms by use of appropriate one-electron functions. Results obtained by this method are contained in Chapter 4; a completely theoretical calculation is included for comparison.

Section II - Expansion of Hamiltonian Matrix Elements

To expand the integral

$$H_{ij} = \int \psi^{i} H \psi^{j} d\tau \qquad (2\text{-}8)$$

the explicit form of ψ^i_j

$$\psi^i = \frac{1}{\sqrt{(2s)!}} \left| \Phi_1^i(r_1) \cdots \Phi_{2s}^i(r_{2s}) \right| = \frac{1}{\sqrt{(2s)!}} \left| \Phi^i \right| \qquad (2\text{-}9)$$

and the comparable expression for ψ^j are substituted into (2-8) to obtain the equation

$$H_{ij} = \frac{1}{(2s)!} \int \left| \Phi^i \right| H \left| \Phi^j \right| d\tau \qquad (2\text{-}10)$$

Here $\Phi_e^i(r_e)$ is the spin-orbital defined by equation (1-23). To simplify the writing, the matrix element H_{ii} required for a diatomic molecule is discussed; the extension to polyatomic molecules and to the case in which i is not equal to j is straightforward.

In a diatomic molecule (a-b) the antisymmetrized spin-orbital product $\left| \Phi^i \right|$ can be written

$$\left| \Phi^i \right| = \left| a_1(r_1) \cdots a_e(r_e)\, b_{e+1}(r_{e+1}) \cdots b_{2s}(r_{2s}) \right|$$

$$= \left| a_1(r_1) \cdots b_{2s}(r_{2s}) \right| \qquad (2\text{-}11)$$

where $a_i(r_i)$, $b_j(r_j)$ are spin-orbital products on nucleus a and b respectively. Corresponding to (2-11) H_{ii} can be expressed as

$$H_{ii} = \frac{1}{(2s)!} \int \left| a_1(r_1) \cdots b_{2s}(r_{2s}) \right| H \left| a_1(r_1) \cdots b_{2s}(r_{2s}) \right| d\tau \qquad (2\text{-}12)$$

It is assumed in the following discussion that within each set of atomic functions the orthonormality condition is satisfied; i.e.,

$$\int a_i(r_i)\, a_{i'}(r_i)\, d\tau = \delta_{ii'} \tag{2-13}$$

$$\int b_j(r_j)\, b_{j'}(r_j)\, d\tau = \delta_{jj'} \tag{2-14}$$

If Slater functions or other non-orthogonal functions are used, orthonormality can be achieved by use of the Schmidt process[31].

Because H is symmetric in the electrons and because the permutation operators, P, generating the determinantal function (2-11) form a group[32], (2-12) can be simplified to

$$H_{ii} = \int a_1(r_1) \cdots b_{2s}(r_{2s})\, |H|\, |a_1(r_1) \cdots b_{2s}(r_{2s})|\, d\tau \tag{2-15}$$

To permit the separation of atomic from interatomic terms, (2-11) is expanded in minors and cofactors from complementary sets of columns[33].

$$\begin{aligned} |a_1(r_1) \cdots b_{2s}(r_{2s})| &= |a_1(r_1) \cdots a_\ell(r_\ell)| \times |b_{\ell+1}(r_{\ell+1}) \cdots b_{2s}(r_{2s})| \\ &\quad - \sum_{u=1}^{\ell} \sum_{v=\ell+1}^{2s} |a_1(r_1) \cdots a_u(r_v) \cdots a_\ell(r_\ell)| \times |b_{\ell+1}(r_{\ell+1}) \cdots b_v(r_u) \cdots b_{2s}(r_{2s})| \\ &\quad + \cdots . \end{aligned} \tag{2-16}$$

With the neglect of multiple interatomic exchanges, (2-16) becomes

$$|a_1(r_1)\cdots b_{2s}(r_{2s})| = \left(1 - \sum_{u,v} P^{uv}\right)\left(|a_1(r_1)\cdots a_\ell(r_\ell)| \times |b_{\ell+1}(r_{\ell+1}) \cdots b_{2s}(r_{2s})|\right) \qquad (2\text{-}17)$$

or, in simplified notation,

$$|a_1(r_1)\cdots b_{2s}(r_{2s})| = \left(1 - \sum_{u,v} P^{uv}\right)\left(|a| \times |b|\right) \qquad (2\text{-}18)$$

Here P^{uv} interchanges electron u on atom a with electron v on atom b. Substitution of (2-18) into (2-15) yields

$$H_{ii} = \int a_1(r_1)\cdots b_{2s}(r_{2s})\left(1 - \sum_{u,v} P^{uv}\right)\left(H\,|a| \times |b|\right) d\tau \qquad (2\text{-}19)$$

since H is symmetric in the electrons. (2-19) is equivalent to

$$\begin{aligned} H_{ii} &= \int a_1(r_1)\cdots b_{2s}(r_{2s})\,(H\,|a| \times |b|)\,d\tau \\ &- \int a_1(r_1)\cdots b_{2s}(r_{2s}) \sum_{u,v} P^{uv}\,(H\,|a| \times |b|)\,d\tau \end{aligned} \qquad (2\text{-}20)$$

Corresponding to (2-18), H can be written

$$H = H_a + H_b + H^I \qquad (2\text{-}21)$$

where

$$\begin{aligned} H_a &= \sum_{i=1}^{\ell}\left(-\tfrac{1}{2}\nabla_i^2 - \frac{Z_a}{r_{ia}}\right) + \sum_{i,i'>i}^{\ell}\frac{1}{r_{ii'}} \\ H_b &= \sum_{j=\ell+1}^{2s}\left(-\tfrac{1}{2}\nabla_j^2 - \frac{Z_b}{r_{jb}}\right) + \sum_{j,j'>j}^{2s}\frac{1}{r_{jj'}} \end{aligned} \qquad (2\text{-}22)$$

$$H^I = -\sum_{i=1}^{\ell} \frac{Z_b}{r_{ib}} - \sum_{j=\ell+1}^{2s} \frac{Z_a}{r_{ja}} + \sum_{i=1}^{\ell}\sum_{j=\ell+1}^{2s} \frac{1}{r_{ij}} + \frac{Z_a Z_b}{r_{ab}}$$

With (2-21), H_{ii} becomes

$$H_{ii} = \int a_1(r_1)\cdots b_{2s}(r_{2s})\left(1 - \sum_{\mu,\nu} P^{\mu\nu}\right)\left(H_a + H_b + H^I\right)(|a| \times |b|)\,d\tau \qquad (2\text{-}23)$$

If the functions $|a|$ and $|b|$ are exact eigenfunctions of the atomic operators H_a and H_b respectively,

$$H_a\,|a| = E_a\,|a|$$
$$H_b\,|b| = E_b\,|b| \qquad (2\text{-}24)$$

Subject to (2-24), (2-13), and (2-14), equation (2-23) reduces to

$$H_{ii} = (E_a + E_b)\left\{1 - \sum_{\mu,\nu} (a_\mu | b_\nu)^2\right\}$$
$$+ \int a_1(r_1)\cdots b_{2s}(r_{2s})\, H^I\, a_1(r_1)\cdots b_{2s}(r_{2s})\,d\tau$$
$$- \sum_{\mu,\nu} \int a_1(r_1)\cdots b_{2s}(r_{2s})\, P^{\mu\nu}(H^I\,|a| \times |b|)\,d\tau \qquad (2\text{-}25)$$

where $(a_\mu | b_\nu)$ is an overlap integral expressed in Dirac notation[34]. Except in the case of hydrogen the atomic functions commonly employed do not satisfy equations (2-24). By the introduction of the quantities $\bar{E}_a$ and $\bar{E}_b$

$$\bar{E}_a = \int a_1(r_1)\cdots b_{2s}(r_{2s})\, H_a\,|a|\,d\tau$$

$$\bar{E}_b = \int b_{\ell+1}(r_{\ell+1})\cdots b_{2s}(r_{2s})\, H_b\,|b|\,d\tau \qquad (2\text{-}26)$$

equation (2-23) can be rewritten as

$$H_{ii} = \bar{E}_a + \bar{E}_b - \sum_{\mu,\nu} \int a_1(r_1)\cdots b_{2s}(r_{2s})\, P^{\mu\nu} \left(\{H_a + H_b\}\, |a|\times|b|\right) d\tau$$

$$+ \int a_1(r_1)\cdots b_{2s}(r_{2s}) \left(1 - \sum_{\mu,\nu} P^{\mu\nu}\right) \left(H^I\, |a|\times|b|\right) d\tau \qquad (2\text{-}27)$$

Definition of H_{ii}^{at} and H_{ii}^{I}

$$H_{ii}^{at} = \bar{E}_a + \bar{E}_b - \sum_{\mu,\nu} \int a_1(r_1)\cdots b_{2s}(r_{2s})\, P^{\mu\nu} \left(\{H_a + H_b\}\, |a|\times|b|\right) d\tau \qquad (2\text{-}28)$$

$$H_{ii}^{I} = H_{ii} - H_{ii}^{at} \qquad (2\text{-}29)$$

permits separate consideration of the two types of terms. Multiplication of a definite integral by a permutation operator does not change the value of the integral; therefore,

$$H_{ii}^{at} = \bar{E}_a + \bar{E}_b - \sum_{\mu,\nu} (P^{\mu\nu})^{-1} \int a_1(r_1)\cdots b_{2s}(r_{2s})\, P^{\mu\nu} \left(\{H_a + H_b\}\, |a|\times|b|\right) d\tau \qquad (2\text{-}30)$$

or

$$H_{ii}^{at} = \bar{E}_a + \bar{E}_b - \sum_{\mu,\nu} \int (P^{\mu\nu})^{-1} a_1(r_1)\cdots b_{2s}(r_{2s}) \left(\{H_a + H_b\}\, |a|\times|b|\right) d\tau \qquad (2\text{-}31$$

Since

$$(P^{\mu\nu})^{-1} = P^{\mu\nu} \qquad (2\text{-}32$$

(2-31) is equivalent to

$$H_{ii} = \bar{E}_a + \bar{E}_b - \sum_{u,v} \int (\rho^{uv} a_1(r_1) \cdots b_{2s}(r_{2s}))(\{H_a + H_b\} |a| \times |b|) d\tau \quad (2\text{-}33)$$

