QUANTUM CHEMICAL CALCULATIONS
ON
HF AND SOME RELATED MOLECULES

by

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Abstract

This thesis reports some quantum chemical calculations directed at elucidating principles useful for refining calculations of electron distribution and other properties for complex molecules. In this work calculations have been made with the valence bond and molecular orbital methods using minimum basis sets of Slater-type orbitals on the ground states of the molecules HF and HO, and on states of HF^+ corresponding to the ionization of either a 1s electron or a $2p\pi$ electron from fluorine in HF. Calculations have been made for molecular energies, bond lengths, force constants, dipole moments, and electron distributions as given by Mulliken population analysis.

For HF, the perfect pairing model with molecule-optimized exponents yields molecular energies about 6 kcal./mole lower than the comparable molecular orbital calculations; the dipole moment calculated by the perfect pairing method is 0.3 D. closer to the experimental value (1.82 D.) than that calculated by the molecular orbital method. The HF equilibrium bond length and force constants are calculated to a reasonable degree of accuracy with the two methods, although the first ionization potentials seem to be better calculated by the molecular orbital method either by Koopman's Theorem

or by taking the difference between the energies of the two states.

The calculations reported in this thesis show clearly that in general free atom exponents are not reliable for calculating molecular properties, and this is important for calculations on larger molecules which most frequently use basis functions appropriate to free atoms. As part of a programme for finding ways of optimizing exponents relatively inexpensively, for use with more complex molecules, an approximation due to Lowdin, for overlap charge distributions in electron repulsion integrals, was tested. The results reported in this thesis show that the method has promise in providing a way of initially optimizing exponents prior to the actual calculation wherein all integrals are evaluated exactly.

Table of Contents

List of Tables

Tables page

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Chapter One

Introduction

Quantum mechanics is important in chemistry for several reasons. In the most fundamental sense, it provides, in principle, the means of determining theoretically all the properties of molecules, either by the time-dependent or the time-independent Schrödinger equation,[1] and, given the properties of individual molecules and the interaction energies between them, statistical mechanics allows predictions to be made for macroscopic collections of molecules. That the possibilities for exact quantum mechanical calculations on individual molecules are somewhat limited, can be assessed by noting that agreement between theory and experiment for the binding energy of the simplest neutral molecule, H_2, has only recently been

reached.[2] Thus, for molecular systems of general interest to the chemist, theoretical treatments must be based on some degree of approximation.

Molecular properties in organic and inorganic chemistry are often discussed in terms of electron distributions,[3,4] and in this vein Platt[5] has argued that a theory of chemistry is primarily a theory of electron density. Early quantum mechanical calculations on atoms and molecules, and experimental studies, especially in structural chemistry, have led to quantum chemical concepts such as orbitals, ionic character, hybridization, and electron pair bonds. These concepts are freely used in discussing electron density in molecules,[6,7] although density distributions can rarely be obtained directly by experiment.

Another use of quantum mechanics in chemistry has evolved with the development, during the last two or three decades, of experimental techniques, such as nuclear magnetic resonance, electron spin resonance, nuclear quadrupole resonance, Mossbauer spectroscopy and photoelectron spectroscopy, which are now widely used by chemists in attempting to gain an improved understanding of chemical bonding. Quantum mechanics has been employed in this context, both for elucidating the basic physics of these experiments, and for developing approximate computational schemes from which calculated

molecular properties can be compared with experimental values. This provides important information for assessing the validity of the models of electron density and chemical bonding used by chemists.

Two major approaches have been developed for approximate calculations on molecules, and these are the molecular orbital method and the valence bond method. The former has been more generally used, mainly because it has been considered to be computationally simpler. Nevertheless, recent developments have led to efficient computational schemes for valence bond calculations, and, moreover, attempts are now being made to develop semi-empirical schemes with this method.[8] Also it has been known for some time that calculations using the perfect pairing model, such as that proposed by Hurley, Lennard-Jones and Pople,[9] which represents an extension to polyatomic molecules of the Heitler-London calculation on H_2,[10] can give better molecular energies than the corresponding molecular orbital calculations.[11] This improvement occurs because electron motions are better correlated in Heitler-London type wave functions than in molecular orbital wave functions.[12] The usefulness of perfect pairing wave functions in polyatomics is closely related to the usefulness of the concept of hybridization, which is itself dependent on the properties of atomic orbitals in molecules. The behaviour

of atomic orbitals in molecules is of general interest, but it is also of particular importance for studying molecules containing the heavier atoms (such as those of the second row of the periodic table and beyond, including transition metals) for which the details of chemical bonding have not yet been established unambiguously in a number of important cases.[13-16] Large basis set calculations on these molecules would seem to be impractical in the near future, and the alternative is to attempt to make reasonable calculations of molecular properties by using well chosen restricted basis sets of atomic orbitals. In any event, large basis set calculations are difficult to interpret in terms of quantum chemical concepts,[17] an example being Mulliken's suggestion[18] that the increase in bond length observed on ionizing a π electron in many diatomic hydrides indicates a degree of π bonding in these molecules, and therefore the involvement of $2p\pi$ atomic orbitals on hydrogen. Although large basis set calculations have been performed for diatomic hydrides, including up to 3d orbitals on hydrogen in the basis set,[19] the chemical significance of hydrogen $2p\pi$ orbitals in bonding has not been determined.

In discussing the valence bond and molecular orbital methods of molecular calculations, one starts with the time-independent Schrödinger equation

$$H\Psi = E\Psi, \qquad (1)$$

where H is the Hamiltonian operator, E is the energy of the system, and Ψ is the state function. In the nonrelativistic approximation, the Hamiltonian operator can be written as

$$H = -\frac{1}{2}\sum_{k=1}^{S}\frac{\nabla_k^2}{m_k} - \frac{1}{2}\sum_{\mu=1}^{N}\nabla_\mu^2 - \sum_{\mu=1}^{N}\sum_{k=1}^{S}\frac{Z_k}{r_{\mu k}} + \sum_{k<\ell}^{S}\frac{Z_k Z_\ell}{r_{k\ell}} + \sum_{\mu<\nu}^{N}\frac{1}{r_{\mu\nu}} \qquad (2)$$

for a collection of N electrons and S nuclei, where the first term represents the summed kinetic energies of the nuclei, the second term represents the summed kinetic energies of the electrons, the third term represents the attraction energy between the electrons and the nuclei, and the fourth and fifth terms represent respectively the nuclear-nuclear repulsions and the electron-electron repulsions. In molecular calculations the Born-Oppenheimer approximation[20] is frequently made. Physically this approximation consists of regarding the motions of the nuclei in a molecule as insignificantly small in comparison to the motions of the electrons, and this is dependent on the masses of the nuclei being very much greater than the masses of the electrons. Thus one regards the nuclei as remaining essentially at rest relative to the motions of the electrons. Using the Born-Oppenheimer approximation, therefore, the wave function is approximated as a function of the electron co-ordinates only, the nuclei being regarded as stationary. Then the electron motions are contained

in the electronic wave function, Ψ_e, which is obtained in principle by solving the equation

$$H_e \Psi_e = E_e \Psi_e , \qquad (3)$$

where

$$H_e = -\frac{1}{2}\sum_{\mu=1}^{N} \nabla_\mu^2 - \sum_{\mu=1}^{N}\sum_{k=1}^{S} \frac{Z_k}{r_{\mu k}} + \sum_{\mu<\nu}^{N} \frac{1}{r_{\mu\nu}} . \qquad (4)$$

In the Born-Oppenheimer approximation, E is E_e plus the nuclear-nuclear repulsion energy.

The molecular orbital and valence bond methods provide schemes for writing down approximate forms of the electronic wave function, Ψ_{approx}, and for calculating the corresponding electronic energies according to (in the Dirac notation)

$$E_e = \frac{\langle \Psi_{approx} | H_e | \Psi_{approx} \rangle}{\langle \Psi_{approx} | \Psi_{approx} \rangle} \qquad (5)$$

The approximate electronic wave functions are obtained according to the variation principle;[21] by which the best wave function is selected according to the criterion of minimum energy.

The Molecular Orbital Method

The molecular orbital method originated from studies by Hund[22] and Mulliken[23] made within a few years of the formulation of quantum mechanics, and this method represents the direct extension to molecules of the atomic

orbital method for atoms.[24,25] For singlet states of a molecule containing 2N electrons, the electronic wave function in molecular orbital theory is approximated by a single determinant as in

$$\Psi_{MO} = (2N)^{-\frac{1}{2}} \text{ DET } | \psi_1(1)\ \overline{\psi_2(2)} \ldots \psi_N(2N-1)\ \overline{\psi_N(2N)} | , \quad (6)$$

where only the diagonal elements of the determinant are defined explicitly. The determinantal form of equation (6) is convenient for ensuring consistency with the antisymmetry principle;[26] $(2N)^{-\frac{1}{2}}$ is the normalization factor. Each molecular orbital is doubly occupied by electrons of opposite spin, β spin being indicated in equation (6) by a bar over the molecular orbital. The molecular orbitals are one-electron functions which extend over the whole molecule and they can be defined to be that set of orthonormal functions, satisfying the conditions

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} , \quad (7)$$

which minimize the electronic energy of the system according to

$$E_{MO} = \frac{\langle \Psi_{MO} | H_e | \Psi_{MO} \rangle}{\langle \Psi_{MO} | \Psi_{MO} \rangle} , \quad (8)$$

where H_e is the electronic Hamiltonian defined in equation (4).

In earlier work on atoms, orbitals were given in

numerical form;[24] in practical applications to molecules, however, they are usually expanded following the procedure reviewed by Roothaan[27] over a set of basis functions as in

$$\psi_i = \sum_{\mu} c_{i\mu} \phi_{\mu} . \qquad (9)$$

Roothaan's procedure consists of determining, by the variation theorem, the coefficients in equation (9) in order to specify the molecular orbitals. Often the basis functions ϕ_{μ} in equation (9) may be identified as atomic orbitals. In practice, a linear combination of atomic orbitals represents an approximation to a molecular orbital wave function because only a restricted number of atomic orbitals are included in the basis set, although, in principle, one may approach as close to the limit as desired. The atomic orbitals in equation (9) may be centred on only one atom in a molecule, however, the convergence to minimum energy is then slow, and, with modern computing facilities, this approximation seems to be of only limited value.[28]

The energy of the determinantal wave function in equation (6), where the one-electron orbitals satisfy the conditions in equation (7), can be expressed[29] as

$$E_{MO} = 2\sum_{i} H_{ii} + \sum_{i}\sum_{j} (2J_{ij} - K_{ij}) , \qquad (10)$$

where

$$H_{ii} = \langle \psi_i | -\tfrac{1}{2}\nabla_i^2 - \sum_k \frac{Z_k}{r_{ik}} | \psi_i \rangle \qquad (11)$$

gives the contribution of one electron in ψ_i to the total electronic energy. The term in equation (11) involving the Laplacian operator represents the kinetic energy of one electron in ψ_i; the second term represents the attraction between an electron in ψ_i and the nuclei. In equation (10), J_{ij} and K_{ij} represent, respectively, Coulomb and exchange electron repulsion integrals defined as

$$J_{ij} = \iint \psi_i(1)\,\psi_i(1)\,\frac{1}{r_{12}}\,\psi_j(2)\,\psi_j(2)\,d\tau_1\,d\tau_2 \qquad (12)$$

and

$$K_{ij} = \iint \psi_i(1)\,\psi_j(1)\,\frac{1}{r_{12}}\,\psi_j(2)\,\psi_i(2)\,d\tau_1\,d\tau_2\,. \qquad (13)$$

The integrals H_{ii}, J_{ij}, and K_{ij}, can readily be expanded in terms of the basis orbitals in equation (9), and, following Roothaan's procedure, a self-consistent field calculation allows the determination of the coefficients, c_i, in equation (9) given the molecular integrals over the basis orbitals.

