THEORETICAL INVESTIGATION OF THE BOND-BOND INTERACTION FORCE CONSTANT IN XF_2 MOLECULES

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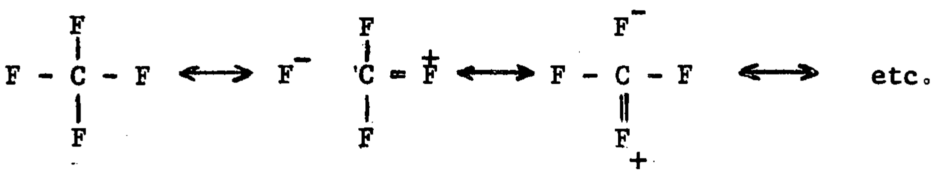
CHAPTER I

INTRODUCTION

The chemistry of fluorine atoms and ions and of molecules containing fluorine has been the object of extensive investigation by chemists for many years. Much of this interest stems from the fact that fluorine combines chemically with other elements in much the same way as hydrogen although the two atoms have greatly different atomic properties. Since fluorine can be directly substituted in many molecules for hydrogen a direct comparison between fluorine substituted and hydrogen substituted compounds can be made to determine the effect on bonding of certain characteristics of the fluorine atom which the hydrogen atom does not exhibit. For instance a comparison of the properties of OF_2 and OH_2 might shed considerable light on the interaction between nonbonded atoms and its relationship to the individual properties of the fluorine and hydrogen atoms. The differences in chemical bonding which might occur because fluorine can contribute to molecular orbitals with several 2p atomic orbitals while hydrogen has essentially only a 1s orbital available for bonding can be investigated. A major purpose of this research project was to investigate in a theoretical manner some of the proposed explanations for the various differences in chemical and physical properties of analogous fluorine and hydrogen compounds. Two major explanations are analyzed in this thesis; the double bond-no bond resonance theory first proposed by Brockway[1] and the interaction between non-bonded atoms which has been of particular interest to molecular spectroscopists.

Brockway[1] first proposed double bond-no bond (DBNB) resonance in 1937 as an explanation of the fact that carbon-fluorine bond distances in fluoromethanes were significantly shorter in compounds containing several fluorine atoms than in the monofluoride molecule. This resonance has been represented by the following structures for CF_4,



$$\begin{array}{c}\mathrm{F}\\|\\\mathrm{F-C-F}\\|\\\mathrm{F}\end{array} \longleftrightarrow \begin{array}{c}\mathrm{F}\\|\\\mathrm{F^{-}\;\;C=\overset{+}{F}}\\|\\\mathrm{F}\end{array} \longleftrightarrow \begin{array}{c}\mathrm{F^{-}}\\ \\\mathrm{F-C-F}\\\|\\\mathrm{F^{+}}\end{array} \longleftrightarrow \text{etc.}$$

If such DBNB resonance structures are of sufficiently low energy, they should stabilize the molecule. This stability would be reflected in stronger and hence shorter C-F bonds. In fluoromethanes containing more than one fluorine atom the C-F bonds would then be shorter than in the methyl fluoride molecule which cannot exhibit such resonance.

This shortening of the C-F bond can be explained by postulating residual attractive forces between the non-bonded fluorines[2]. The assumption of a destabilizing interaction with residual repulsive forces between the non-bonded atoms cannot account for such bond shortenings, although these residual repulsive forces cannot be ruled out for the following reason. When the non-bonded interaction is energetically stabilizing the residual forces between the atoms may be attractive or repulsive. An energetically stabilizing interaction would tend to shorten the C-F bond regardless of the type of residual forces existing between the non-bonded atoms. Many spectroscopists accept the viewpoint that the non-bonded interaction is energetically destabilizing[3]. In the next several paragraphs other chemical phenomena which may be explained by postulating either DBNB resonance or stabilizing non-bonded interactions are presented.

In the disproportionation

$$2CH_3F \longrightarrow CH_4 + CH_2F_2 \qquad \Delta H = -5.2 \text{ kcal.}$$

methane and methylene fluoride are favored over methyl fluoride[4]. DBNB resonance could occur in CH_2F_2 but not in CH_3F. From force constant calculations one deduces that the F···F non-bonded interaction is much larger than the interactions between hydrogen and fluorine or between two hydrogens[3]. Therefore the existence of either significant multiple bonding or of stabilizing non-bonded interactions would tend to drive the reaction to the right.