Corresponding to the operator ρ^{uv}, the modified atomic Hamiltonians, H_a^u and H_b^v, can be introduced with

$$H_a^u = H_a - h_u^a$$
$$H_b^v = H_b - h_v^b \quad (2\text{-}34)$$

and

$$h_u^a = -\frac{1}{2}\nabla_u^2 - \frac{Z_a}{r_{ua}} + \sum_{i \neq u}^{\ell} \frac{1}{r_{ui}}$$
$$h_v^b = -\frac{1}{2}\nabla_v^2 - \frac{Z_b}{r_{vb}} + \sum_{j \neq v}^{2s} \frac{1}{r_{vj}} \quad (2\text{-}35)$$

By use of the definitions (2-34) and (2-35), (2-33) is transformed into

$$H_{ii}^{at} = \bar{E}_a + \bar{E}_b - \sum_{u,v} \left[\int (\rho^{uv} a_1(r_1) \cdots b_{2s}(r_{2s}))\{H_a + H_b\} |a| \times |b| d\tau \right.$$
$$\left. + \int (\rho^{uv} a_1(r_1) \cdots b_{2s}(r_{2s}) (h_u^a + h_v^b) |a| \times |b| d\tau \right] \quad (2\text{-}36)$$

Expansion of $|a|$ and $|b|$ in terms of the diagonal elements[35] leads to

$$|a| = a_1(r_1) \cdots b_{2s}(r_{2s}) + \begin{vmatrix} 0 & a_2(r_1) \\ a_1(r_2) & 0 \end{vmatrix} a_3(r_3) \cdots a_\ell(r_\ell) + \cdots \begin{vmatrix} 0 & a_2(r_1) & a_3(r_1) \\ a_1(r_2) & 0 & a_3(r_2) \\ a_1(r_3) & a_2(r_3) & 0 \end{vmatrix} a_4(r_4) \cdots a_\ell(r_\ell) \cdots \quad (2\text{-}37)$$

and a corresponding set of terms for $|b|$. An examination of the form of the operators (2-34) and (2-35) shows that the only elements contributing to the integral (2-36) come from the leading terms

$$a_1(r_1)\cdots a_\varrho(r_\varrho)\ ;\ b_{\varrho+1}(r_{\varrho+1})\cdots b_{2S}(r_{2S}) \tag{2-38}$$

and secondary terms of the types

$$-\left[a_2(r_1)\,a_1(r_2)\cdots a_\varrho(r_\varrho)\right]\ ;\ -\left[b_{\varrho+2}(r_{\varrho+1})\,b_{\varrho+1}(r_{\varrho+2})\cdots b_{2S}(r_{2S})\right] \tag{2-39}$$

and

$$-\left[a_u(r_1)\,a_1(r_2)\cdots a_\varrho(r_\varrho)\right]\ ;\ -\left[b_v(r_{\varrho+1})\,b_{\varrho+1}(r_v)\cdots b_{2S}(r_{2S})\right] \tag{2-40}$$

Substitution into (2-36) gives rise to the expression

$$\begin{aligned}
H_{il}^{at} = {} & \bar{E}_a + \bar{E}_b - \sum_{u,v}\left(\bar{E}_a^{\,u} + \bar{E}_b^{\,v}\right)(a_u|b_v)^2 - \sum_{u,v}(a_u|b_v)\left\{(a_u|-\tfrac{1}{2}\nabla^2-\frac{z_a}{r_a}|b_v)\right. \\
& \left. + (b_v|-\tfrac{1}{2}\nabla^2-\frac{z_a}{r_a}|a_u) + \sum_{i\neq u}(a_u a_i|b_v a_i) + \sum_{j\neq v}(b_v b_j|a_u b_j)\right\} \\
& + \sum_{u,v}(a_u|b_v)\left\{\sum_{i\neq u}(a_i|b_v)\left[(a_i|-\tfrac{1}{2}\nabla^2-\frac{z_a}{r_a}|a_u) + \sum_{p\neq u,i}(a_i a_p|a_u a_p)\right]\right. \\
& + \sum_{j\neq v}(b_j|a_u)\left[(b_j|-\tfrac{1}{2}\nabla^2-\frac{z_b}{r_b}|b_v) + \sum_{g\neq v,j}(b_j b_g|b_v b_g)\right] \\
& \left. + \sum_{i\neq u}(a_u a_i|a_i b_v) + \sum_{j\neq v}(b_v b_j|b_j a_u)\right\}
\end{aligned} \tag{2-41}$$

The third sum over u and v is composed of terms which are zero in most cases because the $a_u(r)\,(b_v(r))$ and the $a_i(r)\,(b_j(r))$

usually have different symmetries. Even if the terms are not zero by symmetry considerations they are still small because of the orthogonality condition (e.g., if the $a_u(r)$ are eigenfunctions of the one-electron operator

$$-\tfrac{1}{2}\nabla_u^2 - \frac{Z_a}{r_{ua}} \tag{2-42}$$

the sum

$$\sum_{i\neq u}(a_i|b_v)\left(a_i\left|-\tfrac{1}{2}\nabla^2-\frac{Z_a}{r_a}\right|a_v\right)=\sum_{i\neq u}(a_i|b_v)(a_i|a_v)\epsilon_v=0 \tag{2-43}$$

since

$$(a_i|a_v)=0 \tag{2-44}$$

Neglect of these terms, which corresponds to neglect of the secondary terms (2-40), reduces (2-41) to

$$\begin{aligned} H_{ii}^{at} &= \bar{E}_a+\bar{E}_b-\sum_{u,v}\left(\bar{E}_a^u+\bar{E}_b^v\right)(a_u|b_v)^2 \\ &-\sum_{u,v}(a_u|b_v)\left[\left(a_u\left|-\tfrac{1}{2}\nabla^2-\frac{Z_b}{r_b}\right|b_v\right)+\left(b_v\left|-\tfrac{1}{2}\nabla^2-\frac{Z_a}{r_a}\right|a_u\right)\right. \\ &\left.+\sum_{i\neq u}(a_u a_i|b_v a_i)+\sum_{j\neq v}(b_v b_j|a_u b_j)\right] \end{aligned} \tag{2-45}$$

An expansion of H_{ii}^{I} (equation (2-29)) analogous to that used for H_{ii}^{at} is required. By use of the orthonormality relations (equations (2-13) and (2-14)) H_{ii}^{I} can be rewritten as

$$H_{ii}^{I} = \int a_1(r_1)\cdots b_{2S}(r_{2S})\, H^{I} a_1(r_1)\cdots b_{2S}(r_{2S})\, d\tau$$
$$- \sum_{\mu,\nu} \int a_1(r_1)\cdots b_{2S}(r_{2S})\, P^{\mu\nu} (H^{I} |a| \times |b|)\, d\tau \qquad (2\text{-}46)$$

or, with (2-32), as

$$H_{ii}^{I} = \int a_1(r_1)\cdots b_{2S}(r_{2S})\, H^{I} a_1(r_1)\cdots b_{2S}(r_{2S})\, d\tau$$
$$- \sum_{\mu,\nu} \int P_{\alpha}^{\mu\nu} a_1(r_1)\cdots b_{2S}(r_{2S})\, H^{I} |a| \times |b|\, d\tau \qquad (2\text{-}47)$$

Consideration of the expansions (2-38) - (2-40) shows that the secondary terms (2-39) make no contribution to the integral and that the terms (2-40) contribute quantities identical with those neglected in H_{ii}^{at}. If only the leading terms (2-38) are included, (2-47) becomes

$$H_{ii}^{I} = \int \left\{ \left(1 - \sum_{\mu,\nu} P^{\mu\nu}\right) a_1(r_1)\cdots b_{2S}(r_{2S}) \right\} H^{I} a_1(r_1)\cdots b_{2S}(r_{2S})\, d\tau \qquad (2\text{-}48)$$

or, finally

$$H_{ii}^{I} = \sum_{i} \left(a_i \left| -\frac{Z_b}{r_b} \right| a_i\right) + \sum_{j} \left(b_j \left| -\frac{Z_a}{r_a} \right| b_j\right) + \sum_{i}\sum_{j} (a_i b_j | a_i b_j)$$
$$- \sum_{\mu,\nu} (a_\mu | b_\nu)^2 \left[\sum_{i\neq\mu} \left(a_i \left| -\frac{Z_b}{r_b} \right| a_i\right) + \sum_{j\neq\nu} \left(b_j \left| -\frac{Z_a}{r_a} \right| b_j\right) + \sum_{i\neq\mu}\sum_{j\neq\nu} (a_i b_j | a_i b_j) \right]$$
$$- \sum_{\mu,\nu} (a_\mu | b_\nu) \left[\left(a_\mu \left| -\frac{Z_a}{r_a} - \frac{Z_b}{r_b} \right| b_\nu\right) + \sum_{i\neq\mu} (a_i a_\mu | a_i a_\nu) + \sum_{j\neq\nu} (b_j b_\nu | b_j a_\mu) \right] \qquad (2\text{-}49)$$
$$- \sum_{\mu,\nu} (a_\mu b_\nu | b_\nu a_\mu) + \frac{Z_a Z_b}{r_{ab}} \left(1 - \sum_{\mu,\nu} (a_\mu | b_\nu)^2\right)$$

Addition of (2-45) and (2-49) with combination of like terms results in

$$H_{ii} = \bar{E}_a + \bar{E}_b - \sum_{u,v} (\bar{E}_a^u + \bar{E}_b^v)(a_u|b_v)^2 + \sum_i (a_i|-\tfrac{z_b}{r_b}|a_i)$$
$$+ \sum_j (b_j|-\tfrac{z_a}{r_a}|b_j) + \sum_{i,j} (a_i b_j|a_i b_j) + \frac{z_a z_b}{r_{ab}} - \sum_{u,v} (a_u|b_v)^2 \Big[\sum_{i\neq u} (a_i|-\tfrac{z_b}{r_b}|a_i)$$
$$+ \sum_{j\neq v} (b_j|-\tfrac{z_a}{r_a}|b_j) + \sum_{\substack{i\neq u \\ j\neq v}} (a_i b_j|a_i b_j) + \frac{z_a z_b}{r_{ab}} \Big] \qquad (2\text{-}50$$
$$- \sum_{u,v} (a_u|b_v) \Big[2(a_u|-\tfrac{1}{2}\nabla^2 - \tfrac{z_a}{r_a} - \tfrac{z_b}{r_b}|b_v) + 2\sum_{i\neq u} (a_u a_i|b_v a_i)$$
$$+ 2\sum_{j\neq v} (b_v b_j|a_u b_j) \Big] - \sum_{u,v} (a_u b_v|b_v a_u)$$

In view of the method outlined in section I, the quantities $\bar{E}_a, \bar{E}_b, \bar{E}_a^u, \bar{E}_b^v$ are evaluated empirically and the other terms of (2-50) are calculated theoretically.