For open shell systems more than one determinant can be written for a given configuration, and the determinants must be combined according to the appropriate electronic state in order to obtain approximations

to the total wave function of the system. A simple example is the triplet state of a two-electron system for which the total electronic wave function is set up in terms of the orbitals ψ_1 and ψ_2 as

$$\begin{aligned} \psi_{S_z=1} &= |\psi_1(1)\,\psi_2(2)| \\ \psi_{S_z=0} &= \frac{1}{\sqrt{2}}\left(|\psi_1(1)\,\overline{\psi_2(2)}| + |\overline{\psi_1(1)}\,\psi_2(2)|\right) \\ \psi_{S_z=-1} &= |\overline{\psi_1(1)}\,\overline{\psi_2(2)}| \,. \end{aligned} \tag{14}$$

A detailed discussion of the molecular orbital method for open shell systems has been given by Roothaan.[30]

Molecular orbital calculations using the Roothaan procedure and evaluating all molecular integrals without approximation become excessively expensive as the number of electrons in the molecule and the size of the basis set increase. The greater computational effort and expense is due in part to the number of electron-electron repulsion integrals to be evaluated, which increases as approximately the fourth power of the basis set.[31] Also, for large basis sets, it is often found that more time is required to evaluate integrals involving higher members of the basis set than to evaluate integrals involving the lower members of the set. These factors have led to the development of a number of approximate molecular orbital methods suitable

for application on a routine basis to molecules which are too complex to be readily treated using the more complete methods.

In these approximate molecular orbital methods one attempts to make judicious approximations which will simplify the computations so that properties of fairly large molecules can be calculated without either imposing concepts such as preconceived bonding schemes, or eliminating established physical features such as the relative energy levels of atomic orbitals. One development has been to incorporate empirical date into a model such as is done in the Huckel method[32,33] developed for π electrons in organic systems and extended to include all the valence electrons.[34] This method does not explicitly include electron-electron repulsions, but by relating Huckel's Coulomb integrals to valence ionization potentials, and expressing the resonance integrals in terms of the Coulomb and overlap integrals, Hoffmann[35] has discussed charge distributions and conformation energies of a large number of hydrocarbons, and similar methods have been applied to many inorganic molecules.[36,37]

Less drastic approximations are made in the Complete Neglect of Differential Overlap and related methods which are discussed in a recent book by Pople and Beveridge[38] and also in a book edited by Sinanoğlu

and Wiberg.[39] In these methods, emphasis is placed on the valence electrons, and electron repulsion integrals are included, but approximations are made such as

$$\langle \mu\nu | \lambda\sigma \rangle = \delta_{\mu\nu}\,\delta_{\lambda\sigma}\langle \mu\mu | \lambda\lambda \rangle \qquad (15)$$

and

$$\langle \mu | \nu \rangle = \delta_{\mu\nu} \; . \qquad (16)$$

Atomic spectral data are again incorporated in these methods, but a guiding principle is that they are formulated so that the calculated results are invariant to the rotation of axes. This property is required physically, but is not shown by the extended Huckel method. Many applications have been made to the calculation of molecular energies, molecular geometries, charge distributions, ionization potentials, and nuclear magnetic resonance parameters,[40,41,42] and these methods have been established as providing a reasonable balance between computational expense and worthwhile calculations of molecular properties.

The Valence Bond Method

Historically, the valence bond theory provided

the first method for molecular calculations, and this theory originated from the work of Heitler, London, Slater, and Pauling.[43] In this method one assumes a set of basis functions for a molecule, and these functions are most frequently identified as atomic orbitals. In the most complete form of the valence bond method, combinations of determinantal functions are written down for all possible ways of accommodating the electrons in the various atomic orbital functions in accordance with both the Pauli principle,[26] and with the symmetry of the particular electronic state for which the wave function is being expressed. The determinantal functions are defined by the various valence bond configurations for a given electronic state. As an illustrative example, all the valence bond configurations are listed in Table 1 for the $^1\Sigma$ state of HF using a basis set of the 1s atomic orbital at hydrogen, and the 1s, 2s, 2pσ, and 2pπ atomic orbitals at fluorine. The ground state wave function is then obtained by a free mixing of the zero-order wave functions corresponding to all the configurations as in

$$\psi_{VB} = \sum_i c_i \psi_i , \qquad (17)$$

where c_i is the linear mixing coefficient, and ψ_i is the appropriate combination of determinantal functions for the i^{th} valence bond configuration. As examples,

Table 1. Valence bond configurations for the $^1\Sigma$ state of HF

1.	$1s^2\ 2s^2\ \pi_1^2\ \pi_2^2\ \sigma\ h$
2.	$1s^2\ 2s^2\ \pi_1^2\ \pi_2^2\ \sigma^2$
3.	$1s^2\ 2s^2\ \pi_1^2\ \pi_2^2\ h^2$
4.	$1s^2\ 2s\ \pi_1^2\ \pi_2^2\ \sigma^2\ h$
5.	$1s^2\ 2s\ \pi_1^2\ \pi_2^2\ \sigma\ h^2$
6.	$1s^2\ \pi_1^2\ \pi_2^2\ \sigma^2\ h^2$
7.	$1s^2\ 2s^2\ \pi_1\ \pi_2\ \sigma^2\ h^2$
8.	$1s\ 2s^2\ \pi_1^2\ \pi_2^2\ \sigma^2\ h$
9.	$1s\ 2s^2\ \pi_1^2\ \pi_2^2\ \sigma\ h^2$
10.	$1s\ 2s\ \pi_1^2\ \pi_2^2\ \sigma^2\ h^2$
11.	$2s^2\ \pi_1^2\ \pi_2^2\ \sigma^2\ h^2$

The symbols 1s, 2s, π_1, π_2, σ, h refer respectively to 1s, 2s, $2p\pi_1$, $2p\pi_2$, $2p\sigma$ functions at F and the 1s function at H.

the specific forms of the unnormalized zero-order wave functions for the first two configurations in Table 1 are:

$$\Psi_1 = |1s\,\overline{1s}\,2s\,\overline{2s}\,\pi_1\,\overline{\pi}_1\,\pi_2\,\overline{\pi}_2\,\sigma\,\overline{\sigma}| + |1s\,\overline{1s}\,2s\,\overline{2s}\,\pi_1\,\overline{\pi}_1\,\pi_2\,\overline{\pi}_2\,h\,\overline{\sigma}| \qquad (18)$$

and

$$\Psi_2 = |1s\,\overline{1s}\,2s\,\overline{2s}\,\pi_1\,\overline{\pi}_1\,\pi_2\,\overline{\pi}_2\,\sigma\,\overline{\sigma}| \; . \qquad (19)$$

The linear coefficients in equation (17) and the corresponding energies are obtained by application of the variation principle. The technique is well known,[12] and involves solving the secular equation

$$\text{DET}\;|H_{ij} - S_{ij}E| = 0 \qquad (20)$$

for the energies, and

$$\sum_j \sum_i c_i\,(H_{ij} - ES_{ij}) = 0 \qquad (21)$$

for the coefficients. The matrix elements in equations (20) and (21) are defined as

$$H_{ij} = \int \Psi_i^* H_e \Psi_j \, d\tau \qquad (22)$$

and

$$S_{ij} = \int \Psi_i^* \Psi_j \, d\tau \; . \qquad (23)$$

When all the configurations formed from a given basis set are mixed, as in equation (17), the valence

bond method is equivalent to a complete configuration interaction calculation in terms of molecular orbitals expanded over the same basis.[44] Clearly, as the size of a basis set is increased, more configurations can be formed with the appropriate symmetry, and, in the limit, the energies obtained by the valence bond method converge to the eigenvalues for a complete solution of the Schrodinger equation in the Born-Oppenheimer approximation. In less accurate applications of the method, however, it turns out that some configurations can be disregarded. A valence bond study by Harris and Michels[45] on HF for a range of bond lengths, has shown that mixing the six most important configurations leads to a calculated molecular energy only 0.35 kcal./mole above that obtained from the mixing of all eleven configurations. The five configurations which may be neglected, with only small error, either correspond to charge distributions in the sense H^--F^+, which is contrary to chemical experience based on the concept of electronegativity, or correspond to configurations involving excitation of electrons from the fluorine 1s core. Similarly, calculations by Maglagan and Schnuelle[8] for BeH_2 show, for the particular case of using free atom exponents and a Be-H distance of 1.34 Å, that the effect of neglecting those valence bond configurations, where Be is more negatively charged than H, and neglecting

also those configurations where Be is non-bonding, raises the total energy by only 1.2 kcal./mole. These considerations indicate ways of selecting for approximate calculations those valence bond configurations which are most significant to a given basis set. A consequence of such a selection is an appreciable saving in computational effort and expense, and this becomes more important for larger molecules.

A more restricted form of the valence bond method is that which involves perfect pairing,[9] and this method is usually based on hybrid rather than natural atomic orbitals. In this approach, electron pair bonds are constructed between orbitals in a molecule, and the total electronic wave function is given in terms of the determinantal functions appropriate to the various spin couplings for the electron pair bonds. As an example of this approach, one can consider BeH_2, for which two electron pair bonds are assumed to be formed from the overlap of the 1s orbitals (designated l_1 and l_2) on each hydrogen with the appropriate directed hybrid functions h_1 and h_2 at the Be atom. For this example, the unnormalized perfect pairing wave function is written as

$$\Psi_{pp} = |h_1 h_2 \bar{l}_2 \bar{l}_2| - |\bar{h}_1 h_2 l_1 \bar{l}_2| - |h_1 \bar{h}_2 \bar{l}_1 l_2| + |\bar{h}_1 \bar{h}_2 l_1 l_2|, \quad (24)$$

where one electron pair bond is formed by the overlap

of l_1 and h_1, and the other bond is formed by the overlap of l_2 and h_2. Two interpretations can be given to Ψ_{pp}.[46] In the first, Ψ_{pp} involves only neutral configurations at Be, and h_1 and h_2 are the digonal hybrids formed from the 2s and 2pσ atomic orbitals at Be. The second interpretation allows for ionic character in the BeH bonds by expressing h_1 and h_2 as suitable combinations of the 1s orbitals at H and the digonal hybrids as in

$$\begin{aligned} h_1 &= N(d_1 + kl_1) \\ h_2 &= N(d_2 + kl_2) \ , \end{aligned} \qquad (25)$$

where k is a measure of the ionic character of the bond and may be taken as a variation parameter; N is the normalization factor.