In both the structural and thermodynamic phenomena mentioned above, the effects are much less striking when other halogens are substituted for fluorine. The non-bonded interaction force constant between two chlorines is calculated to be less than between two fluorines[3]. If this interaction is stabilizing one would not expect methane and methylene chloride to be as heavily favored over methyl chloride as the corresponding fluoride compounds.[4]

The relative significance of DBNB resonance in fluoromethanes compared with other halomethanes is demonstrated by the greater ability of fluorine, compared with the heavier halogens, to donate a pair of electrons to the carbon atoms of aromatic rings. A relative measure of this donating ability is given by the numerical values of the substituent constant, σ, in the Hammett equation[5]. The substituent constant is a measure of the electron donating or electron withdrawing power of a substituent on an aromatic ring, a σ value greater than zero indicating the former. A substituent on a benzene ring will produce different electronic effects at the meta and para positions. As a result σ values vary depending on the position of interest in the aromatic ring. The substituent effect at the meta and para positions are denoted by σ_m and σ_p, respectively. The quantity of $\sigma_p - \sigma_m$ has been suggested as a measure of the ability of a substituent to add (or withdraw) electrons to a π system by a resonance phenomenon. This suggestion is approximately correct since inductive effects (such as the electronegativity of the substituent) perturb the meta and para positions to approximately the same extent whereas resonance effects essentially show up at the ortho or para position. Values of $\sigma_p - \sigma_m$ for fluorine, chlorine, bromine, and iodine are 0.275, 0.146, 0.159 and 0.076, respectively.[5]

The vibrational frequencies of OF_2, NF_2, CF_2, OCl_2 and OH_2 are listed in Table I. In a large number of nonlinear symmetric triatomic

TABLE I

VIBRATIONAL FREQUENCIES OF SOME NON-LINEAR SYMMETRIC TRIATOMIC MOLECULES

Frequency*	OF_2[6]	NF_2[7]	CF_2[8]	OCl_2[9]	OH_2[10]
ν_1 (sym. str.)	929	1069.6	1222	630.7	3651.7
ν_2 (sym. bend.)	461	573.4	668	296.4	1595.0
ν_3 (antisym. str.)	828	930.7	1102	670.8	3755.8

*All frequencies are given in cm^{-1}.

molecules, ν_3, the antisymmetric stretching frequency is larger than ν_1, the symmetric stretching frequency. This behavior is illustrated by OCl_2 and OH_2. But, in the carbon, nitrogen and oxygen difluorides ν_1 is larger than ν_3. Significant multiple bonding and/or stabilizing non-bonded interaction between the fluorines would tend to produce this frequency inversion shown by these molecules. Figure 1 shows a DBNB resonance structure for XF_2 and a schematic diagram of its symmetric and antisymmetric stretching modes. As one X-F bond is compressed, multiple bonding should become increasingly important for that bond. If DBNB resonance structures contribute significantly to the resonance hybrid, they would facilitate motion in the antisymmetric stretching mode, thus lowering ν_3. ν_1 would be relatively unaffected by such resonance structures but may possibly be increased by a small amount.

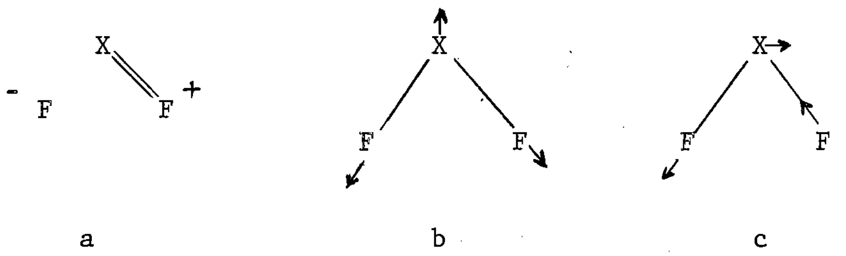
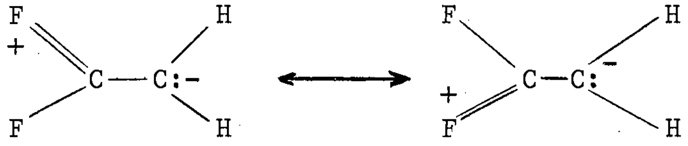


Figure 1. For the XF_2 Molecule a) a DBNB Resonance Structure, b) the Symmetric Stretching Mode, and c) the antisymmetric stretching mode.