Matrix elements $H_{ij}\ (i\neq j)$ are expanded by a procedure similar to that used for H_{ii} . The resulting expressions are generally much simpler than equation (2-50) since only a few elements of the Hamiltonian contribute non-zero terms. If ψ^i and ψ^j of

$$H_{ij} = \int \psi^i H \psi^j d\tau \qquad (2\text{-}51)$$

differ by more than two atomic orbitals,

$$H_{ij} = 0 \qquad (2\text{-}52)$$

to the approximation used above.

Section III - Interaction Operator Method

The difficulty of molecular calculations has led to the introduction of approximations whose validity has never been investigated. Among these is the "interaction operator method" which has been frequently employed[36]. In this section use is made of the expansion developed in Section II (equation 2-50) to establish a criterion for the applicability of the interaction operator method.

It was shown above (equations (2-24) and (2-25)) that functions $|a|$ and $|b|$, if atomic eigenfunctions, lead to the matrix element

$$H_{ii} = (E_a + E_b)\left\{1 - \sum_{\mu,\nu} (a_\mu|b_\nu)^2\right\} + \int a_1(r_1)\cdots b_{25}(r_{25})\left(1 - \sum_{\mu,\nu} P^{\mu\nu}\right)(H^I|a|\times|b|)\,d\tau \qquad (2\text{-}53)$$

The interaction operator method assumes that use of equation (2-53) with $\bar{E}_a$ and $\bar{E}_b$ (equation 2-26) substituted for E_a and E_b is a valid procedure in the case that $|a|$ and $|b|$ are not atomic eigenfunctions. If ψ^i is considered an adequate representation of the system, the energy is

$$E = \frac{(\bar{E}_a + \bar{E}_b)\left(1 - \sum_{\mu,\nu} (a_\mu|b_\nu)^2\right) + \int a_1(r_1)\cdots b_{25}(r_{25})\left(1 - \sum_{\mu,\nu} P^{\mu\nu}\right)(H^I|a|\times|b|)\,d\tau}{\left(1 - \sum_{\mu,\nu} (a_\mu|b_\nu)^2\right)} \qquad (2\text{-}54)$$

or

$$E = \bar{E}_a + \bar{E}_b + \frac{\int a_1(r_1)\cdots b_{25}(r_{25})\left(1-\sum_{\mu,\nu} P^{\mu\nu}\right)(H^I\,|a|\times|b|)\,d\tau}{\left(1-\sum_{\mu,\nu}(a_\mu|b_\nu)^2\right)} \qquad (2\text{-}55)$$

The dissociation energy of the system is just

$$E-\bar{E}_a-\bar{E}_b = \frac{\int a_1(r_1)\cdots b_{25}(r_{25})\left(1-\sum_{\mu,\nu} P^{\mu\nu}\right)(H^I\,|a|\times|b|)\,d\tau}{\left(1-\sum_{\mu,\nu}(a_\mu|b_\nu)^2\right)} \qquad (2\text{-}56)$$

i.e., the energy resulting from the use of the interaction operator alone.

Comparison of (2-53) and (2-54) with the expansion (2-50) shows that the interaction operator method assumes equalities of the form

$$(a_\mu|b_\nu)\left(b_\nu\left|-\tfrac{1}{2}\nabla^2-\frac{Z_a}{r_a}\right|a_\mu\right) \cong (a_\mu|b_\nu)^2\left(a_\mu\left|-\tfrac{1}{2}\nabla^2-\frac{Z_a}{r_a}\right|a_\mu\right) \qquad (2\text{-}57)$$

and

$$(a_\mu a_i\,|\,b_\nu a_i) \cong (a_\mu|b_\nu)(a_\mu a_i\,|\,a_\mu a_i) \qquad (2\text{-}58)$$

Equation (2-57) is exact if the a_μ are eigenfunctions of one-electron operators (equation 2-42); for orthogonalized Slater functions (2-57) is no longer exact but is still a rather good approximation. In any problem, the validity of the method depends primarily on the correctness of (2-58). Table 2 shows some results obtained with integrals calculated for HF. It is seen that the interaction operator approximation introduces an error on the order of 20% in each

Table 2

Required Integral	Interaction operator Approximation		Correct Value (a.u.)	Approx. Value (a.u.)
$(H_{1s}F_{2\pi}/F_{2s}F)_{2\pi}$	(H_{1s}/F_{2s})	$(F_{2s}F_{2\pi}/F_{2s}F)_{2\pi}$	.3635	.4440
$(H_{1s}F_{2\sigma}/F_{2s}F_{2\sigma})$	"	$(F_{2s}F_{2\sigma}/F_{2s}F)_{2\sigma}$	.3742	.4440
$(H_{1s}F_{2s}/F_{2s}F_{2s})$	"	$(F_{2s}F_{2\sigma}/F_{2s}F)_{2s}$	.3670	.4440
$(H_{1s}F_{2\pi}/F_{2\sigma}F_{2\pi})$	$(H_{1s}/F_{2\sigma})$	$(F_{2\sigma}F_{2\pi}/F_{2\sigma}F)_{2\pi}$	.2036	.2726
$(H_{1s}F_{2\sigma}/F_{2\sigma}F_{2\sigma})$	"	$(F_{2\sigma}F_{2\sigma}/F_{2\sigma}F_{2\sigma})$	.2300	.3056
$(H_{1s}F_{2s}/F_{2\sigma}F_{2s})$	"	$(F_{2\sigma}F_{2s}/F_{2\sigma}F_{2s})$	.2124	.2836

integral. Since the terms involved form a considerable part of the dissociation energy, the error introduced into the final result is expected to be large and the interaction operator method inapplicable in HF. To draw general conclusions from this calculation is inadvisable; specific tests should be made with (2-58) for each problem. As it seems likely, however, that for comparable molecular dimensions a comparable error will result, great caution must be exercised in application of the interaction operator approximation.

Chapter 3 - INTEGRAL EVALUATION

The most time-consuming portion of molecular calculations is the numerical evaluation of the Schrödinger integrals. Their difficulty dictates the use of simple one-electron functions and limits the accuracy achievable in practice. Exact methods for computing many of the required integrals have been developed. In cases for which exact calculation is too tedious, approximate methods can be introduced. This chapter discusses the exact and approximate evaluation of molecular integrals with special reference to those necessary for HF and HF_2^-.

Section I - Exact Methods

In any problem involving one-electron atomic functions and a Hamiltonian of the type given in equation (1-2) only three-dimensional and six-dimensional integrals appear; i.e. the integrals require volume integration over the coordinates of one electron (three-dimensional) or, when that part of the Hamiltonian including electron interaction terms ($\frac{1}{r_{ii'}}$) is being considered, over the coordinates of two electrons. The types of integrals required are evident from the expansion of matrix elements (Chapter 2). The simplest are the dimensionless overlap integrals

$$(A_u | B_v) = \int A_u(r_1) B_v(r_1) d\tau \qquad (3\text{-}1)$$

Here the capital letters A_u, B_v represent only the orbital part of the spin-orbits a_u, b_v appearing in the integrals of (2-50). It is assumed that the integration over the spins has been performed. Corresponding to the kinetic energy operator, the kinetic energy integrals have the form

$$(A_u | -\tfrac{1}{2}\nabla^2 | B_v) = -\tfrac{1}{2} \int A_u(r_1) \nabla_1^2 B_v(r_1) d\tau \qquad (3\text{-}2)$$

The general one-electron integral resulting from the potential energy operators is

$$(A_u | \frac{1}{r_c} | B_v) = \int A_u(r_1) B_v(r_1) \frac{d\tau}{r_{1c}} \qquad (3\text{-}3)$$

then, correspondingly, the $\frac{1}{r_{ii'}}$ terms lead to the two-electron repulsion integral

$$(A_u B_v | C_s D_t) = \int A_u(r_1) B_v(r_2) C_s(r_1) D_t(r_2) \frac{d\tau}{r_{12}} \qquad (3\text{-}4)$$

Special cases with some of the A,B,C,D and some of the u,v,s,t equivalent occur frequently.

The method used for solving the integrals (3-1) through (3-4) depends largely on the functions used for the Au, Bv .... . Here real Slater orbitals[24] of the form

$$A_u(r) = N r^{n^*-1} e^{-\delta r} S_{lm}(\theta, \phi) \qquad (3\text{-}5)$$

are considered*. The quantity n^* is closely related to the principal quantum number, n; for n less than or equal to 3

$$n^* = n \tag{3-6}$$

δ is defined by the relation

$$\delta = \frac{Z - s}{n^*} \tag{3-7}$$

where Z is the nuclear charge and s is a shielding constant determined by semi-empirical rules developed by Slater. The functions $S_{\ell m}(\theta, \phi)$ are real surface harmonics

$$S_{\ell m} = P_\ell^m(\cos\theta) \begin{Bmatrix} \cos m\phi \\ \sin m\phi \end{Bmatrix} \tag{3-8}$$

For other one-electron functions differing only superficially from the Slater orbitals (e.g. by having the single r term replaced by a polynomial or the single exponential by sum of exponentials) simple generalizations of the methods outlined below are applicable.