In general, within the perfect pairing model, for a closed-shell molecule with n electron-pair bonds, there will be 2^n determinants in the electronic wave function. Hurley, Lennard-Jones, and Pople have shown[9] that, provided that the orbitals involved in any eletron pair bond are orthogonal to all other orbitals in a molecule, a comparatively simple expression can be written in closed form for the electronic energy corresponding to the perfect pairing wave function of the molecule. The evaluation of this expression is related to the methods which are discussed in chapter two for evaluating the Hamiltonian and overlap matrix elements

in equations (22) and (23).

A useful criterion for different methods for molecular calculations is provided by the agreement between calculated and experimental molecular properties. Calculations performed using the valence bond and molecular orbital methods with comparable basis sets, enable comparisons to be made between the two methods.

Detailed comparisons of the valence bond and molecular orbital methods have been made for H_2.[47] Using a minimum basis set of Slater-type orbitals with energy-optimized exponents, the valence bond method predicts[48] an equilibrium bond length of 0.743 Å and a binding energy of 85.94 kcal./mole. The experimental values are 0.741 Å and 109.98 kcal./mole respectively, while the corresponding quantities from the molecular orbital method[49] are 0.732 Å and 80.27 kcal./mole with a minimum basis set. The molecular orbital method becomes much less reliable as the bond distance is increased, and this is associated with the overemphasis of ionic contributions in the molecular orbital method.[49] Karo and Olsen[50] have compared the molecular orbital and valence bond methods for the ground state ($^1\Sigma$) of LiH using a basis set of numerical 1s, 2s, and 2p orbitals at Li and a Slater 1s orbital at H. At the equilibrium bond length of 1.56 Å, both methods predict a dipole moment of 6.05 D, which may be compared with the experimental

value of 5.88 D.;[51] and at this bond distance, the valence bond method gives a molecular energy which is 0.4 kcal./mole lower than that given by the molecular orbital method. Again, as the internuclear distance increases, the molecular orbital method becomes relatively less reliable. Maglagan and Schnuelle[8] have noted that the valence bond method generally gives lower molecular energies than the molecular orbital method for molecules in which the model of electron pair bonds is frequently used. By contrast, the molecular orbital method is comparatively better for delocalized systems such as benzene, although, as noted previously, with sufficient refinement the two methods merge. A detailed comparison has recently been made by Mitchell and Thirunamachandran[46] for BeH_2 employing a basis set of Slater-type orbitals with energy-optimized exponents. The molecular energy calculated with the perfect pairing model is 15 kcal./mole below that for the molecular orbital method, and the calculated Be-H distances are 1.35 Å and 1.37 Å for the perfect pairing and molecular orbital methods respectively. A further interesting comparison between the molecular orbital and valence bond methods has been made by Harrison and Allen[52] for the ground $^3B_1$ state and two low excited states $^1A_1$ and $^1B_1$ of CH_2. Using a basis set of Gaussian lobe functions, these authors calculate the bond angles of

the $^3B_1$, $^1A_1$, and $^1B_1$ states to be 131°, 111°, and 154° according to the molecular orbital method, and using the valence bond approach the corresponding angles are 138°, 108°, and 148° which are to be compared with experimental equilibrium bond angles of ~135°, 103°, and 140° for the three states.[53] Finally, the $^1A_1$-$^1B_1$ vertical transition is 0.96 kcal./mole closer to the experimental value using the valence bond method.

Aims of the Thesis

This study follows recent calculations by Mitchell and Thirunamachandran[46,54] on BeH_2, in which the molecular orbital and valence bond methods have been compared using a minimum basis set of energy-optimized Slater-type orbitals. The work on BeH_2 indicates that the perfect pairing model provides a very good approximation for this molecule, and further comparative calculations are necessary in order to provide basic information with which to assess these methods on a wider basis. HF was chosen as a suitable molecule for continuing this work because the computational effort is reduced for diatomic hydrides, and the large electronegativity dif-

ference between H and F contrasts with the much smaller difference in electronegativities between neighbouring atoms in BeH_2. Although many calculations have already been made on HF using large basis sets,[19,55] it still seems worthwhile to make a direct comparison of the different models for molecular calculations using an energy-optimized minimum basis set of Slater-type orbitals, in part because the large basis set calculations are difficult to interpret in terms of quantum chemical concepts. Connected with the perfect pairing model is the concept of hybridization, and in this work, attempts are made to compare the atomic orbital hybridization at F in HF and HF^+, and also to compare with the hybridization at O in the diatomic HO which is isoelectronic with HF^+. Calculations on HF^+ were made for states in which a 1s or a $2p\pi$ electron has been ionized from fluorine in the neutral molecule.

Since minimum basis set calculations are performed in the various semi-empirical molecular orbital methods currently being used,[38,39] and because these methods have been designed especially for evaluating properties of related series of molecules, it seems necessary, in order to gain a better understanding of these semi-empirical methods, to know just how well minimum basis set calculations are able, in principle, to give useful

calculated values of properties such as bond lengths, ionization potentials, dipole moments, and molecular energies. This is especially so for more complicated molecules, such as those containing an atom of the second row of the Periodic Table or beyond, for which computational expense most often requires calculations to be carried out using restricted basis sets.

It is hoped that the calculations on HF, HF^+, and HO reported in this thesis can contribute both to a better understanding of the reliability of minimum basis set computations for calculating molecular properties of basic interest to the chemist, and to a better awareness of the value and limitations of the perfect pairing model and the use of hybridization in molecular wave function calculations. Finally, a preliminary attempt is made to assess the value of an approximation, proposed by Lowdin,[56] for simplifying molecular integrals for the purpose of optimizing atomic orbital exponents. The need for suitable integral approximations is greatest for more complex molecules, but it is necessary to assess the applicability of any approximations by comparing results obtained using the approximations with those from the more complete calculations and also with experimental results, and this indicates in part the reason for this study on HF.

Chapter Two

Calculations on HF, HF^+, and HO

In principle, quantum chemical calculations on molecules can give direct information about electronic distribution by squaring the electronic wave function; some assessment of the reliability of actual calculations may be obtained by comparing calculated molecular properties with those measured experimentally. In Tables 2 and 3 results are collected from a number of recent calculations on $HF_{^1\Sigma}$, $HF^+_{^2\Pi}$, and $HO_{^2\Pi}$, which are of special interest to this thesis. The main part of this chapter describes the details of the calculations which have been carried out during this work, and the results in Tables 2 and 3 provide a reference for assessing the results which are discussed in chapter three.

Table 2. Results of some previous calculations of molecular properties for $HF_{^1\Sigma}$

Wave function			Molecular properties				
Model	Basis set	Ref.	Energies (a.u.)**	H-F Distance (a.u.)	Dipole Moments (D.)	Ionization Potl.(1π)(eV)	Force Constants $\cdot 10^5$(dynes/cm)
mo	min. STO free atom exp.	57	-99.4915	1.733	1.12		
mo	min. STO opt. exp.	58	-99.5361	1.733	1.44		
vb	min. STO opt. exp.	59	-99.563*	1.860			
mo + ci	min. STO opt. exp.	58	-99.5640	1.733	1.30		
mo	ext. GTO opt. atom exp.	60	-99.8873	1.743		14.00	9.60
mo	ext. GTO opt. exp.	55	-100.0622	1.733			
mo	ext. STO opt. exp.	19	-100.0708	1.696		14.6*	11.22
Experimental			-100.5271	1.7238	1.8195	16.06	9.657

* The value is taken from a graph
**1 a.u.= 27.205e.V.

Table 3. Results of some previous calculations of molecular properties of $HF^{+}_{2\pi}$ and $HO_{2\pi}$

Wave function $HO_{2\pi}$			Molecular properties				
Model	Basis set	Ref.	Energies (a.u.)	Bond distance (a.u.)	Dipole Moments (D.)	Ionization Potl.(1)(eV)	Force Constants $\cdot 10^5$(dynes/cm)
mo	ext. GTO opt. atom exp.	60	-75.2872	1.813		11.7	
vb	H.-Fock a.o.	61	-75.325	1.80			
mo	H.-Fock a.o.	61	-75.327	2.00			
mo	ext. STO opt.exp.	19	-75.4208	1.80		11.3*	7.79
Experimental			-75.778	1.834	1.66	13.2	9.216
	$HF^{+}_{2\pi}$						
mo	ext. GTO opt. atom exp.	60	-99.3734	1.96			
mo	ext. STO opt. exp.	62	-99.53*	1.85		14.45	
Experimental							

Basis Functions

As seen in Table 2, a number of different types of functions have been used as bases for molecular calculations. In principle, any set of functions which is complete may be used to expand a molecular wave function; in practice the choice of functions is determined by the computational effort required to obtain a desired level of convergence. Most often the basis functions used in molecular calculations are related in some way to atomic orbital functions. Traditionally, the Hartree-Fock method for atoms leads to atomic orbitals which are in numerical form, however, these tabulated functions are too unwieldy to be useful in molecular computations. In more recent work analytic expressions are used to represent atomic orbitals and these analytic atomic orbitals are expressed as

$$\phi_{nlm} = \sum R_i(r) \cdot Y_{lm}(\theta, \phi), \qquad (26)$$

where Y_{lm} represents the appropriate spherical harmonics (listed for example by Pauling and Wilson[43]), and the $R_i(r)$ are some type of radial function. One commonly used representation of the radial functions is that given by Slater[63] and expressed as

$$R_{ni} = N_i \cdot r^{n_i - 1} \cdot \exp(-\alpha_i r), \qquad (27)$$

where n_i and α_i are the principal quantum number and orbital exponent respectively; N_i is a normalization factor. This form was proposed by Slater in order to approximate, in a simple way, the radial functions from the Hartree-Fock calculations for atomic orbitals. The radial function in equation (27), when combined with a spherical harmonic defines a Slater-type orbital. Slater-type orbitals have no radial nodes, however, they do converge efficiently in atomic and molecular calculations. An alternative radial function is the Gaussian function, conveniently expressed as

$$R_{nl} = N \cdot r^{n+l} \cdot \exp(-\alpha \cdot r^2). \qquad (28)$$

The use of Gaussian functions was first proposed by Boys,[64] because integrals required in molecular calculations are more easily obtained using Gaussian functions than Slater functions. This advantage must be weighed against the fact that these functions provide much slower convergence for molecular energies than do Slater-type orbitals; in fact it requires about half the number of Slater basis functions as Gaussian functions to obtain a given molecular energy.