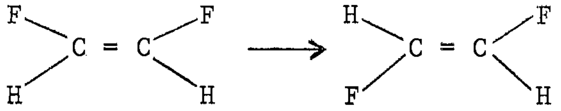
The non-bonded distance in XF_2 changes as the molecule vibrates in its symmetric stretching mode but this distance is almost constant as the molecule moves in its antisymmetric mode. The existence of a stabilizing non-bonded interaction between the fluorines would tend to increase ν_1 leaving ν_3 relatively unaffected.

Vinylidene fluoride has an F-C-F angle 12° smaller than its H-C-H angle.[11] This would not be expected on the basis of electrostatic repulsion between the non-bonded fluorines but is anticipated if this interaction is stabilizing. Pitzer[12] has suggested resonance structures of the type



for unsaturated hydrocarbons. If these structues were unimportant the carbon atomic orbitals which form bonds with the fluorines would be sp^2 hybrids. The above structures would introduce added p character into the C-F bonds at the expense of the C-C bond. Since the angle between sp^2 orbitals is larger than between sp^3 orbitals one would expect a smaller F-C-F angle in compounds in which the above structures are important. This same argument applies to the smaller F-C-F angle in CHF_3 compared to CH_2F_2.[13] In this case the C-F bond experiences an increase in p character at the expense of the C-H bond.

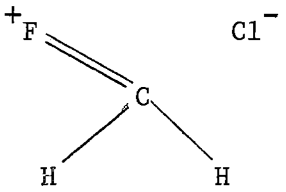
The cis to trans conversion of 1,2-difluoroethylene is not the



$\Delta H = 0.928$ kcal

thermodynamically favored reaction compared to the reverse process.[14] Such a result is unexpected on the basis of bond dipole-dipole repulsions. Stabilizing non-bonded interactions in these molecules would favor the cis form. Resonance structures similar to those drawn for vinylidine fluoride[12] have been used to explain the greater stability of the cis form compared with the trans form of difluoroethylene.

Lucken[15] has measured ^{35}Cl nuclear quadrupole resonance frequencies of various chloromethanes. For those molecules for which structures such as



might be drawn the NQR frequencies of ^{35}Cl are considerably lower than in compounds where structures of this type cannot be drawn. Such lowering in this frequency is expected as the ionicity of the C–Cl bond is increased.

Lucken[15] has performed an approximate Huckel molecular orbital calculation on the model illustrated in Figure 2 where X might be a

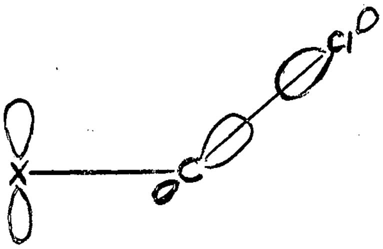
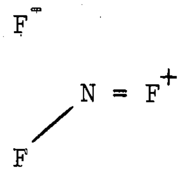


Figure 2. An Atomic Orbital Diagram for Lucken's Calculation.

fluorine atom. Double bonding is provided for by combining ψ_X with an antibonding orbital of the carbon-chlorine bond. His calculation can account for the shortening of the C–F bond length in the fluoromethane series and the anomalously low quadrupole resonance frequencies of chlorine in molecules where multiple bonding might take place. His calculation is very sensitive to the choice made for the electronegativity of X and the values chosen for the resonance integrals derived in the calculation. A less arbitrary molecular orbital approach would be desired to further test the significance of multiple bonding in these molecules.

Kaufman[16] has explained why the N-F bond energy observed in NF_2 is larger than this same quantity observed in NF_3. First the geometry of NF_2 is more favorable for multiple bonding than the geometry of NF_3. In NF_2 the p orbitals available for π-bonding are perpendicular to the plane containing the NF_2 molecule. NF_3 has a pyramidal structure similar to ammonia. The most favored geometry for a DBNB resonance structure of NF_3



would be a planar structure where the 2p orbitals on nitrogen and fluorine, perpendicular to the plane, could come into maximum coincidence. Since more significant energetic factors favor the pyramidal structure this geometry would not be favorable for multiple bonding in NF_3. Secondly, multiple bonding in NF_2 may occur through use of a half-filled atomic orbital on nitrogen whereas NF_3 has only a fully occupied nitrogen non-bonded atomic orbital.