With functions of the form (3-5) all the integrals in which

$$A = B = C = D \tag{3-9}$$

* For the considerations of Chapter 2 to be exactly applicable, orthogonalized Slater functions have to be used. Since these are linear combinations of the simple Slater functions, equation (3-5), the methods described below are unaffected.

i.e. one-center integrals, can be done directly. The one-center repulsion integrals (3-4) are most easily performed by using r_{12} as a variable of integration.

For the two-center case

$$A \neq B \tag{3-10}$$

and

$$C=A,\ D=B \tag{3-11}$$

$$C = B,\ D = A \tag{3-12}$$

or

$$C = D = A \neq B \tag{3-13}$$

transformation to spheroidal coordinates[37] permits the expression of the integrals (3-1) in closed form in terms of sums of exponentials times polynomials[38]. In the integrals (3-4) the $\frac{1}{r_{12}}$ term is troublesome. If spheroidal coordinates are employed, an expansion[39] of $1/r_{12}$

$$\frac{1}{r_{12}} = \frac{2}{R} \sum_{\ell=0}^{\infty} \sum_{m=0}^{\ell} \lambda_{\ell m}\, Q_\ell^m(\xi_1) P_\ell^m(\xi_2) P_\ell^m(\eta_1) P_\ell^m(\eta_2) \cos m(\phi_1-\phi_2) \qquad \xi_1 > \xi_2 \tag{3-14}$$

is found useful. Here

$$\lambda_{\ell 0} = 2\ell+1\,; \quad \lambda_{\ell m} = (-1)^m (4\ell+2) \left\{ \frac{(\ell-m)!}{(\ell+m)!} \right\}^2 \quad m>0 \tag{3-15}$$

the P_ℓ^m, Q_ℓ^m are Legendre functions[40] of the first and second kind and $\xi_1, \eta_1, \phi_1; \xi_2, \eta_2, \phi_2$ are the spheroidal coordinates of the two electrons.[38] Coulomb integrals (3-11) again yield closed expressions composed of sums of exponentials times polynomials[38]. Exchange (3-12) and ionic

integrals (3-13) result in slowly converging non-terminating sums of complex functions[41].

The values of some of these functions have been tabulated in terms of their dependence on δ [42]. In Tables 9-11 (Chapter 4) the one- and two-center integrals required for HF and HF_2^- are listed.

For three- and four-center integrals, spheroidal coordinates are not well suited. An expansion of orbitals centered on one nucleus, a, about a second nucleus, b, can be made by use of an addition theorem[43] for Bessel functions

$$\frac{e^{-Kr_{ia}}}{r_{ia}} = \sum_{m=0}^{\infty} (2m+1) \frac{K_{m+1/2}(Kr_{ab}) I_{m+1/2}(Kr_{ib}) P_m(\cos\theta_{ib})}{\sqrt{r_{ab} r_{ib}}} \qquad (3\text{-}16)$$

where $I_{m+1/2}$ and $K_{m+1/2}$ are Bessel functions of purely imaginary argument of the first and second kind, respectively. Application of (3-16) reduces the three- or four-center problem to the two-center case.

The difficulties encountered in computing the resulting expressions are, however, so enormous as to discourage all but the professional computer.

Section II - Approximate methods: Exponential expansion and point-charge

The difficulties inherent in the exact computation of molecular integrals involving Slater functions suggest that

approximation methods be investigated. As long as the variation function (see Chapter 1) is composed of only a few terms, the accuracy possible in any calculation is severely limited. The approximation of integrals is permissible, therefore, if the resultant error is small compared to that arising from the use of a poor wave function. In most of the two-center integrals great care is needed to ascertain that the methods used yield sufficiently accurate results. Since three and four-center integrals make only a small contribution to the matrix elements a rather large percentage error in their values (on the order of five percent) can usually be tolerated. It is primarily in these multicenter integrals that time can be saved by the use of approximation without significantly affecting the accuracy of the final result.

Several useful approximation methods can be obtained by use of an expansion similar to that expressed by equation (3-16). Since the functions Au and Bv of equation (3-4) are members of a complete set, C_s and D_t can be expanded about nucleus a and b, respectively, in terms of Au and Bv; i.e.

$$C_s(r_1) = \sum_{i=1}^{\infty} (A_i / C_s) A_i(r_1) \qquad (3\text{-}17)$$

and

$$D_t(r_2) = \sum_{j=1}^{\infty} (B_j / D_t) B_j(r_2) \qquad (3\text{-}18)$$

By use of (3-17) and (3-18) the charge distributions $A_u(r_1)\,C_s(r_1)$ and $B_v(r_2)\,D_t(r_2)$ can be replaced by the expressions

$$A_u(r_1)\,C_s(r_1) = \sum_{i=1}^{\infty} (A_i|C_s)\,A_u(r_1)\,A_i(r_1) \tag{3-19}$$

and

$$B_v(r_2)\,D_t(r_2) = \sum_{j=1}^{\infty} (B_j|D_t)\,B_v(r_2)\,B_j(r_2) \tag{3-20}$$

The magnitude of the charge present in the distributions (3-19) and (3-20) is obtained by integrating over all space. Since the $A_u(r_1)\,A_i(r_1)$ and the $B_v(r_2)\,B_j(r_2)$ are orthonormal sets, the only terms in the expansions (3-19) and (3-20) that contribute to the total charge are the term

$$(A_u|C_s)\,A_u(r_1)\,A_u(r_1) \tag{3-21}$$

from (3-19) and the term

$$(B_v|D_t)\,B_v(r_2)\,B_v(r_2) \tag{3-22}$$

from (3-20). All the other products in (3-19) and (3-20) affect only the first (dipole) and higher moments of the charge distributions. At a sufficiently large distance

the potential of a charge distribution is well approximated by use of the zero moment alone. This suggests use of expressions of the form

$$A_u(r_1)\,C_s(r_1) \cong (A_u/C_s)\,A_u(r_1)\,A_u(r_1) \tag{3-23}$$

and

$$B_v(r_2)\,D_t(r_2) \cong (B_v/D_t)\,B_v(r_2)\,B_v(r_2) \tag{3-24}$$

in the evaluation of the integrals (3-3) and (3-4). A procedure comparable to that used in obtaining (3-23) and (3-24) yields the relations

$$A_u(r_1)\,C_s(r_1) \cong (C_s/A_u)\,C_s(r_1)\,C_s(r_1) \tag{3-25}$$

and

$$B_v(r_2)\,D_t(r_2) \cong (D_t/B_v)\,D_t(r_2)\,D_t(r_2) \tag{3-26}$$

Since the choice between (3-23) and (3-25) or between (3-24) and (3-26) is purely arbitrary, it appears best to use some form of mean. Introduction of the arithmetic mean gives the expression

$$(A_u(r_1)\,C_s(r_1)) \cong \tfrac{1}{2}\,(C_s/A_u)\left\{A_u(r_1)A_u(r_1) + C_s(r_1)\,C_s(r_1)\right\} \tag{3-27}$$

the geometric mean yields

$$A_u(r_1)\,C_s(r_1) = (C_s/A_u)\left\{[A_u(r_1)\,A_u(r_1)]\times[C_s(r_1)\,C_s(r_1)]\right\}^{1/2} \qquad (3\text{-}28)$$

Substitution of (3-27) and (3-28) into (3-3) results in the approximate forms

$$(A_u\,|\,\tfrac{1}{r_b}\,|\,C_s) \cong \tfrac{1}{2}\,(C_s/A_u)\left[(A_u\,|\,\tfrac{1}{r_{1b}}\,|\,A_u) + (C_s\,|\,\tfrac{1}{r_{1b}}\,|\,C_s)\right] \qquad (3\text{-}29)$$

and

$$(A_u\,|\,\tfrac{1}{r_b}\,|\,C_s) \cong (C_s/A_u)\left[(A_u\,|\,\tfrac{1}{r_b}\,|A_u)\times(C_s\,|\,\tfrac{1}{r_b}\,|\,C_s)\right]^{1/2} \qquad (3\text{-}30)$$

For the integral (3-4), expressions (3-27), (3-28) and the comparable approximations for $B_\nu(r_2)\,D_\ell(r_2)$ are needed. With their use, the formulae

$$(A_u B_\nu\,|\,C_s D_\ell) \cong \tfrac{1}{4}\,(A_u/C_s)(B_\nu/D_\ell)\left[(A_u B_\nu\,|\,A_u B_\nu) + (A_u D_\ell\,|\,A_u D_\ell) + (C_s B_\nu\,|\,C_s B_\nu) + (C_s D_\ell\,|\,C_s D_\ell)\right] \qquad (3\text{-}31)$$

and

$$(A_u B_\nu\,|\,C_s D_\ell) = (A_u\,|\,C_s)(B_\nu\,|\,D_\ell)\left[(A_u B_\nu\,|\,A_u B_\nu)\times(A_u D_\ell\,|\,A_u D_\ell)\times(C_s B_\nu\,|\,C_s B_\nu)\times(C_s D_\ell\,|\,C_s D_\ell)\right]^{1/4} \qquad (3\text{-}32)$$

result. Instead of transforming the charge distributions by means of the expansions (3-19) and (3-20), it is possible to determine the value of the charge directly; e.g., the magnitude of the total charge present in the distribution $A_u(r_1)\,C_s(r_1)$ is equal to the integral

$$(A_u / C_s) \tag{3-33}$$

By use of the point charge approximation, the potential of $A_u(r_1)\,C_s(r_1)$ at a point b can now be written as

$$\frac{(A_u / C_s)}{r_{\bar{ac},b}} \tag{3-34}$$

where $r_{\bar{ac},b}$ is the distance from the center of charge of $A_u(r_1)\,C_s(r_1)$ to the point b. In terms of (3-34) the integral (3-3) becomes

$$(A_u / \frac{1}{r_b} / C_s) = \frac{(A_u / C_s)}{r_{\bar{ac},b}} \tag{3-35}$$

Similarly the integral (3-4) can be expressed in the form

$$(A_u B_v / C_s D_t) = \frac{(A_u / C_s)(B_v / D_t)}{r_{\bar{ac},\bar{bd}}} \tag{3-36}$$

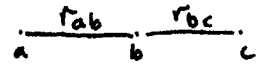
where $r_{\bar{ac},\bar{bd}}$ represents the distance between the center of $A_u(r_1)\,C_s(r_1)$ and $B_v(r_2)D_t(r_2)$. For the special case of (3-4) involving only three centers, the modified formula

$$(A_u B_v / A_u D_t) = (B_v / D_t)(A_u / \frac{1}{r_{\bar{bd}}} / A_u) \tag{3-37}$$

can be used.