In the present study, the interest centres mainly on the use of minimum basis set calculations and assessing the possibilities for calculating properties of large molecules; therefore Slater-type radial functions

combined with the appropriate spherical harmonics are used as basis sets. To overcome the lack of orthogonality which occurs for pure Slater-type orbitals of the same symmetry on the same centre, orthogonalized Slater-type orbitals are constructed according to the Schmidt orthogonalization procedure.[65] For orbitals on the same centre this procedure consists of reinstating the radial nodes which were neglected in the approximation implicit in equation (27). In the general case, to Schmidt orthogonalize a function ϕ_1 to another function ϕ_2, one takes

$$\phi_{1orthog} = \phi_1 - S\,\phi_2 \quad , \tag{29}$$

where

$$S = \langle \phi_1 | \phi_2 \rangle \quad . \tag{30}$$

When normalized, $\phi_{1orthog}$ defines the function ϕ_1 which has been Schmidt orthogonalized to ϕ_2.

The Slater functions used as a basis set for the study of HF consist of a 1s function at H and 1s, 2s, $2p\sigma$ and the degenerate pair of $2p\pi$ functions at F. The formulation of the energy expressions is simplified if all valence orbital functions are orthogonalized to the F1s core, and this is achieved by Schmidt orthogonalizing both H1s and F2s individually to F1s.

In the perfect pairing model of HF there is one

electron pair bond constructed from the overlap of the 1s atomic orbital at H with a hybrid formed from the 2s and 2pσ atomic orbitals at F. The second hybrid formed from these two atomic orbitals at F is regarded as a non-bonding orbital, and is doubly occupied. These two hybrids may be expressed as

$$d_1 = \sin\alpha\ 2s + \cos\alpha\ 2p\sigma \qquad (31)$$

and

$$d_2 = \sin\beta\ 2s' + \cos\beta\ 2p\sigma' \qquad (32)$$

where d_1 is the bonding hybrid and d_2 is the non-bonding hybrid. The primes in the expression for d_2 allow for the possibility that the radial functions used for the bonding hybrid could be different from those used for the non-bonding hybrid; α is a variation parameter which determines the mixing of the atomic orbitals in d_1, and β is chosen so as to ensure that d_1 and d_2 are orthogonal by taking

$$\tan\beta = -S_{pp} / (S_{ss} \cdot \tan\alpha), \qquad (33)$$

where S_{ss} is the overlap integral between the 2s and 2s' functions and S_{pp} is the overlap between 2p and 2p'.

Valence Bond and Molecular Orbital Wave Functions

In the perfect pairing model the ground state wave function of HF can be written in unnormalized form as a combination of two determinants as in

$$\Psi_{pp} = |\, 1s\, \overline{1s}\, \pi_1 \overline{\pi}_1 \pi_2 \overline{\pi}_2\, d_2\, \overline{d}_2\, h\, \overline{d}_1 \,| + |\, 1s\, \overline{1s}\, \pi_1 \overline{\pi}_1 \pi_2 \overline{\pi}_2\, d_2 \overline{d}_2\, d_1 \overline{h} \,|, \quad (34)$$

where there is a single electron pair bond between the hybrid d_1 and the orbital combination designated h in equation (34); 1s, π_1, and π_2 refer to doubly occupied non-bonding orbitals at F. Allowance is made in equation (34) for the possibility of ionic character in the H-F σ bond, expected since F is more electronegative than H, by forming the electron pair bond between the hybrid d_1 and a linear combination of the 1s function at H with d_1 defined as

$$h = N_\gamma (\sin\gamma \cdot a + \cos\gamma \cdot d_1) , \quad (35)$$

In equation (35), a is the H_{1s} atomic orbital orthogonalized to the F_{1s} core, and γ is a variation parameter which gives a measure of the ionic character of the H-F σ bond. This formulation corresponds to the second interpretation given to Ψ_{pp} on page 18.

When d_1, d_2, and h, as given by equations (31), (32), and (35) are substituted into equation (34), Ψ_{pp} can be expanded as

$$\psi_{pp} = \sum_{i=1}^{15} c_i \psi_i \,, \qquad (36)$$

where each ψ_i corresponds to a valence bond configuration expressed in terms of the orthogonalized Slater-type orbitals. The fifteen ψ_i which can be formed from the expansion of ψ_{pp}, are listed in Table 4. The coefficients c_i in equation (36) are then determined by the values of the parameters α, β, and γ. For the special case that $2s \equiv 2s'$ and $2p \equiv 2p'$, corresponding to the minimum basis set situation, only three of the fifteen configurations in Table 4 are different, and in this case the wave function obtained by solving the secular equation for these three structures is equivalent to the perfect pairing wave function in equation (34). These perfect pairing and valence bond wave functions for the ground state of HF are to be compared with the corresponding molecular orbital wave functions discussed below; howver, consideration is first given, within the perfect pairing framework, to some doublet states of HF^+ which are of interest in interpreting results from photoelectron spectroscopy[66] and electron spectroscopy for chemical analysis[67] on the neutral HF molecule. Two states of HF^+ are considered in an approximate way. The first is a $^2\Sigma$ state

Table 4. Zero-order wave functions in equation (36) for the $^1\Sigma$ state of HF

1. $\Psi_1 = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2s}'2s\bar{2s}|$
2. $\Psi_2 = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2s}'2p\bar{2p}|$
3. $\Psi_3 = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2p}'2s\bar{2s}|$
4. $\Psi_4 = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2p}'2p\bar{2p}|$
5. $\Psi_5 = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2s}'2s\bar{a}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2s}'a\bar{2s}|$
6. $\Psi_6 = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2s}'2p\bar{a}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2s}'a\bar{2p}|$
7. $\Psi_7 = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2s}'2s\bar{2p}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2s}'2p\bar{2s}|$
8. $\Psi_8 = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2p}'2s\bar{a}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2p}'a\bar{2s}|$
9. $\Psi_9 = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2p}'2p\bar{a}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2p}'a\bar{2p}|$
10. $\Psi_{10} = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2p}'2s\bar{2p}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2p}'2p\bar{2s}|$
11. $\Psi_{11} = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2p}'2s\bar{2s}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2s}'2s\bar{2s}|$
12. $\Psi_{12} = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2p}'2p\bar{2p}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2s}'2p\bar{2p}|$
13. $\Psi_{13} = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2p}'2s\bar{2p}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2s}'2s\bar{2p}|$
    $+ |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2p}'2p\bar{2s}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2s}'2p\bar{2s}|$
14. $\Psi_{14} = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2p}'2s\bar{a}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2s}'2s\bar{a}|$
    $+ |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2p}'a\bar{2s}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2s}'a\bar{2s}|$
15. $\Psi_{15} = |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2p}'2p\bar{a}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2s}'2p\bar{a}|$
    $+ |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2s'\bar{2p}'a\bar{2p}| + |1s\bar{1}s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 2p'\bar{2s}'a\bar{2p}|$

Symbols are as in the text.

obtained by the ionization of an electron from the F_{1s} orbital in the neutral HF; the second is a $^2\pi$ state obtained by removing an electron from a $2p\pi$ atomic orbital at F. In the perfect pairing approximation, the appropriate wave functions for these two states of HF^+ may be expressed in unnormalized form as

$$\Psi_{PP_{^2\Sigma}} = |1s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 d_2\bar{d}_2 h\bar{d}_1| + |1s\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2 d_2\bar{d}_2 d_1\bar{h}| \quad (37)$$

and

$$\Psi_{PP_{^2\Pi}} = |1s\bar{1s}\pi_1\pi_2\bar{\pi}_2 d_2\bar{d}_2 h\bar{d}_1| + |1s\bar{1s}\pi_1\pi_2\bar{\pi}_2 d_2\bar{d}_2 d_1\bar{h}| + |1s\bar{1s}\pi_1\bar{\pi}_1\pi_2 d_2\bar{d}_2 h\bar{d}_1| + |1s\bar{1s}\pi_1\bar{\pi}_1\pi_2 d_2\bar{d}_2 d_1\bar{h}|, \quad (38)$$

where $S_z=\frac{1}{2}$ in both cases. The wave function in equation (38) also represents an approximation within the perfect pairing model for the ground state of the diatomic species HO which is isoelectronic with HF^+.

Wave functions in the molecular orbital approach have been constructed so as to enable as close a comparison as possible with the valence bond and perfect pairing wave functions discussed above. Consequently, the molecular orbitals were constructed from only the valence basis orbitals. The molecular orbitals which would involve mainly the inner basis orbitals, were simply taken to be core atomic orbitals as was done in the perfect pairing calculations. On this basis, the electronic wave function for the ground state of HF in

the molecular orbital approximation can be expressed as

$$\psi_{MO} = | \, 1s\,\overline{1s}\,\pi_1\overline{\pi_1}\,\pi_2\overline{\pi_2}\,\sigma_1\overline{\sigma_1}\,\sigma_2\overline{\sigma_2} \, | \,, \qquad (39)$$

where σ_1 and σ_2 are respectively the bonding and essentially non-bonding molecular orbitals, defined as

$$\sigma_1 = N_\delta \left(\sin\delta \cdot a + \cos\delta \cdot d_1 \right) \qquad (40)$$

and

$$\sigma_2 = N_\epsilon \left(\sin\epsilon \cdot a + \cos\epsilon \left(\sin\zeta \cdot d_1 + \cos\zeta \cdot d_2 \right) \right), \qquad (41)$$

in such a way as to be useful for discussing hybridization in this model. In equations (40) and (41) N_δ and N_ϵ are normalization factors; δ and ζ (along with α) are variation parameters, and ϵ is fixed by the condition that σ_1 and σ_2 are mutually orthogonal. Since the F_{1s} core orbital has the same symmetry as σ_1 and σ_2, a free mixing of this core orbital must lead to a slight lowering of energy by the variation principle. The corresponding approximate wave functions in the molecular orbital approximation for the $^2\Sigma$ and $^2\pi$ electronic states of HF^+ formed by removing either an F_{1s} or an $F_{2p\pi}$ electron from HF are expressed as

$$\psi_{MO\,^2\Sigma} = | \, 1s\,\pi_1\overline{\pi_1}\,\pi_2\overline{\pi_2}\,\sigma_1\overline{\sigma_1}\,\sigma_2\overline{\sigma_2} \, | \qquad (42)$$

and

$$\psi_{HO_2\pi} = |1s\,\overline{1s}\,\pi_1\pi_2\overline{\pi}_1\sigma_1\overline{\sigma_1}\,\sigma_2\overline{\sigma_2}| + |1s\,\overline{1s}\,\pi_1\overline{\pi}_1\pi_2\sigma_1\overline{\sigma_1}\,\sigma_2\overline{\sigma_2}| \quad (43)$$

Computational Details

Given the electronic wave function of a molecule and the electronic Hamiltonian, the electronic energy of the system is obtained by equation (5). When the determinantal wave functions defined in the previous section are substituted into equation (5), the expression for the electronic energy involves functions of the type

$$H_{ij} = \langle \Psi_i | H_e | \Psi_j \rangle \quad (44)$$

and

$$S_{ij} = \langle \Psi_i | \Psi_j \rangle \ , \quad (45)$$

where Ψ_i and Ψ_j are many-electron determinantal functions. The general procedures for the evaluation of these many-electron matrix elements in terms of coefficients and one and two-electron molecular integrals have been given by Lowdin[68] and are fully discussed by Slater.[69] The latter treatment was followed in this work with all expressions for the overlap and Hamilto-

nian matrix elements being evaluated by hand by determining the appropriate coefficients, in terms of the overlap integrals, for all the molecular integrals occurring for the particular basis set. Computer programmes were written to sum all these contributions and consideration is now given to the methods employed to obtain the various molecular integrals.