In summary, many experimental phenomena hint at the existence of multiple bonding and/or stabilizing non-bonded interactions in XF_2 and other fluorine containing molecules. No extensive molecular orbital calculation has been accomplished to support either theory although the

Huckel calculation by Lucken indicates multiple bonding could be important in these molecules. Kaufman's explanation, using a half-filled orbital on nitrogen to explain bonding differences in NF_2 and NF_3 would not explain the frequency inversion found in OF_2 since this oxygen contains only filled non-bonded atomic orbitals. It appears that more extensive molecular orbital calculations would be useful in establishing the significance of DBNB resonance or multiple bonding in fluorine compounds. These calculations have been performed on OF_2. The techniques are explained and the results are discussed later in the thesis. Force constant calculations have been performed which point out the relationship between vibronic coupling of the double bond-no bond type and non-bonded interactions which may exist in these molecules. The techniques and results of these calculations are given in the next chapter.

CHAPTER II

THE VIBRATIONAL PROBLEM

XF_2 molecules have three vibrational degrees of freedom. Associated with each of these degrees of freedom is a fundamental frequency and a normal coordinate. Displacement of the nuclei of a molecule from their equilibrium position according to one of its normal coordinates will lead to simple motion in which all the nuclei move in phase with the same frequency. Such vibrations are called normal vibrations. The apparently random vibration of an actual molecule may be described as a sum of normal vibrations each with its own frequency and phase factor. The normal vibrations of a symmetric nonlinear triatomic molecule are illustrated in Figure 3.

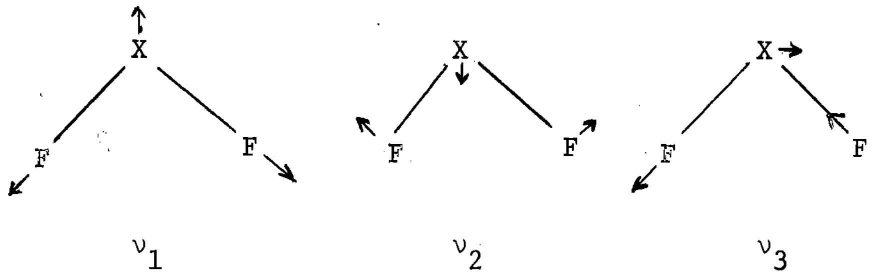


Figure 3. Schematic Diagrams Representing the Symmetric Stretching Mode With Frequency ν_1, the Symmetric Bending Mode of Frequency ν_2, and the Antisymmetric Stretching Mode of Frequency ν_3.

In general, normal coordinates may be defined quantitatively by the following relationship,

$$Q_k = \sum_{i=1}^{3N} l_{ki} q_i \qquad k = 1,2 \cdots 3N \tag{1}$$

where Q_k denotes the normal coordinates of the molecule, N represents the number of atoms in the molecule and the q_i are the 3N mass-weighted cartesian displacement coordinates defined by the set of equations

$$q_i = m_j \Delta X_i . \qquad \begin{matrix} j = 1,2 \cdots N \\ i = 1,2, \cdots 3N \end{matrix} \tag{2}$$

The mass of the j^{th} atom is given by m_j and ΔX_i is one of the three cartesian displacement coordinates of the j^{th} atom. The coefficients, l_{ki} in (1), are chosen so that in terms of the normal coordinates, Q_k, the kinetic energy, T, and the potential energy, V, of the nuclei have the form

$$2T = \sum_{k=1}^{3N} \dot{Q}_k^2 \quad \text{and} \quad 2V = \sum_{k=1}^{3N} \lambda_k Q_k^2 \tag{3}$$

where $\dot{Q}_k$ is the time derivative of Q_k and the λ_k are related to the vibrational frequencies, ν_k, of the normal modes by

$$\lambda_k = 4\pi^2 \nu_k^2 . \tag{4}$$

For a nonlinear molecule six of the normal modes correspond to translational and rotational modes of zero frequency. The remaining 3N-6 modes are vibrational modes corresponding to the 3N-6 fundamental frequencies.