To determine the adequacy of the expansion formulae (3-29) through (3-32) and of the point charge expressions (3-35) through (3-37), it is necessary to apply them to specific examples of the integrals (3-3) and (3-4).

Hirschfelder et al,[44] have computed the exact values of some three-center integrals with u, v, s, t all corresponding to hydrogen functions. They considered only the case of all three nuclei on one line,



In Tables 3 and 4 the results obtained by them are compared with those computed with the various approximation methods. It is seen that the geometric mean expansion (3-28) is consistently superior to the other approximations. Since the greatest error introduced is on the order of four percent, the geometric mean can be considered a satisfactory method of calculation. At large ρ ($r_{ab} > 2$) the simpler point charge approximation also yields usable results.

If the orbitals A_u (r) and C_s (r) belong to different symmetry species, their product A_u (r) C_s (r) corresponds to a distribution of zero charge. The dipole and multipole moments of the distribution now make an important contribution to the potential. Many terms in the expansion (3-19) may have to be included. Until the rapidity of convergence has been determined, the value of the method for calculating integrals containing distributions of zero charge remains in doubt.

Table 3

Integral $(A_{1s}/\frac{1}{r_c}/B_{1s})$ in (a.u.)

r_{ab} (a.u.)	r_{cb} (a.u.)	Exact Value (a.u.)	Arith. Mean (a.u.)	Geom. Mean (a.u.)	Point Charge (a.u.)
1.0	1.0	.500	.515	.503	.573
2.0	2.0	.1925	.213	.198	.205
3.0	3.0	.0780	.086	.081	.077
4.0	4.0	.0321	.037	.032	.031
1.2	4.1	.1724	.1744	.1729	.171

Table 4

Integral $(A_{1s}B_{1s}/B_{1s}C_{1s})$

r_{ab} (a.u.)	r_{bc} (a.u)	Exact Value (a.u)	Arith. Mean (a.u.)	Geom. Mean (a.u.)	Point Charge (a.u.)
1.0	1.0	.395	.399	.395	.738
2.0	2.0	.143	.150	.143	.173
3.0	3.0	.040	.044	.0395	.041
4.0	4.0	.010	.0108	.0097	.009

Integral $(A_{1s}C_{1s}/B_{1s}C_{1s})$

r_{ab} (a.u)	r_{bc} (a.u)	Exact Value (a.u)	Arith. Mean (a.u)	Geom. Mean (a.u)	Point Charge (a.u)
1.0	1.0	.419	.421	.417	.57
2.0	2.0	.188	.199	.191	.197
3.0	3.0	.079	.086	.081	.078
4.0	4.0	.032	.036	.032	.031

Section 111 - Approximate Methods: Normal function expansion

In Chapter 1 it is suggested that one-electron orbitals composed of functions other than exponentials can be used to simplify molecular calculations. One set of functions, that related to the solutions of the harmonic oscillator problem and the normal distribution function, is investigated in this section; i.e., functions of the type

$$\sum_{\ell} P_{\ell m}(r)\, e^{-\delta_\ell r^2} \tag{3-38}$$

are examined. Here $P_{\ell m}(r)$ is a polynomial of order n and δ_ℓ is a coefficient, which has yet to be specified.

The functions (3-38) are introduced because multi-center integrals constructed from them are easily evaluated. Their simplicity arises from the fact that expansions of the type (3-16) are here replaced by the simple expression

$$e^{-K r_{1a}^2} = e^{-K(r_{1b}^2 + r_{ab}^2 - 2 r_{ab} z_{1b})} \tag{3-39}$$

if r_{ab} is assumed to lie along the z-axis.

To be useful in a variation function or in the approximation of molecular integrals, expression (3-38) has to be related to the orbital of exponential type that is being replaced. The method employed for this fitting process depends on the accuracy desired. For use in a variation function (1-28), the simplest form of (3-38),

a polynomial times a normal function, should suffice. Since hydrogen-like and Slater functions are exact or approximate eigenfunctions of the one electron operator

$$-\tfrac{1}{2}\nabla^2 - \frac{Z}{r} \qquad (3\text{-}40)$$

the variation principle [45] (equations (1-7) and (1-8)) can be used to determine the coefficients δ_ℓ . In approximating orbitals other than the one corresponding to the ground state of (3-39), the orthogonality condition (1-9) has to be included in the calculation.

An approximation more accurate than that provided by a single term of (3-38) is required for the calculation of integrals. With a series of terms, the variation procedure becomes too complicated because of the requirement (1-9) and because of the presence of non-linear parameters. Some other method of fitting the functions (3-38) has to be employed. Since integral properties of (3-38) are being used, a likely procedure consists of choosing the coefficients δ_ℓ by equating certain moments of the exact and approximate functions. To approximate the hydrogen 1s orbital by the expression

$$e^{-r} \cong a_1 e^{-\delta_1 r^2} + a_2 e^{-\delta_2 r^2} \qquad (3\text{-}41)$$

the equations

$$\int_0^\infty e^{-r} r^n dr = a_1 \int_0^\infty e^{-\delta_1 r^2} r^n dr + a_2 \int_0^\infty e^{-\delta_2 r^2} r^n dr \qquad n=1,2,3,4 \qquad (3\text{-}42)$$

are solved for a_1, a_2, δ_1 and δ_2 . Overlap integrals

obtained from the two sides of (3-41) are compared in Table 5. Since the deviations are large, the coefficients in (3-41) are redetermined by fitting the exact and approximate function directly at the four points

$$r = 0.0,\ 0.5,\ 1.5,\ 3.0 \tag{3-43}$$

The overlap integrals obtained with the new coefficients (see Table 5) are seen to be in better agreement with the exact values. This improvement suggests the testing of a three-term function

$$e^{-r} = a_1 e^{-b_1 r^2} + a_2 e^{-b_2 r^2} + a_3 e^{-b_3 r^2} \tag{3-44}$$

whose coefficients are determined by equating it to the exponential at six points,

$$r = 0.0,\ 0.5,\ 1.0,\ 2.0,\ 2.5,\ 4.0 \tag{3-45}$$

Table 5 shows that highly accurate overlap integrals can be computed with a three-term expression. To determine whether the other molecular integrals (3-3) and (3-4) can be evaluated with corresponding accuracy requires additional computations. The results obtained here only indicate the usefulness of the normal functions in molecular calculations.

Table 5

Normal Function Expansion

r_{ab} (a.u.)	1s Overlap Integral* (a.u.)	Moment Approximation* (2 term)(a.u.)	Directly Fitted Function* (2 term) (a.u.)	Directly Fitted Function* (3 term) (a.u.)
0.0	1.000	1.000	1.000	1.000
0.5	.960	.925	.942	.959
1.0	.858	.749	.821	.857
2.0	.586	.551	.564	.585
3.0	.349	.358	.307	.343

*All integrals are normalized to 1 for R=0.

Chapter 4 TREATMENT OF HF AND HF_2^-

A quantum-mechanical discussion of the hydrogen bond requires the selection of a system simple enough to permit the use of quantitative methods. The bifluoride ion (FHF^-), as it exists in crystalline KHF_2[46], appears excellently suited for calculation because of the simplicity of the system as a whole and because of the well-defined nature of the hydrogen bond itself. In this chapter, the method outlined in chapters 1 and 2 is applied to FHF^- after its applicability to highly ionic structures is tested by a treatment of HF.

Section 1: Hydrogen Fluoride

For this calculation HF is considered to consist of eight electrons in the field of two nuclei 1.738 a.u. apart.[47] The fluorine 1s electrons are collapsed into the fluorine nucleus, leaving a net positive charge of seven. As pointed out in Chapter 1, such an approximation procedure requires a careful check on the error introduced. In Table 6 some of the 1s integrals are compared with the results obtained by replacing them with a point charge. The excellent agreement indicates that the error resulting from the neglect of the 1s fluorine electrons is not significant.

Since HF has a closed-shell structure, the choice

Table 6

Integrals of the Fluorine 1s Electron

Integral	Approximation Formula	Exact Value (a.u.)	Approximate Value (a.u.)
$(F_{1s}/\frac{1}{r_H}/F_{1s})$	1/R	.57537	.57537
$(HF_{1s}/F_\sigma F_{1s})$	$(H/\frac{1}{r_F}/F_\sigma)$	.23833	.23905
(HF_{1s}/HF_{1s})	$(H/\frac{1}{r_F}/H)$	.52582	.52644

of orbitals for the variation function is straightforward. The hydrogen 1s orbital and the fluorine 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals are used. From these, the variation function is constructed by the selection of all possible singlet structures with the correct symmetry. Two covalent structures, each corresponding to the existence of one valence-bond, are possible; i.e; the structure with a bond between the hydrogen 1s orbital and the fluorine $2p_\sigma$ orbital*

$$\psi_{H-\sigma} = \psi^1 - \psi^2 \tag{4-1}$$

where

$$\psi^1 = \frac{1}{(2\cdot 8!)^{1/2}} \left| \sigma(1)\beta(1)\, H(2)\alpha(2)\, S(3)\beta(3) \cdots y(8)\alpha(8) \right| \tag{4-2}$$

and

$$\psi^2 = \frac{1}{(2\cdot 8!)^{1/2}} \left| \sigma(1)\alpha(1)\, H(2)\beta(2)\, S(3)\beta(3) \cdots y(8)\alpha(8) \right| \tag{4-3}$$

and the structure with a bond between the hydrogen 1s and the fluorine 2s orbital

$$\psi_{H-S} = \psi^3 - \psi^4 \tag{4-4}$$

where

$$\psi^3 = \frac{1}{(2\cdot 8!)^{1/2}} \left| S(1)\beta(1)\, H(2)\alpha(2)\, \sigma(3)\beta(3) \cdots y(8)\alpha(8) \right| \tag{4-5}$$