The basis set, as described above, becomes contaminated by the orthogonalization procedures, however, the one and two-electron molecular integrals over the basis orbitals are readily expanded in terms of one and two-electron integrals involving only Slater-type orbitals. A procedure due to Magnusson and Zauli[70] provides a convenient way of obtaining those electron-electron repulsion integrals which involve a charge distribution on a single centre such as

$$\langle \psi_1^a \psi_2^a \mid \psi_3^a \psi_4^b \rangle , \qquad (46)$$

where a and b are the two nuclei and ψ_1 to ψ_4 are Slater-type orbitals on the indicated centres. This procedure involves expressing the integral in (46) as

$$\langle \psi_3^a \mid V^a_{(\psi_1 \psi_2)} \mid \psi_4^a \rangle , \qquad (47)$$

where $V^a_{(\psi_1 \psi_2)}$ is the potential due to the charge distribution $\psi_1^a \psi_2^a$ centred on a. Potentials of this type for Slater-type orbitals have been tabulated by Magnus-

son and Zauli,[70] and some extensions and corrections have been reported by Mitchell.[71] When using polar co-ordinates (r, θ , ϕ) at each centre, the integral in (47) involves six variables; however, by introducing the elliptical co-ordinates μ and v, defined as

$$\mu = \frac{1}{R}(r_a + r_b) \qquad (48)$$

and

$$\nu = \frac{1}{R}(r_a - r_b) \ , \qquad (49)$$

where R is the inter-nuclear distance, the integral in (47) can readily be expressed in terms of the three variables μ, v, and ϕ, where ϕ measures the angle of rotation about the inter-nuclear axis a-b. Also for the known form of the Slater-type orbitals and the potential V, the integration over ϕ is trivial and can be done analytically. Thus the evaluation of the integral in (47) requires integration over the two co-ordinates μ and v, and to cover all space the respective ranges are 1 to ∞ and -1 to +1. The evaluation of integrals of the type in (46) was performed using two-dimensional Gaussian quadrature[72] with Legendre polynomials of order 16; and as an illustration of this technique, an integral involving a single variable with limits p and q is given in this approximation by

$$\int_p^q f(x)\,dx = \frac{q-p}{2} \sum_{i=1}^{n} a_i\, f\left(x_i \frac{q-p}{2} + \frac{q+p}{2}\right), \qquad (50)$$

where x_i is the i^{th} root of the Legendre polynomial of order n, and a_i are tabulated constants associated with each x_i. The form of equation (50) can be directly extended to any number of variables.

One advantage of this approach for the evaluation of the two-electron integrals of the type in (46) is that all the one-electron integrals can be obtained by the same methods at the same time. The overlap and nuclear attraction integrals respectively, written in general as

$$\langle \psi_i \mid \psi_j \rangle \qquad (51)$$

and

$$\langle \psi_i \mid \frac{z}{r} \mid \psi_j \rangle \qquad (52)$$

represent special cases of the integral in (47). Furthermore, the kinetic energy integrals

$$\langle \psi_i \mid -\tfrac{1}{2} \nabla^2 \mid \psi_j \rangle \qquad (53)$$

can be expressed in terms of overlap integrals as shown by Roothaan[73] who gave the expression

$$-\tfrac{1}{2}\nabla^2 (n,l,m) = -\tfrac{1}{2}\alpha^2 \Big\{ (n,l,m) - 2(2n/2n-1)^{1/2} (n-1,l,m) + \frac{(n+l)(n-l-1)}{[2n(2n-1)(2n-2)(2n-3)]^{1/2}} (n-2,l,m) \Big\} \qquad (54)$$

for the effect of the kinetic energy operator on a Slater-type orbital represented by (nlm) with exponent α.

The method used in going from (46) to (47) is not applicable in a convenient way for evaluating the electron-electron repulsion exchange integrals of the type

$$\langle \psi_1^a \psi_2^b \mid \psi_3^a \psi_4^b \rangle . \qquad (55)$$

Exact numerical values of these integrals were obtained by using a computer programme written by Pitzer, Wright and Barnett[74] and translated into Fortran IV by Mitchell. Since these integrals were much the most time consuming, an approximation proposed by Lowdin[58] was also used to obtain values of the integrals. Lowdin's approximation consists of expressing the charge distribution $\psi_1^a \psi_2^b$ as

$$\psi_1^a \psi_2^b \simeq S_{12}\left[\lambda_1(\psi_1^a \psi_1^a) + \lambda_2(\psi_2^b \psi_2^b)\right], \qquad (56)$$

where S_{12} is the overlap integral between ψ_1 and ψ_2, and λ_1 and λ_2 are determined by the condition that the dipole moments of the charge distributions on the right and left hand sides of (56) are equal. Substitution of (56) into (55) yields

$$\langle \psi_1^a \psi_2^b \mid \psi_3^a \psi_4^b \rangle \simeq S_{12}\left[\lambda_1(\psi_1^a \psi_1^a \psi_3^a \psi_4^b) + \lambda_2(\psi_2^b \psi_2^b \psi_3^a \psi_4^b)\right], \qquad (57)$$

and the right hand side now involves integrals which can be evaluated by the numerical method discussed above.

Secular equations for wave functions of the type in equation (36) were solved with computer programmes from Quantum Chemistry Programme Exchange.[75,76] For the molecular orbital and perfect pairing calculations, the molecular energies were minimized by varying the relevant mixing parameters by making successive five point per variable grid searches until the energy converged to the fifth decimal place (energies in atomic units). The optimum orbital exponents were obtained by varying the individual exponents in turn until self-consistency was achieved in the exponent values to two decimal places. The bond distances corresponding to minimum energies for the various wave functions were obtained by determining the orbital exponents for minimum energy for a series of bond distances, and then interpolating exponents linearly and calculating energies for the intermediate lengths, thereby allowing estimation of the equilibrium distance.

Chapter Three

Results and Discussion

Using the wave functions and procedures described in chapter two, a series of calculations have been made for HF, HF^+, and HO in their ground states, and also for HF^+ in the $^2\Sigma$ state obtained on ionizing a fluorine core 1s electron from HF. Computations have been made using molecule-optimized exponents for the Slater-type functions, and the resulting wave functions, molecular energies, one-electron energies, Mulliken populations, dipole moments, H-F bond distances and force constants are reported in Tables 5 - 12. Included in these tables are comparative results obtained from calculations using free atom exponents.[77]

Table 5. Orbital exponents and molecular properties for different wave functions of HF at the experimental bond distance (1.733 a.u.)

	Orbital exponents				Molecular properties *			
Wave function	H1s	F2s	F2pσ	F2pπ	Energy (a.u.)	Dipole Moment (D)	Ionization potentials (1σ)(eV)	(1π)(eV)
pp a	1.34	2.55	2.60	2.49	-99.5450	1.73	713.29	12.39
pp b	1.38	2.56	2.59	2.49	-99.5449	1.77		
pp c	1.00	2.56	2.55	2.55	-99.4956	1.44	712.32	12.45
mo a	1.32	2.56	2.67	2.50	-99.5355	1.44	714.07	12.66
mo b	1.36	2.56	2.63	2.49	-99.5346	1.55		
mo c	1.00	2.56	2.55	2.55	-99.4908	1.12	714.12	13.32

All F1s exponents have been optimized at 8,65.
* All properties have been calculated exactly.
a - All orbital exponents have been optimized completely.
b - Orbital exponents have been optimized with the Lowdin approximation in (56).
c - Free atom exponents have been used.

Table 6. Variation parameters and Mulliken populations for different wave functions of HF at the experimental bond distance (1.733 a.u.)

	Variation parameters					Mulliken populations		
Wave function	$\sin\alpha$	$\sin\gamma$	$\sin\delta$	$\sin\zeta$	$\sin\epsilon$	H1s	F2s	F2pσ
pp a	0.1203	0.9344				0.685	1.999	1.316
pp b	0.1281	0.9313				0.679	1.999	1.322
pp c	0.0875	0.9438				0.702	2.000	1.298
mo a	0.4000		0.6000	0.0344	-0.1970	0.773	1.944	1.284
mo b	0.2797		0.5922	-0.0422	-0.1488	0.744	1.945	1.312
mo c	0.3094		0.6250	-0.0219	-0.2042	0.781	1.959	1.260

a, b, c, - are as in Table 5.

Table 7. Orbital exponents and molecular properties for different wave functions of HF at calculated equilibrium bond distances

	Orbital exponents				Molecular properties			
Wave function	H1s	F2s	F2pσ	F2pπ	Energy (a.u.)	Bond length (a.u.)	Dipole Moment(D.)	Force constant
pp a	1.33	2.55	2.60	2.49	-99.5456	1.77	1.72	8.3
pp b	1.35	2.55	2.58	2.49	-99.5410	1.79	1.83	7.1
pp c	1.00	2.56	2.55	2.55	-99.5088	1.93	1.31	7.1
mo a	1.31	2.56	2.66	2.50	-99.5356	1.75	1.41	8.5
mo b	1.35	2.56	2.62	2.49	-99.5263	1.76	1.71	7.6
mo c	1.00	2.56	2.55	2.55	-99.5021	1.91	0.89	7.2

All F1s exponents have been optimized at 8.65.

a - All orbital exponents have been optimized exactly.

b - The Lowdin approximation in (56) has been used for calculating exponents and molecular properties.

c - Free atom exponents have been used and molecular properties have been calculated exactly.

Table 8. Variation parameters and Mulliken populations for different wave functions of HF at calculated equilibrium bond distances

Wave function	Variation parameters					Mulliken populations		
	$\sin\alpha$	$\sin\gamma$	$\sin\delta$	$\sin\xi$	$\sin\epsilon$	H1s	F2s	F2pσ
pp a	0.1188	0.9378				0.694	1.999	1.306
pp b	0.1376	0.9313				0.682	1.999	1.319
pp c	0.0700	0.9613				0.769	2.000	1.232
mo a	0.4938		0.5875	0.1000	-0.2301	0.777	1.948	1.275
mo b	0.3125		0.5750	-0.0313	-0.1428	0.721	1.936	1.343
mo c	0.3375		0.6563	0.0187	-0.2185	0.860	1.965	1.175

a, b, c, - are as in Table 7.