Potential Energy Functions

Although it is convenient to express the potential energy of the nuclei in normal coordinates it is physically more meaningful to express this quantity in terms of internal coordinates (coordinates describing the internal configuration of the molecule without specifying translational or rotational coordinates). The potential energy may be expanded in a Taylor series about the minimum where V_o is the potential

$$2V = 2V_o + 2\Sigma\left(\frac{\partial V}{\partial R_t}\right)_{V_o} R_t + \Sigma\Sigma\left(\frac{\partial^2 V}{\partial R_t \partial R_{t'}}\right) R_t R_{t'} + \cdots \qquad (5)$$

energy of the molecule at equilibrium and R_t represents one of the 3N-6 internal coordinates. If the internal coordinates are independent and the harmonic oscillator approximation is invoked (5) becomes

$$2V = \Sigma\Sigma\left(\frac{\partial^2 V}{\partial R_t \partial R_{t'}}\right)_{V_o} R_t R_{t'} = \Sigma\Sigma f_{tt'} R_t R_{t'} \qquad (6)$$

where $f_{tt'}$ are the force constants for this potential energy function. For an XF_2 molecule the above equation may be written as

$$V = \frac{1}{2} f_r(\Delta r_1)^2 + \frac{1}{2} f_r(\Delta r_2)^2 + \frac{1}{2} f_\alpha(\Delta\alpha)^2 + f_{rr}(\Delta r_1 \Delta r_2) + f_{r\alpha}(\Delta r_1 \Delta\alpha) + f_{r\alpha}(\Delta r_2 \Delta\alpha) \qquad (7)$$

where Δr_1 and Δr_2 are displacement coordinates of the X-F bonds and $\Delta\alpha$ is a displacement coordinate of the F-X-F angle as illustrated in Figure 4. The force constant of the X-F bond is denoted by f_r, f_α

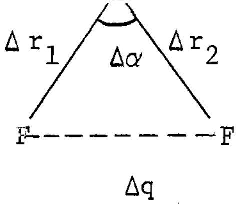


Figure 4. Internal Displacement Coordinates of XF_2

corresponds to the force constant of the F-X-F angle, and f_{rr} and $f_{r\alpha}$ are the bond-bond and the bond-angle interaction force constants, respectively. The force field corresponding to this potential energy expression is called the general valence force field (GVFF). Through these force constants, fundamental understanding of the nature of chemical bonding in the molecule may be attained. The technique involved in obtaining force constants from the frequency data will not be discussed here as it is described thoroughly in several references.[17,18] Equation (7) contains four unknown force constants for an XF_2 molecule but there are only three fundamental frequencies. In the absence of other supplementary data the problem is under-determined. As a result it is only possible to solve for three of the force constants in terms of a fourth one.

An approximate quadratic force field widely employed by chemists to reduce the number of unknowns is the Urey-Bradley force field (UBFF). The potential energy expression for this force field may be written as

$$2V = 2K'r(\Delta r_1 + \Delta r_2) + K(\Delta r_1^2 + \Delta r_2^2) + 2H'(\Delta\alpha) + H(\Delta\alpha)^2 + 2F'q(\Delta q) + F(\Delta q)^2 \quad (8)$$

where K', H' and F' are $(\partial V/\partial r_i)_{V_o}$, $(\partial V/\partial\alpha)_{V_o}$ and $(\partial V/\partial q)_{V_o}$ respectively and K, H, and F are $(\partial^2 V/\partial r_i^2)_{V_o}$, $(\partial^2 V/\partial\alpha^2)_{V_o}$ and $(\partial^2 V/\partial q^2)_{V_o}$ respectively and r and q are the X-F bond distance and the F···F non-bonded distance, respectively, as illustrated in Figure 4. Note that an extra internal displacement coordinate, Δq, denoting the displacement of the non-bonded fluorines, has been introduced and this set of internal coordinates is not independent. Therefore the $(\partial V/\partial R_t)_{V_o}$ in equation

(5) may not be set equal to zero as the potential energy in each coordinate is not necessarily at a minimum when the molecule is at its equilibrium geometry. Therefore K', H' and F' remain in equation (8) while such terms are absent in (7). Expressing Δq as a function of Δr_1, Δr_2 and Δq and substituting it in equation (8) allows one to relieve this dependency, and derive the following expression.