---

*The molecular axis is assumed to be the z axis.

and

$$\Psi^4 = \frac{1}{(2\cdot 8!)^{1/2}} \left| s(1)\alpha(1)\, H(2)\beta(2)\sigma(3)\beta(3) \cdots y(8)\alpha(8) \right| \quad (4\text{-}6)$$

Of these two structures, only the first is likely to make a significant contribution. The second requires promotion of an electron from a fluorine 2s to a fluorine 2p orbital with a concomitant promotion energy of 0.76 a.u.; i.e.

$$E(F: 2s^2 2p^5;\ ^2P_{Av}) - E(F: 2s 2p^6;\ ^2S) = 0.76 \quad (4\text{-}7)$$

(see Table 7). This energy so destabilizes the structure (4-4) that it can safely be neglected. In addition to the covalent structures, (4-1) and (4-4), the ionic singlet structures

$$\Psi_{H^+F^-} = \Psi^5 = \frac{1}{(8!)^{1/2}} \left| \sigma(1)\beta(1)\sigma(2)\alpha(2) \cdots y(8)\alpha(8) \right| \quad (4\text{-}8)$$

and

$$\Psi_{H^-F^+} = \Psi^6 = \frac{1}{(8!)^{1/2}} \left| H(1)\beta(1) H(2)\alpha(2)\, s(3)\beta(3) \cdots y(8)\beta(8) \right| \quad (4\text{-}9)$$

have to be considered. The high fluorine ionization potential, (o.64a.u.),[48] and the low electron affinity of hydrogen, (0.026a.u.)[49] indicate that the contribution of structure (4-8) is small; it is not included in the calculations carried out below.

Table 7, Atomic energies (a.u.)*

State	Energy (exp.)	Energy (calc.)
H: 1s; ^2S	- 0.5	- 0.5
F: $2s^2 2p_\pi^4 2p_\sigma$; $^2P_{Av}$	-24.2269	-26.0094
F^+: $2s^1 2p_\pi^4 2p_\sigma$; $^3P_{Av}$	-22.8324	-23.3105
F^+: $2s^2 2p_\pi^4$;	-23.4505	-25.4486
F^-: $2s^2 2p_\pi^4 2p_\sigma^2$; ^1S	-24.3610	-25.5682
F: $2s^1 2p^6$; ^2S	-23.46214	

* Measured from F: 2s; S as the zero of energy.

From the two remaining singlet structures, (4-1) and (4-8), the variation function

$$\Psi_0 = a_1 \Psi_{H-F} + a_2 \Psi_{H^+F^-} = a_1 \Psi_c + a_2 \Psi_i \qquad (4\text{-}10)$$

is constructed. Determination of the coefficients a_1 and a_2 requires evaluation of the elements

$$\int \psi^i H \psi^j d\tau \qquad i,j = 1,2,5 \qquad (4\text{-}11)$$

and

$$\int \psi^i \psi^j d\tau \qquad i,j = 1,2,5 \qquad (4\text{-}12)$$

Application of equation (1-50) to (4-10) and (4-12) yields the necessary expansions. These are given in detail on page 69. According to the method outlined in Chapter 2, the atomic terms appearing in the matrix elements are to be evaluated by means of spectroscopic data. All the required values, except one, correspond to spectroscopic states of the isolated atoms (see Table 7) and are, therefore, obtainable from the compilation prepared by Moore.[48] For the configuration F^+: $2s^2\ 2p^3$ an approximate interpolation[50] is used. By the Slater theory for complex atoms[51] the desired level is $\frac{3}{25}\ F^2$ above F^+: $2s^2\ 2p^4$; ^1D. Accurate evaluation of F^2 is not possible since the spacing[48] of ^3P, ^1D, and of ^1D, ^1S, is not agreement with first-order theory;

Expansions of HF Matrix Elements

$$\int \Psi' H \Psi' d\tau = \bar{E}(H: 1s;\ ^2S) + \bar{E}(F: 2s^2 2p_\pi^4 2p_\sigma;\ ^2P_{AV}) - (H|s)^2$$
$$+ \bar{E}(F^+: 2s^2 2p_\pi^4 2p_\sigma;\ ^3P_{AV}) + (H|\tfrac{-Z_F}{r_F}|H) + 4(x|-\tfrac{1}{r_H}|x) + 2(s|-\tfrac{1}{r_H}|s)$$
$$+ (\sigma|-\tfrac{1}{r_H}|\sigma) + \tfrac{Z_F}{r_{HF}} + 4(Hx|Hx) + 2(Hs|Hs) + (H\sigma|H\sigma) - (Hs|sH)$$
$$- 2(Hx|xH) - (H|s)^2\{4(x|-\tfrac{1}{r_H}|x) + (s|-\tfrac{1}{r_H}|s) + (\sigma|-\tfrac{1}{r_H}|\sigma) + \tfrac{Z_F}{r_{HF}}\}$$
$$- (H|s)\{2(H|-\tfrac{1}{2}\nabla^2 - \tfrac{Z_F}{r_F} - \tfrac{1}{r_H}|s) + 8(sx|Hx) + 2(ss|Hs) + 2(s\sigma|H\sigma)\}$$

$$\int \Psi' H \Psi^2 d\tau = \bar{E}(F^+, 2s^2 2p_\pi^4)(H|\sigma)^2 + (H|\sigma)^2\{4(x|-\tfrac{1}{r_H}|x) + 2(s|-\tfrac{1}{r_H}|s)$$
$$+ \tfrac{Z_F}{r_{HF}}\} + (H|\sigma)\{2(H|-\tfrac{1}{2}\nabla^2 - \tfrac{Z_F}{r_{HF}} - \tfrac{1}{r_H}|\sigma) + 8(\sigma x|Hx) + 4(\sigma s|Hs)\}$$
$$+ (\sigma H|H\sigma)$$

$$\int \Psi' H \Psi^5 d\tau = \bar{E}(F: 2s^2 2p_\pi^4 2p_\sigma\ ^2P_{AV})(H|\sigma) + (H|\sigma)\{4(x|-\tfrac{1}{r_H}|x)$$
$$+ 2(s|-\tfrac{1}{r_H}|s) + \tfrac{Z_F}{r_{HF}} + (\sigma|-\tfrac{1}{r_H}|\sigma)\} + (H|-\tfrac{1}{2}\nabla^2 - \tfrac{1}{r_H} - \tfrac{Z_F}{r_{HF}}|\sigma) + 4(Hx|\sigma x)$$
$$+ 2(Hs|\sigma s) + (H\sigma|\sigma\sigma)\}$$

$$\int \Psi^5 H \Psi^5 d\tau = \bar{E}(F^-: 2s^2 2p_\pi^4 2p_\sigma^2;\ ^1S) + 4(x|-\tfrac{1}{r_H}|x) + 2(\sigma|-\tfrac{1}{r_H}|\sigma)$$
$$+ \tfrac{Z_F}{r_{HF}} + 2(s|-\tfrac{1}{r_H}|s)$$

$$\int \Psi' \Psi' d\tau = 1 - (H|s)^2$$

$$\int \Psi' \Psi^2 d\tau = (H|\sigma)^2$$

$$\int \Psi' \Psi^5 d\tau = (H|\sigma)$$

$$\int \Psi^5 \Psi^5 d\tau = 1$$

i.e.,

$$\frac{^1S - {}^1D}{^1D - {}^3P} = 1.16 \qquad (4\text{-}13)$$

instead of the predicted ratio of 1.5. A simple average of the F^2 values obtained from the ^3P, ^1D and the ^1D, ^1S differences is used. The resulting energy spacing between $F : 2s^2\ 2p_\pi^4$ and $F^+: 2s^2\ 2p^4$; $^3P_{AV}$ is given by the relation

$$E = \frac{5}{4}\left[E(^1D) - E(^3P)\right] + \frac{1}{6}\left[E(^1S) - E(^1D)\right] \qquad (4\text{-}14)$$

For comparison with the experimental energies, calculated values for the atomic terms are also listed in Table 7. The latter were obtained by application of the Slater theory.[51]

To evaluate the integrals (p.69) Slater orbitals are introduced. Although it has been suggested that the best screening constants for molecules are different from those determined for atoms, isolated atom values are used. (see Table 8). With the methods outlined in Chapter 3 all the integrals appearing in the matrix elements (p.69) can be computed exactly. In Tables 9, 10, and 11, the resulting values are listed. Substitution of these integrals into the expansions on page 69 yields numerical values for the matrix elements (see Table 12). If these are inserted into the secular equation (1-19), the ground state energy and wave function for HF are obtained. In Table 13, the total energy of the

Table 8

Slater Function Parameters

Orbitals	Symbol	S_{lm}	N	n^*	δ
H_{1s}	H	1	$(\frac{1}{\pi})^{1/2}$	1	1
F_{1s}	F_{1s}	1	$(\frac{\delta^3}{\pi})^{1/2}$	1	8.7
F_{2s}	s	1	$(\frac{\delta^5}{3\pi})^{1/2}$	2	2.56
$F_{2p\sigma}$	σ	$\cos\theta$	$(\frac{\delta^5}{\pi})^{1/2}$	2	2.56
F_{2p_x}	x	$\sin\theta\cos\phi$	"	2	2.56
F_{2p_y}	y	$\sin\theta\sin\phi$	"	2	2.56

Table 9

One-center integrals (a.u.)

$(H/-\frac{1}{2}\nabla^2-\frac{1}{r_H}/H)$	−0.5000
$(s/-\frac{1}{2}\nabla^2-\frac{Z_F}{r_F}/s)$	−7.8677
$(\sigma/-\frac{1}{2}\nabla^2-\frac{Z_F}{r_F}/\sigma)$	−5.6832
$(x/-\frac{1}{2}\nabla^2-\frac{Z_F}{r_F}/x)$	−5.6832
(ss/ss)	9.9300
$(\sigma\sigma/\sigma\sigma)$	1.0020
(xx/xx)	0.9300
(sx/sx)	0.9300
$(s\sigma/s\sigma)$	0.9300
$(\sigma x/\sigma x)$	0.8940
(xy/xy)	0.8940
$(s\sigma/\sigma s)$	0.2056
(sx/xs)	0.2056
$(\sigma x/x\sigma)$	0.0540
(xy/yx)	0.0540

Table 10

H - F Two-center integrals (a.u.)