Table 9. Orbital exponents and molecular properties for different wave functions of $HF^{+}\,^{1}\Sigma$ at HF experimental bond distance (1.733 a.u.)

	Orbital exponents					Molecular properties	
Wave function	H1s	F1s	F2s	F2pσ	F2pπ	Energy (a.u.)	Dipole Moment (D.)
pp a	1.49	8.97	2.77	3.03	2.97	-74.1245	2.70
pp b	1.50	8.97	2.77	3.02	2.97	-74.1245	2.73
pp c	1.00	8.65	2.56	2.55	2.55	-73.5303	3.80
mo a	1.49	8.97	2.77	3.03	2.96	-74.1103	2.81
mo b	1.50	8.97	2.77	3.02	2.96	-74.1102	2.80
mo c	1.00	8.65	2.56	2.55	2.55	-73.5316	3.83

a, b, c_T are as in Table 7.

Table 10. Variation parameters and Mulliken populations for different wave functions of $HF^{+}{}^{1}\Sigma$ at HF experimental bond distance (1.733 a.u.)

	Variation parameters					Mulliken populations		
Wave function	$\sin\alpha$	$\sin\gamma$	$\sin\delta$	$\sin\zeta$	$\sin\epsilon$	H1s	F2s	F2pσ
pp a	0.1625	0.7938				0.466	1.999	1.536
pp b	0.1625	0.7888				0.459	1.999	1.542
pp c	0.0000	0.3719				0.146	2.000	1.854
mo a	0.4125		0.4000	0.0000	-0.1157	0.452	1.951	1.597
mo b	0.3625		0.4031	-0.0187	-0.1024	0.451	1.954	1.595
mo c	0.0469		0.1719	-0.0500	-0.0555	0.108	2.033	1.859

a, b, c,- are as in Table 7.

Table 11. Orbital exponents and molecular properties for a series of wave functions for $HF^{+}_{2\pi}$ and $HO_{2\pi}$

	Orbital exponents					Molecular properties		
Wave function	H1s	F1s	F2s	F2pσ	F2pπ	Energy (a.u.)	Bond length (a.u.) **	Dipole Moment(D.)
HF pp a	1.48	8.64	2.63	2.74	2.67	-99.1983	1.73	2.44
b	1.48	8.64	2.63	2.73	2.67	-99.1983	1.73	2.44
c	1.00	8.65	2.56	2.55	2.55	-99.0989	1.73	2.79
d	1.43	8.64	2.63	2.71	2.68	-99.2031	1.84	2.55
HF mo a	1.47	8.64	2.63	2.74	2.67	-99.1835	1.73	2.46
b	1.47	8.64	2.63	2.74	2.67	-99.1835	1.73	2.46
c	1.00	8.65	2.56	2.55	2.55	-99.0900	1.73	2.87
HO* pp b	1.28	7.66	2.24	2.27	2.18	-75.1154	1.83	1.16

* Calculation for $HO_{2\pi}$

** 1.73 is a fixed value for the bond length.

a, b, c, - are as in Table 7.

d - The Lowdin approximation has been used for calculating exponents and molecular properties.

Table 12. Variation parameters and Mulliken populations for a series of wave functions for $HF^{+}_{^2\Pi}$ and $HO_{^2\Pi}$

	Variation parameters					Mulliken populations		
Wave function	sin α	sin γ	sin δ	sin ζ	sin ϵ	H1s	F2s	F2pσ
pp a	0.1560	0.8391				0.525	1.999	1.476
pp b	0.1563	0.8375				0.523	1.999	1.478
pp c	0.0656	0.9313				0.384	2.000	1.616
pp d	0.1594	0.8438				0.534	1.999	1.467
mo a	0.0734		0.4563	-0.1391	-0.0311	0.530	1.948	1.522
mo b	0.0734		0.4563	-0.1391	-0.0311	0.530	1.948	1.522
mo c	0.2911		0.3625	-0.0438	-0.1115	0.373	1.982	1.645
pp b*	0.1500	0.9881				0.863	1.999	1.139

* Calculation for $HO_{^2\Pi}$
a, b, c, - are as in Table 7.
d - is as in Table 11.

Atomic Orbital Exponents

The first choice of variables for molecular calculations with a basis set of Slater-type orbitals concerns the selection of appropriate orbital exponents. In semi-empirical schemes, free atom exponents are usually used,[38,39] however, examination of the optimized exponent values in Tables 5, 7, 9, and 11 shows that in certain cases the exponent values are considerably modified from atomic values; and this indicates that in general the choice of suitable exponent values is not a trivial one.

Looking first at the exponent values for HF in Tables 5 and 7, a significant change has occurred in the H1s exponent, from 1.00 for the free atom value to the optimized value of about 1.32, depending on the particular wave function. As the distance of maximum probability for a Slater-type orbital is given by

$$r_{max} = n/\alpha \,, \qquad (58)$$

where n is the principal quantum number and α is the orbital exponent, an increase in an exponent value corresponds to a contraction of the Slater-type orbital. The H1s orbital appears to be contracted in HF compared with the free H atom, and the contraction can be related, in part at least, to a transfer of charge from

H to F expected by electronegativity arguments and shown by the Mulliken populations in Tables 6 and 8. This charge transfer results in H becoming positively charged and the electronic density at H is in consequence held more tightly. The optimized exponents for the F1s, F2s, and F2pπ orbitals experience only small changes from the free atom values, although an increase of around 0.1 is shown by the F2pσ orbital. Previous experience[46,78,79] has indicated that exponent values often tend to increase by this amount for orbitals involved in bonding, and this can be related to the Virial Theorem.[80] When highly polarizable excited orbitals are involved in bonding however, the changes in exponent values may be large.[81] Similar exponent values are found from both the perfect pairing and molecular orbital calculations for HF, the greatest difference for the calculated equilibrium bond length is 0.06 for F2pσ.

The results for HF and $HF^{+}_{1\pi}$ show that the F1s exponent is not sensitive to changes in the valence shell electronic structure, and this is expected for a core orbital which has a very low polarizability. As shown in Table 9 however, on ionizing an F1s electron from HF this exponent value is increased very significantly. In general, for this ionization all the exponents are increased and this corresponds to a

contraction of the atomic orbitals which is expected since the remaining electrons will be held more tightly in the positively charged species, as has been noted in previous calculations on C_2H_2 and $C_2H_2^+$ by Goodman and Griffith,[82] although these workers did not optimize the H1s exponent which they fixed at 1.20. In $HF^+{}_{2\Sigma}$ the F1s exponent now has a value of 8.97 which is very close to the value (9.00) obtained by Slater's rules.[63] The H1s exponent in $HF^+{}_{2\Sigma}$ is 0.5 larger than the free atom value, and 0.2 larger than that for HF. Again, this increase for $HF^+{}_{2\Sigma}$ can be associated with the large transfer of electronic charge from H to F. It may be noted that the effect of this charge transfer is that $HF^+{}_{2\Sigma}$ approximates to the situation represented by H^+-F where the electron distribution at F tends towards spherical symmetry. This is reflected in the F2pσ and F2pπ exponents being more nearly equal than, for example, in HF. The optimum exponent values in the perfect pairing and molecular orbital models are nearly identical, the greatest difference being 0.01, and again this can by rationalized by the tendency to approach H^+-F.

The optimum exponent values for $HF_{2\pi}$, listed in Table 11, are intermediate between the exponent values for HF and those for $HF^+{}_{2\Sigma}$. With the same doubly occupied F1s core, the F1s exponent for $HF^+{}_{2\pi}$ has the value of 8.65 equal both to that for the free atom, and that

for HF. The contraction of the H1s orbital in $HF^+_{2\pi}$ is less than that in $HF^+_{2\Sigma}$ but greater than the H1s contraction in HF.

The results in Tables 5 - 12 give evidence that calculations of molecular properties such as bond lengths and dipole moments with minimum basis sets are much improved if molecule-optimized exponents are used rather than free atom exponents. In applying this result to more complex molecules, it will be necessary to have convenient and relatively inexpensive methods for optimizing Slater orbital exponents, and with this in mind consideration has been given to obtaining optimal exponents when the time-consuming electron repulsion integrals involving two two-centre charge distributions are evaluated using the approximation due to Lowdin in equation (56). The first point to note is that in all cases in Tables 5, 7, 9, and 11, the optimum exponents obtained using the Lowdin approximation are quite similar to the values from exact calculations and therefore are rather different from free atom values; in the cases of $HF^+_{2\Sigma}$ and $HF^+_{2\pi}$ the agreement is very close. For these cases the contraction in the H1s orbitals, as reflected in the large H1s exponent values, reduces the numerical values of the two-centre exchange integrals with the consequence that the errors introduced by the approximation are reduced also. Likewise, for these two states of HF^+, the molecular properties cal-

culated with the Lowdin approximation are very similar to those from the exact calculations, and even for neutral HF the errors introduced are not large considering the saving in computation time. This suggests it could be advantageous to investigate further in this context.

Molecular Energies

As noted in Tables 2 and 3, (with the exception of $HF^{+}{}_{2\Sigma}$), molecular energies lower than the values reported in Tables 5, 7, and 11 have been given previously for the molecular species of interest here. However, the intention in the present work is to restrict the basis sets to forms which have applications to more complex molecules, and consequently the results obtained will be discussed more in relation to similar calculations, rather than to those with the extended basis sets noted in Tables 2 and 3.

The molecular energies for HF at the calculated equilibrium bond distances listed in Table 7, show that the perfect pairing model gives a molecular energy (-99.5456 a.u.) which is 6.27 kcal./mole lower than that from the molecular orbital model (-99.5356 a.u.) for a minimum basis set of Slater-type orbitals with energy-optimized exponents. Using the Lowdin approx-

imation for the two-centre exchange integrals in the way described above, the perfect pairing wave function gives a molecular energy (-99.5410 a.u.) 9.22 kcal./mole lower than the molecular orbital calculation (-99.5263 a.u.), and this perfect pairing energy is 2.88 kcal./mole higher than that obtained when all integrals are evaluated exactly. Using free atom exponents[77] and evaluating all integrals exactly, the molecular energy for HF for the perfect pairing wave function (-99.5088 a.u.) is 3.20 kcal./mole lower than that for the molecular orbital wave function (-99. 5021 a.u.) but it is 23.07 kcal./mole above that obtained with energy-optimized exponents. Similarly, the energy for HF calculated with the molecular orbital model is 21.00 kcal./mole higher when free atom exponents are used instead of molecule-optimized exponents. Thus for the three different sets of calculations in Table 7, the perfect pairing model yields lower energies than the corresponding molecular orbital calculations, and the use of free atom exponents gives energies more than 20 kcal./mole higher than the energies obtained with molecule-optimized exponents. As expected, results in Table 5 show similar trends for calculations on HF with the bond length fixed at the experimental value (1.733 a.u.).