Integral	r=1.738 (a.u.)	r=2.136 (a.u.)	r=2.534 (a.u.)
(H/s)	0.47737	0.36255	0.26716
(H/σ)	0.30497	0.25171	0.19668
$(H/\frac{1}{r_F}/H)$	0.52644	0.43205	0.38833
$(\sigma/\frac{1}{r_H}/\sigma)$	0.64844	0.51270	0.42235
$(x/\frac{1}{r_H}/x)$	0.53216	0.44472	0.38061
$(s/\frac{1}{r_H}/s)$	0.57093	0.46738	0.39450
$(s/\frac{1}{r_H}/\sigma)$	0.17871	0.12220	0.08758
$(H/\frac{1}{r_H}/\sigma)$	0.37741	0.25039	0.15971
$(H/\frac{1}{r_H}/s)$	0.36932	0.23834	0.15031
$(H/\frac{1}{r_F}/\sigma)$	0.23905	0.18542	0.13786
$(H/\frac{1}{r_F}/s)$	0.45187	0.32707	0.23240
$(H/z_F/s)$	0.2691		
$(H/z_F/\sigma)$	0.5000		

Table 10 (cont.)

Integral	r=1.738 (a.u.)	r=2.136 (a.u.)	r=2.534 (a.u.)
(Hs/Hs)	0.49994	0.43477	0.37973
(Hx/Hx)	0.48667	0.42357	0.36115
(Hσ/Hσ)	0.52649	0.45717	0.39750
(Hσ/Hs)	0.10331	0.08747	0.07194
(Hx/sx)	0.36346	0.2276	0.1545
(Hσ/sσ)	0.37420	0.2364	0.1624
(Hs/ss)	0.36704	0.2305	0.1588
(Hx/σx)	0.20355	0.1549	0.1118
(Hσ/σσ)	0.22997	0.1741	0.1241
(Hs/σs)	0.21236	0.1601	0.1169
(Hs/sH)	0.16642	0.07084	0.04782
(Hσ/σH)	0.11497	0.08188	0.05212
(Hx/xH)	0.02795	0.01132	0.00540

Table 11

F-F Two-center integrals (a.u.)
(r = 4.272 (a.u.))

(s'/s^2)	0.00940
(s'/σ^2)	0.01360
(σ'/σ^2)	0.01956
(x'/x^2)	0.00262
$(s'/\frac{1}{r_{F^2}}/s')$	0.23407
$(s'/\frac{1}{r_{F^2}}/\sigma')$	0.03089
$(\sigma'/\frac{1}{r_{F^2}}/\sigma')$	0.23994
$(x'/\frac{1}{r_{F^2}}/x')$	0.23114
$(s'/\frac{1}{r_{F'}}/s^2)$	0.00479
$(\sigma'/\frac{1}{r_{F'}}/s^2)$	0.00631
$(s'/\frac{1}{r_{F'}}/\sigma^2)$	0.00745
$(\sigma'/\frac{1}{r_{F'}}/r^2)$	0.00966
$(x'/\frac{1}{r_{F'}}/x^2)$	0.00196
$(s's^2/s's^2)$	0.23407
$(\sigma'x^2/x'x^2)$	0.03089
$(\sigma'\sigma^2/\sigma's^2)$	0.03322
$(\sigma's^2/\sigma's^2)$	0.23994
$(\sigma'\sigma^2/\sigma'\sigma^2)$	0.24670
$(x's^2/x's^2)$	0.23114
$(x'\sigma^2/x'\sigma^2)$	0.23656
(xx^2/xx^2)	0.22854

Table 11 (cont.)

$(x'y^2/x''y^2)$	0.22747
$(x's^2/x''\sigma^2)$	0.02972
$(\sigma'\sigma^2/\sigma^2\sigma'')$	0.00019
$(\sigma's^2/s^2\sigma'')$	0.00009
$(\sigma'x^2/x^2\sigma'')$	0.00000
$(s's^2/s^2s')$	0.00004
$(s'x^2/x^2s')$	0.00000
$(x'x^2/x^2x')$	0.00000
$(x'y^2/y^2x')$	0.00000
$(\sigma'\sigma'/\sigma^2\sigma')$	.00973
$(\sigma's'/\sigma^2s')$	.00924
$(\sigma'x'/\sigma^2x')$	.00899
$(s'\sigma'/s^2\sigma')$	.00444
$(s's'/s^2s')$	.00439
$(s'x'/s^2x')$	.00436
$(\sigma'\sigma'/s^2\sigma')$	.00667
$(\sigma's'/s^2s')$	.00635
$(\sigma'x''/s^2x')$	..00618
$(s'\sigma'/\sigma^2\sigma')$	.00651
$(s's'/\sigma^2s')$	.00642
$(s'x'/\sigma^2x')$	.00638
$(x'\sigma'/x^2\sigma')$	.00120
$(x's'/x^2s')$	.00121
$(x'x'/x^2x')$	.00125
$(x'y'/x^2y')$	.00118

Table 12

HF Matrix Elements - Numerical values
(a.u.)

Matrix Element	Completely Theoretical Method	Semi-Theoretical Method
$H_{cc}=H_{11}+H_{12}$	23.10331	21.47132
$H_{ii}=H_{55}$	26.10796	24.90076
$H_{ci}=2^{\frac{1}{2}}H_{15}$	11.64407	10.82362
$I_{cc}=I_{11}+I_{12}$	0.86513	0.86513
$I_{ii}=I_{55}$	0.43129	0.43129
$I_{ci}=2^{\frac{1}{2}}I_{15}$	1.00000	1.00000

Table 13

Energy, wave function, and dipole moment of HF

	Completely Theoretical Method	Semi-Theoretical Method	Experimental Values
HF-total energy (a.u.)	26.73073	24.93906	-
F -total energy (a.u.)	26.0094	24.2269	-
H -total energy (a.u.)	0.5000	0.5000	-
D_e for HF (a.u.)	0.2213	0.2122	0.2249
D_e for HF	138.7	133.0	141.1
a_1^2 -coefficient of 4_c	1.00	.2066	
a_2^2 -coefficient of 4_i	0.015	.5347	
μ-dipole moment of HF (Debye units) expressed as H $\rightarrow$ F	-0.57	2.27	1.91

molecule, its dissociation energy (De), and the squares of the coefficients of the wave function (4-10) are listed. From the known coefficients of the function the dipole moment can be computed by use of the equation

$$\mu = 1.738 - \sum_{\ell=1}^{8} \bar{z}_\ell \qquad (4\text{-}15)$$

where

$$\bar{z}_\ell = \int \bar{\psi}_0 \, z_\ell \, \psi_0 \, d\tau \qquad (4\text{-}16)$$

and z_ℓ is the z-coordinate of the ℓth electron with the fluorine nucleus as origin. The term 1.738 in (4-15) arises from the unit positive charge on the hydrogen nucleus. The integrals, appearing in equation (4-16) are listed in Table 10. The value of the dipole moment is given in Table 13.

To evaluate the results of the calculation, experimental values of the dissociation energy[53] and the dipole moment[54] are shown in Table 13. It is seen that both the completely theoretical and semi-theoretical methods give excellent values for the energy. However, for the dipole moment, the completely theoretical method gives an entirely incorrect result, while the semi-theoretical method calculates a value in reasonable agreement with experiment.

Some explanation is required for the good energy value computed with the incorrect theoretical wave function. The

nodeless character of the Slater functions causes F_{2s} orbital energy to be too large and the $F^+;2s\ 2p_\pi^4 2p_\sigma$ energy to be too small in absolute value. The consequent decrease in the repulsion from the (S/H) overlap terms stabilizes the covalent structure and, accidentally, leads to nearly the correct energy value.

The results obtained with the semi-theoretical method indicate that it is satisfactory for the treatment of highly ionic molecules. The 20% error in the dipole moment is not large when consideration is given to its sensitivity to the form of the wave function. A two-term variation function (4-10) cannot be expected to give higher accuracy. It is likely that inclusion of the neglected structures (4-4) and (4-7) would improve the answer.

Section II: The Bifluoride Ion

The success of the semi-theoretical method in the HF calculation (Section 4-1) suggests that meaningful results can be obtained by its application to other systems. In this section, a treatment of the bifluoride ion (FHF^-) is presented. An attempt is made to compute the energy of FHF^- and to demonstrate the symmetric position of the hydrogen nucleus.

To simplify the calculation, FHF^- is considered as an isolated system. Nevertheless, a fluorine-fluorine distance (4.272 a.u.) which was determined in an investigation[46] of a KHF_2 crystal is used. It is assumed that the K^+ ions and the other FHF^- ions present in the crystal are so far removed from the one under consideration that they introduce only a minor perturbation.

Two hydrogen positions are considered in this calculation. In one, the hydrogen is located at the center of the fluorine-fluorine line, and in the other, the hydrogen is on the same line at a distance of 1.738 a.u. from the nearer fluorine.* The distance in the unsymmetric case was was selected because it permits the use of many of the integrals computed for H F.

Since the point-charge approximation has been justified for 1s electrons (section 4-1), FHF^- is here treated as a system composed of sixteen electrons in the field of two fluorine nuclei, each of charge plus seven, and one hydrogen nucleus of charge plus one. Only three singlet structures are included. Two contain a single valence bond between

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* In the following discussion the fluorine nearer to the hydrogen is labelled one (F^1) and the other is labelled two (F^2).

the hydrogen and one fluorine

$$\Psi_1 = \Psi_{F_0'-H\ F^{2-}} = \frac{1}{(2\cdot16!)^{1/2}} \left| \sigma'^2(1)\beta(1)\, H(2)\alpha(2) \cdots y'(8)\alpha(8)\, \sigma^2(9)\beta(9) \cdots y^2(16)\alpha(16) \right| \tag{4-17}$$

and

$$\Psi_2 = \Psi_{F'-\ H-F_F^{2-}} = \frac{1}{(2\cdot16!)^{1/2}} \left| \sigma'^2(1)\beta(1) \cdots y'(8)\alpha(8)\, \sigma^2(9)\beta(9)\, H(10)\alpha(10) \cdots y^2(16)\alpha(16) \right| \tag{4-18}$$

and the third is completely ionic

$$\Psi_3 = \Psi_{F'-\ H^+\ F^{2-}} = \frac{1}{(16!)^{1/2}} \left| \sigma'^2(1)\beta(1)\sigma^2(2)\alpha(2) \cdots y'(8)\alpha(8)\, \sigma^2(9)\beta(9) \cdots y^2(16)\alpha(16) \right| \tag{4-19}$$

Other structures which have the required symmetry are neglected for reasons identical to those used in the discussion of HF (p.66). With the structures (4-17), (4-18), and (4-19) a variation function

$$\Psi_0 = a_1 \Psi_1 + a_2 \Psi_2 + a_3 \Psi_3 \tag{4-20}$$

is constructed. The matrix elements arising in the evaluation of the coefficients a_i (i 1,2,3) of (4-20) can be expanded by use of equation (1-50) in a form generalized to include the three-center case. The resulting expansions are not reproduced here because of their extreme length; if desired, they can be obtained from the author. Among the terms composing the expansion are those arising from the exchange of two electrons on different fluorine nuclei. Since the

overlap integrals (x^1/x^2) and (y^1/y^2) are much smaller than the other overlap integrals (Table 11), terms corresponding to x^1,x^2 and y^1,y^2 exchanges are neglected. For computing the matrix elements, three-center integrals are needed in addition to the two-center integrals listed in Tables 10 and 11. The necessary three-center integrals are computed with the approximation formulae discussed in section 3-II. Equations (3-29) and (3-32) are used for most of the integrals; those including distributions of zero charge are approximated by means of a single term normal function expansion (3-38). In Table 14, and 15 values for the three-center integrals are listed. All the necessary atomic terms, except one, are the same as those used in HF (Table 7). The one new term, F:2s $2p^6$; ^2S, is taken from Moore[48]. Values for the matrix elements are given in Table 16. Solution of the secular equation results in the energies and coefficients listed in Table 17.

From the total energy of FHF^- and the known values of the energy of F^- and HF, the energy of the reaction*

$$F^- + HF \rightarrow FHF^- \qquad (4\text{-}21)$$

can be computed (Table 17). For the symmetric case, the value of 36.5 kcal. is obtained. No experimental data are

* Zero point vibrations are neglected in this calculation.

Table 14

Three-center Integrals - Hydrogen symmetric (approximate values a.u.).

$(H\sigma^1/s^2\sigma^1)$	.1201
(Hs^1/s^2s^1)	.1157
(Hx^1/s^2x^1)	.1134
$(H\sigma^1/\sigma^2\sigma^1)$	.08453
(Hs^1/σ^2s^1)	.08130
(Hx^1/σ^2x^1)	.07968
$(H\sigma^1/H\sigma^2)$	.00894
(Hs^1/Hs^2)	.00409
$(H\sigma^1/Hs^2)$	.006065
$(H\sigma^2/s^2\sigma^1)$	.003405
$(Hs^2/s^2\sigma^1)$	.003216
$(Hx^2/x^2\sigma^1)$	.00004
$(H\sigma^1/\sigma^2H)$	.02892
$(H/\frac{1}{r_{F^2}}/s^1)$	.1174
$(H/\frac{1}{r_{F^2}}/\sigma^1)$	.08250
$(\sigma^1/\frac{1}{r_H}/\sigma^2)$	.01764
$(s^1/\frac{1}{r_H}/s^2)$	.00807
$(x^1/\frac{1}{r_H}/x^2)$	.00237
$(s^1/\frac{1}{r_H}/\sigma^2)$	.01244

Table 15

Three-center integrals - Hydrogen unsymmetric
(approximate values a.u.).

$(H/\frac{1}{r_{F^2}}/s')$	.14392	$(Hs^2/s's^2)$	.1423
$(H/\frac{1}{r_{F^2}}/\sigma')$	.09309	$(Hx^2/s'x^2)$	.1379
$(H/\frac{1}{r_{F'}}/s^2)$	.09378	$(H\sigma^2/\sigma'\sigma^2)$	.09550
$(H/\frac{1}{r_{F'}}/\sigma^2)$	.06990	$(Hs^2/\sigma's^2)$	.09206
$(s'/\frac{1}{r_H}/s^2)$	.00446	$(Hx^2/\sigma'x^2)$	.08914
$(\sigma'/\frac{1}{r_H}/\sigma^2)$	.01023	$(H\sigma'/H\sigma^2)$	.00895
$(s'/\frac{1}{r_H}/\sigma^2)$	.00688	(Hs'/Hs^2)	.00410
$(\sigma'/\frac{1}{r_H}/s^2)$	.00668	$(Hs'/H\sigma^2)$	.00606
$(x'/\frac{1}{r_H}/x^2)$	.00118	$(H\sigma'/Hs^2)$	.00608
$(H\sigma'/s^2\sigma')$	.1869	$(H\sigma^2/\sigma^2\sigma')$	.00209
(Hs'/s^2s')	.1822	$(Hs^2/s^2\sigma')$	.00189
(Hx'/s^2x')	.1797	$(H\sigma'/\sigma'\sigma^2)$	.00002
$(H\sigma'/\sigma^2\sigma')$	.1429	$(Hs'/s'\sigma^2)$	.00324
(Hs'/σ^2s')	.1341	$(Hx'/x'\sigma^2)$	.00003
(Hx'/s^2x')	.1297	$(H\sigma'/\sigma^2H)$	.02542
$(H\sigma^2/s'\sigma^2)$	.1474		

Table 16

FHF^- Matrix Elements a.u.

	Symmetric	Unsymmetric
H_{11}	36.26086	37.03629
H_{22}	36.26086	31.43090
H_{33}	49.25928	49.26159
H_{12}	2.13528	1.91168
H_{13}	17.61327	21.32146
H_{23}	17.61327	13.79433
I_{11}	0.73601	0.75159
I_{22}	0.73601	0.64294
I_{33}	0.99832	0.99832
I_{13}	0.35597	0.43129
I_{23}	0.35597	0,27815

Table 17

Energy and Wave Function of FHF^- (a.u.)

	Symmetric	Unsymmetric
Energy of FHF^-	49.37101	49.36982
Energy of Reaction $F^- + HF \rightarrow FHF^-$	0.0582 (36.5 kcal.)	0.0570 (35.7 kcal.)
a_1^2 -coefficient of Ψ_1	0.0795	0.11215
a_2^2 -coefficient of Ψ_2	0.0795	0.02611
a_3^2 -coefficient of Ψ_3	0.5732	0.6018

available for comparison with this result. Davies[56] has calculated an energy of 43.1 kcal. by an electrostatic method. Westrum and Pitzer[57] give a value of 27 kcal. This was obtained from Ketelaar's[58] statement that the energy lies somewhere between 27 and 55 kcal. The value of 36.5 kcal. presented in this thesis awaits an experimental test.

In the hope of determining whether the potential function for the hydrogen has a central minimum, the unsymmetric case was calculated (Table 17). The small change in the energy of the system (0.8 kcal.) resulting from a 0.398 a.u. (0.21A) shift of the hydrogen does not give an unequivocal answer concerning the potential function. Either two potential wells or a very flat minimum could exist. To determine which is the actual situation, additional calculations with the hydrogen located in other positions must be made.

From Table 17, it is seen that in both the symmetric and the unsymmetric configuration, the completely ionic structure (4-19) makes the largest contribution to the wave function. Consideration of the matrix elements (Table 16) shows that the ionic structure alone is unstable with respect to dissociation into F^- and HF. The additional energy, supplied by the partly covalent structures (4-17) and (4-18), is required to stabilize the ion.

In the unsymmetric case (Table 17) the structure (4-17)

with a short H-F bond makes a considerably larger contribution than do either of the covalent structures in the symmetric case. Correspondingly, the contribution of the long-bonded structure is almost negligible. The ionic structure, in contrast, has approximately the same coefficient in the two configurations.

Application of the above considerations to other hydrogen-bonded systems is not attempted in this thesis. It is likely that detailed examination of the matrix elements will permit generalization of the results. If key integrals can be determined, their variation from atom to atom can be a valuable criterion of hydrogen bond strength. The development of this suggestion is left for the future.

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PROPOSITIONS

1. The translocation of liquids and dissolved materials is of major importance in plants. Mechanisms for translocation have been suggested and circumstantially verified. Some direct experimental tests are proposed.

2. The problem of bird navigation is difficult to attack primarily because of the lack of suitable experimental techniques. An experiment of use in testing theories of navigation is proposed.

3. Since cones are known to be responsible for color vision in man, differences among the cones are assumed to exist. It is proposed that microabsorption techniques be used in an attempt to find the different kinds of cones. The reflecting microscope appears well suited for this approach.

4. It is proposed that insect-produced galls are ideal systems for studying the mechanism of organization in living tissues.

5. A simple proof of the Rumer method for determining the valence structures is proposed.

6. A study of $NaHF_2$ has indicated that the F-F distance is considerably larger than that in KHF_2. It is proposed that a new investigation be made to determine the F-F distance more precisely and to find the position of the hydrogen nucleus.

7. Highly accurate wave functions have been calculated for H_2^+ and H_2. It is proposed that these be expanded in terms of hydrogenic orbitals as a means of testing the promotion energy method.

8. It is proposed that some curve fitting procedures can be simplified by the use of Gauss' method for numerical integration.

9. In employing atomic functions for molecular calculations there is no necessity for having the functions centered on the nuclei of the system. It is proposed that Feynman's theorem[1] be used as a criterion for the position of the origin of the atomic functions.

10. To avoid disputes over the origin of this proposition, it is presented in the form

a^5 b^2 c^6 d^4 e^{23} f^4 g^1 h^4 i^{10} j^0 k^1 ℓ^3 m^4 n^5 o^6

p^1 q^1 r^{11} s^{10} t^{12} u^5 v^1 w^0 x^2 y^1 z^1

The solution of the anagram provides the answer to one of the pressing problems of present day science.

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