Previously, Ransil[57] has used a minimum basis set of Slater-type orbitals for a molecular orbital calcula-

tion on HF at the experimental bond distance and reported an energy of -99.4785 a.u. using orbital exponents obtained from Slater's rules (H1s=1.00, F1s=8.70, F2s=2.60, F2p=2.60). An energy 0.0006 a.u. (0.38 kcal./mole) higher than Ransil's energy was obtained with the computer programme used in this study for the same values of bond length and orbital exponents. This difference is attributed to the use in this work of the pure 1s atomic orbital at F in the molecular orbital wave function in equation (39). By the variation principle this constraint must raise the energy compared with the case when all atomic orbitals of the same symmetry type are freely mixed to form the molecular orbitals.

When the same values are given separately to the F2s and the F2pσ exponents in the hybrids d_1 and d_2, the perfect pairing wave function in equation (34) corresponds to a free mixing of the configurations $(F2s)^2(H1s)^1(F2p\sigma)^1$, $(F2s)^2(F2p\sigma)^2$, and $(F2p\sigma)^2(H1s)^1(F2s)^1$, (omitting the common core $(F1s)^2(F2p\pi_1)^2(F2p\pi_1)^2$). Previously, Silk and Murrell,[59] using a minimum basis set of Slater-type orbitals, mixed these three configurations in combination with three more configurations corresponding to H^-F^+. Silk and Murrell gave the same exponent values for the F2pσ and F2pπ orbitals and calculated an equilibrium bond length of 1.86 a.u. in only

fair agreement with the experimental value (1.733 a.u.). Molecular energies for the perfect pairing wave function in equation (34) can not be compared directly with Silk and Murrell's because they mixed more configurations, but at 1.4 a.u. where they find the H^-F^+ configurations to contribute only slightly, the programmes used in this work give a molecular energy (-99.4725 a.u.) 1.25 kcal./mole higher than their published value (-99.4745 a.u.), using their exponents.

As for HF, calculations on $HF^+{}_{^1\Sigma}$ using optimized orbital exponents give lower molecular energies for the perfect pairing wave function than for the molecular orbital model. When exponents are optimized for exact calculation of all molecular integrals, the perfect pairing energy is 8.91 kcal./mole lower than the molecular orbital energy. As noted above, the use of the Lowdin approximation yields exponents in close agreement with those from the exact calculation, and the increase in energy in using Lowdin exponents is only 0.07 kcal./mole. A very great difference occurs when free atom exponents are used; in the perfect pairing model the molecular energy is then 373 kcal./mole above the value obtained with molecule-optimized exponents and the corresponding value for the molecular orbital model is 363 kcal./mole. This large difference between energies obtained using free atom exponents and those obtained

with optimized exponents, emphasizes that electronic relaxation must be included in calculations of E.S.C.A. energies. As noted in the section on orbital exponents, however, this study does indicate that it may be possible to use Slater's rules[63] or something similar[77] for estimating exponents when the positive ion is formed by the removal of a core electron.

The comparison of perfect pairing and molecular orbital energies for $HF^{+}{}_{^2\pi}$ is similar to that reported above for HF and $HF^{+}{}_{^2\Sigma}$, and the details are to be found in Table 11. The interest in the energy of $HF^{+}{}_{^2\pi}$ in this work is mainly in relation to calculating the first ionization potential of HF with a minimum basis set of Slater-type orbitals.

The energies are presented in Table 5 for the ionizing of an F1s electron (1σ) or an F2pπ elèctron (1π) as calculated assuming no reorganization of the remaining electrons (this is usually referred to as Koopman' Theorem[83]). A value of 13.32 e.V. is calculated for the 1π ionization potential with free atom exponents, and a bond length of 1.733 a.u., and this is to be compared with the experimental value[84] of 16.06 e.V. by photoelectron spectroscopy. Using Koopmans' Theorem and exponents given by Slater's rules, Pople and Beveridge[38] report a value of 12.65 e.V. with the molecular orbital theory, and with Slater-type orbitals optimized for HF

(Table 5) calculated values of 12.66 and 12.39 e.V. are obtained for the molecular orbital and perfect pairing models respectively. In principle, an improved calculation of the vertical ionization potential is made by taking the differences between the molecular energies of HF and $HF^{+}_{2\pi}$ for the H-F bond length, but surprisingly the first ionization potential calculated this way has a value in less good agreement for both the perfect pairing and the molecular orbital model using either optimized or free atom exponents , than the value obtained with Koopmans' Theorem. Thus at the experimental bond length (1.733 a.u.) energy differences between Tables 5 and 11 give a value of 10.90 e.V. from the molecular orbital method using free atom exponents. The reasons for the less good agreement in taking the differences between the state energies is not clear, although presumably it is related in part to the restricted form of the basis set.

As noted already, the differences between using free atom exponents and molecule-optimized exponents are much larger for calculating the energy of ionizing an F1s electron. Using Koopmans' Theorem, this ionization potential is calculated to be 714.12 e.V. when using free atom exponents and the molecular orbital method. This value can be compared with the values of 706.26 e.V. and 691.57 e.V. obtained respectively with free atom

exponents and molecule-optimized exponents when differences in the molecular orbital energies for HF and $HF^{+}{}_{2\Sigma}$ in Tables 5 and 9 are taken. Unfortunately, these numbers can not be compared with experiment since HF does not seem to have been studied by E.S.C.A. yet.

Bond Lengths and Force Constants

Equilibrium bond lengths have been calculated using the perfect pairing and molecular orbital wave functions for various sets of orbital exponents, and the method for obtaining the equilibrium distance has been described on page 41. The results in Table 7 show that the molecular orbital method using molecule-optimized exponents gives an equilibrium bond distance of 1.75 a.u. which is only 0.02 a.u. (0.01 Å) longer than the experimental value of 1.733 a.u.[53] The perfect pairing method gives a calculated value of 1.77 a.u.. Using exponent values obtained with the Lowdin approximation, the calculated equilibrium bond lengths are within 0.02 a.u. (0.01 Å) of the best calculated values, and therefore are in reasonable agreement with experiment. It is significant that the calculations with free atom exponents give bond lengths in poor agreement with experi-

mental values. Thus using free atom exponents,[77] the perfect pairing model predicts an equilibrium bond length 0.20 a.u. greater than that obtained using optimized exponents. Likewise, the molecular orbital calculation gives a bond distance 0.18 a.u. larger with free atom exponents than that obtained with molecule-optimized exponents. Thus for these calculations, the error in calculated bond lengths using free atom exponents is an order of magnitude greater than the error introduced using exponent values optimized with Lowdin's approximation.

As discussed above, and shown in Table 11, the optimum orbital exponent values for $HF^{+}_{2\pi}$ calculated with and without Lowdin's approximation are very nearly equal. Therefore it seems reasonable to calculate the equilibrium bond length of $HF^{+}_{2\pi}$ by using the Lowdin approximation for optimizing exponents at different bond distances. The calculated equilibrium value of 1.84 a.u. is close to the value (1.85 a.u.) calculated recently by Richards and Raftery,[62] although appreciably lower than the value of 1.96 a.u. quoted by Pople[60] using a basis set of Gaussian functions derived from atomic wave functions. No experimental value for the equilibrium distance in $HF^{+}_{2\pi}$ is presently available. The Lowdin approximation has also been used for a preliminary calculation on the equilibrium distance in HO

for which the experimental value is 1.83 a.u.[53] in the $^2\Pi$ state. Using the Lowdin approximation, the optimized exponent values at 1.83 a.u. are H1s=1.28, O1s=7.66, O2s=2.24, O2pσ=2.27, and O2pπ=2.18 and with these exponents the calculated equilibrium distance is 1.91 a.u., 0.08 a.u. longer than the experimental value. As there is less charge transfer from H in HO compared with $HF^+_{2\Pi}$ the Lowdin approximation may be less reliable for HO. It is possible, therefore, that a calculation with all integrals evaluated exactly would give an improved value for the equilibrium bond distance in HO.

Like bond lengths, values of force constants are often used to give information about the nature of the bonding. The calculation of a force constant depends on calculating molecular energies as a function of the displacement from equilibrium, and in the harmonic approximation,[29] the stretching force constant (k) for a diatomic molecule is obtained from

$$E = \frac{k}{2} (r - r_e)^2 \qquad (59)$$

where E is the molecular energy calculated at a bond length r, and r_e is the calculated equilibrium bond distance. The force constant, therefore, is readily determined from a plot of E versus $(r-r_e)^2$. Using molecule-optimized exponents, HF stretching force constants equal to 8.3×10^5 dynes/cm and 8.5×10^5

dynes/cm are obtained from the perfect pairing and molecular orbital models respectively, and these values are to be compared with an experimental value of 9.66 x 10^5 dynes/cm.[60] The correspondence to the experimental value is less good by about 1 x 10^5 dynes/cm when free atom exponents are used to calculate the force constant.

Electron Distributions

The calculated charge distributions in the molecules of interest in this work are determined by the values of the variation parameters α, γ, δ and ζ in equations (31),(35),(40), and (41). Experimentally, information relating to charge distributions is obtained by measurements of dipole moments and of the higher moments,[85,86] and these moments may be calculated from molecular wave functions. Thus, for a molecule, the dipole moment, which is a vector quantity, is given by

$$\underset{\sim}{\mu} = -e \langle \Psi | \underset{\sim}{r} | \Psi \rangle \qquad (60)$$

for a state function Ψ; $\underset{\sim}{r}$ is a sum of the electron position vectors. For diatomic hydrides with cylindrical symmetry about the internuclear axis, the dipole moment is directed along this axis with magnitude

$$\mu = -e\langle \psi_e | z | \psi_e \rangle + \sum_i e z_i r_i \,, \tag{61}$$

where ψ_e is the electronic wave function, z is the sum of components along the internuclear axis of electron positions, r_i and Z_i are respectively the position and charge of the i^{th} nucleus.

Another convenient measure of electron distributions which is used frequently for molecular wave functions expressed as a basis of atomic orbital functions is provided by the population analysis due to Mulliken.[87] In the molecular orbital model, when the i^{th} molecular orbital is expressed as

$$\psi_i = \sum_u c_{iu}\, \phi_u \,, \tag{62}$$

the total electron population of ϕ_u in the linear combination of atomic orbitals - molecular orbital method, is given by

$$P_u^{mo} = \sum_i n_i \left\{ c_{iu}^2 + \sum_{u \neq v} c_{iu}\, c_{iv}\, S_{uv} \right\} \,, \tag{63}$$

where

$$S_{uv} = \langle \phi_u | \phi_v \rangle \,. \tag{64}$$

The summation over i is over all occupied molecular orbitals ψ_i and n_i is the occupation number. Implicit in equation (63) is that the overlap charge distribution has been partitioned equally between the two centres

involved. An equivalent population analysis for valence bond wave functions is obtained according to the following procedure:[88]

$$\Psi_{vb} = \sum_i c_i \Psi_i \quad , \tag{65}$$

where the zer-order wave function Ψ_i corresponds to a configuration with occupancy n (i) for the atomic orbital ϕ_u. Then the total electron population in ϕ_u in the valence bond method is given by

$$P_u^{vb} = \sum_i n_u(i) \left\{ c_i^2 + \sum_{j \neq i} c_i c_j S_{ij} \right\} , \tag{66}$$

where

$$S_{ij} = \langle \Psi_i | \Psi_j \rangle . \tag{67}$$

Some of the variation parameters in equations (35) and (40) provide measures of electron distributions. Thus for the perfect pairing model an increase in $\sin\gamma$ indicates an increase in the charge at H; $\sin\gamma$ equal to 1.00 implying no charge transfer while $\sin\gamma$ equal to 0.0 corresponds to transfer of one electron from H. Similarly in the molecular orbital model $\sin\delta$ is a measure of the charge at H in the bonding molecular orbital. Quantitatively, as the values of either $\sin\gamma$ or $\sin\delta$ decrease, one may expect the His orbital population to decrease and correspondingly the dipole moment to increase. In both the molecular orbital and perfect pair-

ing models, as used in this work, sin α is a measure of the sp hybridization at F. As sin α increases, the hybrid designated d_1 has more F2s character, and correspondingly the hybrid designated d_2 has less F2s character. The trends in these various measures of electron distribution will now be examined for the different molecular wave functions.

Looking first at the results in Tables 7 and 8 for the calculated HF equilibrium distances, the agreement to 0.01 in the values of sin γ or sin δ using the exactly-optimized and the Lowdin-optimized exponents is reflected in the H1s populations being similar for either set of exponents. The H1s populations are, however, slightly higher for the molecular orbital model (0.78) than for the perfect pairing model (0.69); and this is consistent with the calculated dipole moment being higher for the perfect pairing calculation (1.72 D.) than for the molecular orbital model (1.41 D.). The experimentally-measured dipole moment of HF is 1.82 D..[89] With free atom exponents, the charge redistribution on formation of HF is calculated to be less, and this is reflected in the lower calculated values of the dipole moment, being 1.31 D. and 0.89 D. for the perfect pairing and molecular orbital calculations respectively. Similar trends in results are found for the calculations at experimental distance of 1.733 a.u..

The values of sin α in Tables 6 and 8 indicate that the perfect pairing model is consistent with somewhat less sp hybridization than the molecular orbital method, and although it is well known that the concept of hybridization is not necessary in the molecular orbital theory,[12] results of comparing values of sin α are consistent with the Mulliken populations on the F2s orbital being 0.05 greater in the perfect pairing calculation than in the molecular orbital calculation. Nevertheless, the hybridization at F in HF is small in both models, as expected from the average 2s to 2p promotion energy, which from atomic spectral data is estimated to be 20.8 e.V.[12] The results obtained are consistent with the bonding hybrid d_1 being essentially F2pσ, and therefore, the non-bonding hybrid designated d_2 being mainly F2s in character.

Even though the sp hybridization at F seems to be small, the hybrids have been looked at in a different way for the purpose of molecular calculations. This extension involved assigning one orbital exponent to d_1 and a different exponent to d_2 without regard to the basis Slater-type orbitals; that is the Slater exponents are selected such that

$$\alpha_{2s} = \alpha_{2p} \tag{68}$$

and

$$\alpha_{2s'} = \alpha_{2p'}, \tag{69}$$

with

$$\alpha_{2s} \neq \alpha_{2s'}. \tag{70}$$

With these basis functions, the energy was completely minimized for the perfect pairing wave function. The optimized exponents were found to be H1s=1.35, F1s=8.65, F2pπ=2.49, d_1=2.62 and d_2=2.55. The optimum exponents for d_1 and d_2 are within 0.02 of the optimum values of F2pσ and F2s in Table 7, however, this approach results in a perfect pairing energy of -99.5459 a.u. which is 0.19 kcal./mole lower than the previous best perfect pairing energy, and a calculated equilibrium H-F distance of 1.75 a.u. which is 0.02a.u. better than the perfect pairing calculation using the more conventional basis of atomic orbitals. Assigning exponents to hybrids rather than natural atomic orbitals might be expected to give greater improvements in the calculations of properties of molecules in which the hybridization of atomic orbitals is suggested to occur to a greater extent than at F in HF.

An interesting observation from all the results is that with the single exception of the molecular orbital calculation for $HF^+_{2\pi}$ atomic orbital hybridiza-

tion at F is less when free atom exponents are used instead of molecule-optimized exponents. This suggests that one should perhaps be cautious in deducing conclusions regarding possibilities of hybridization purely from considerations related to data for free atoms, although it may be noted that in the limit of complete transfer of electronic charge from H to F, the hybridization picture becomes irrelevant. It is not too clear at present, but the fact that the molecular orbital calculation of $HF^{+}{}_{2\pi}$ is out of line may be related to this consideration. Another odd feature of this calculation is that the Mulliken population for F2s is indicated to be greater than 2. This result is associated with the equal partitioning of overlap charge between the two centres in the Mulliken analysis. This is not realistic and is well known to yield negative populations in some cases.[90]

The results in Tables 10 and 12 show that large modifications occur in the calculated electron distributions for $HF^{+}{}_{2\Sigma}$ and $HF^{+}{}_{2\pi}$ when free atom exponents are used instead of molecule-optimized exponents. However, when the Lowdin approximation is used for determining orbital exponents for these molecular species, the Mulliken populations and dipole moments are in close agreement with those from the exact calculations. As expected, the charge transfer from H to F increases in

the series HF, $HF^{+}_{^2\pi}$, $HF^{+}_{^2\Sigma}$, and this is reflected in the values for the Mulliken populations and the calculated dipole moments. Also, as noted above, the H1s exponent tends to increase with this charge transfer.

A further comparison with $HF^{+}_{^2\pi}$ is provided by a preliminary calculation on $HO_{^2\pi}$ with the perfect pairing model and utilizing the Lowdin approximation. In this case it turns out that $\sin\gamma$ is close to unity and, correspondingly, the H1s electron population is 0.86. This is to be expected because of the much lower electronegativity of O compared with F in the species being considered. The smaller charge transfer compared with F results in a lower dipole moment; our calculated value of 1.16 D. is to be compared with the experimental value of 1.66 D.[91] for HO.

Concluding Remarks

The interest in finding useful methods for deriving wave functions with applications to complex molecules stems from many considerations, but without doubt there is currently much interest in developing quantum chemical methods with applications to molecular systems as diverse as those of biological interest[93] and those present in structures of the solid state.[92] Inevitably, methods

with application to complex systems must first be tested on simpler molecules. On the whole, the molecular orbital method has proved most useful in applications to complex systems so far,[38,39] but recent advances in computational techniques have indicated the feasibility of making valence bond calculations on a more routine basis to polyatomic molecules,[8,45] and it has been known for some time that calculations in the perfect pairing model can be formulated readily with comparatively simple expressions for molecular energies.[9,69] Probably in the future, wave functions for complex molecules will be written so as to represent some hybrid of the molecular orbital and perfect pairing schemes, such as is built into many conventional bonding models (eg. the localized and delocalized components of the electronic structure of benzene). In part, this thesis has been directed at comparing the molecular orbital and perfect pairing models for some simple diatomic hydrides, and this represents an extension of the recent work by Mitchell and Thirunamachandran on BeH_2.[46] We can conclude that for minimum basis set calculations, both the perfect pairing and molecular orbital models provide reasonable accounts of a number of basic properties of HF, $HF^+ {}^2\Sigma$ and $HF^+ {}^2\Pi$. More specifically, calculations of molecular energies using wave functions in the perfect pairing framework are between 6 and 10 kcal/mole lower than those from

corresponding calculations using molecular orbital wave functions. Equilibrium bond lengths calculated with both the perfect pairing and molecular orbital models are within 0.04 a.u. (0.02 Å) of the experimental value for HF; where comparison with experimental data is possible dipole moments seem to be better predicted with the perfect pairing model, although, force constants and ionization potentials are calculated with similar reliabilities with the perfect pairing and molecular orbital methods. To some extent this contrasts with the situation for BeH_2, where the perfect pairing model seems to be preferable to the molecular orbital model; in part this contrast can be associated with the greater electronegativity difference between H and F; thus in the limit of H^+F^- both the perfect pairing and the molecular orbital models would merge with the ionic model.

The comparisons made here between calculations with free atom exponents and those with molecule-optimized exponents show that free atom exponent values can not in general be considered appropriate for calculations which attempt to evaluate properties such as bond lengths and dipole moments. Often semi-empirical methods[38] give the same exponent values to the different 2p orbitals, which, in a molecular environment, are often inequivalent. This restriction is made in part for simplicity

and in part to maintain rotational invariance.[94] Nevertheless, it should be noted that this constraint does introduce error compared with the situation where the symmetrically different 2p orbitals have different exponents. It may be noted that in this work, the perfect pairing calculations for HF gave much better calculations of the H-F equilibrium distance than that reported by Silk and Murrell,[59] even though these workers used a larger set of basis configurations for their valence bond wave functions. The difference in bond length seems to be due to the allowance in this work of different $2p\sigma$ and $2p\pi$ exponents, whereas Silk and Murrell constrained theirs to have a single value. For this basis set with Slater-type orbitals it seems therefore that the choice of orbital exponents is quite crucial for estimating molecular properties. Further studies of the changes in exponents from free atom values are necessary to enable reasonable predictions of suitable exponents for larger molecules.

The determination of molecule-optimized exponent values by means of exact calculations does, however, become very expensive for large molecules, and for this reason it is important that there are approximate schemes available for limiting the computational effort. One way is to approximate the molecular integrals by drastically limiting the number that need to be calculated

exactly. This study has shown that an approximation proposed by Lowdin,[56] when applied to calculating some two-centre electron-repulsion exchange integrals, predicts optimum exponent values which are close (0.04 for all cases considered here) to the values obtained from calculations in which all integrals are evaluated exactly. The approximation as used here does make a substantial saving in computational expense for the diatomic hydrides considered in this thesis, but to be really useful for more complex molecules it would be necessary for the Lowdin approximation to be made for all overlap charge distributions occurring in electron-repulsion integrals. Nevertheless, the results obtained here encourage the belief that the use of the Lowdin approximation should be considered further for estimating suitable exponent values prior to a calculation where all molecular integrals are evaluated exactly.

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