$$2V = (K + aF + bF')(\Delta r_1^2 + \Delta r_2^2) + (H + cF + dF')\Delta\alpha^2 + 2(eF + fF')\Delta r_1 \Delta r_2 + 2(gF + hF')(\Delta r_1 \Delta\alpha + \Delta r_2 \Delta\alpha) \qquad (9)$$

In this expression "a" through "h" are functions of the geometry of the molecule and have been tabulated by Overend and Scherer.[19] Equation (9) contains four unknowns, K, H, F and F', which must be evaluated from three fundamental frequencies, unless additional data is available. Before a solution of this problem can be obtained a relationship between two of these force constants must be found.

In determining this relationship it has been common to assume that the interaction between non-bonded atoms is essentially of the van der Waals' type,[20] the potential energy of which may be represented by a Lennard-Jones expression of the form

$$V = \frac{a}{q^{12}} - \frac{b}{q^6} . \qquad (10)$$

Figure 5 illustrates a rough plot of the potential energy of such an interaction against the non-bonded distance q. For the range of typical non-bonded distances found in most molecules, the potential energy is repulsive and the second term in equation (10) is negligible. With

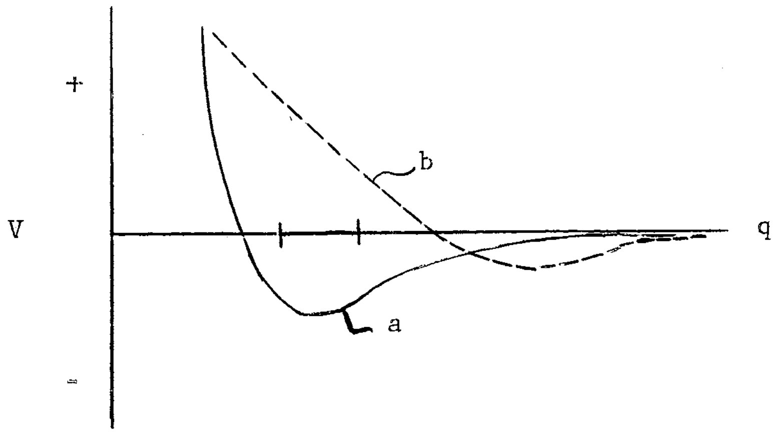


Figure 5. Curve a - Stabilizing Non-bonded Interaction.
Curve b - van der Waal's Interaction.
├──┤ Typical Non-bonded Distance Range in Molecules.

this assumption and the equations

$$F' = \frac{1}{q}\left(\frac{\partial V}{\partial q}\right)_{q_0} \quad \text{and} \quad F = \left(\frac{\partial^2 V}{\partial q^2}\right)_{q_0}$$

where q_0 is the equilibrium non-bonded distance of a "typical" molecule one arrives at an expression relating F and F', i.e., $F' = -0.1F$. Whether this practice is valid or not is subject to some question[2,21] but since F' is usually quite small it does not affect the calculation to a large degree. Therefore, the force constants K, H and F may be determined from the three fundamental frequencies of an XF_2 molecule.

Before presenting the results of the GVFF and UBFF calculations for these triatomic difluoride molecules, a brief discussion concerning the bond-bond interaction force constant, f_{rr}, will clarify its physical significance. When one bond of a molecule is distorted, the electronic structures of the other bonds are affected and their properties changed. Linnett and Hoare[22] have considered ten symmetrical triatomic molecules theoretically and have found the following relationships:

> If f_{rr} is positive, breaking one bond leaves the other bond stronger and shorter.
>
> If f_{rr} is negative, breaking one bond leaves the other bond weaker and longer.

Linnett and Hoare also state that if the two bonds concerned contain only localized electrons, the cross term, f_{rr}, tends to be negative while f_{rr} tends to be positive if the bonds contain delocalized electrons.

GVFF Calculations

Duchesne and Burnelle[23] have completed extensive force constant calculations on OF_2. They have obtained values for f_r, f_α and f_{rr} as a function of $f_{r\alpha}$. Their allowed solutions for f_{rr} as a function of $f_{r\alpha}$ are shown in Figure 6. For the negative values of f_{rr} shown in this figure f_r and f_α take on physically unreasonable values. They

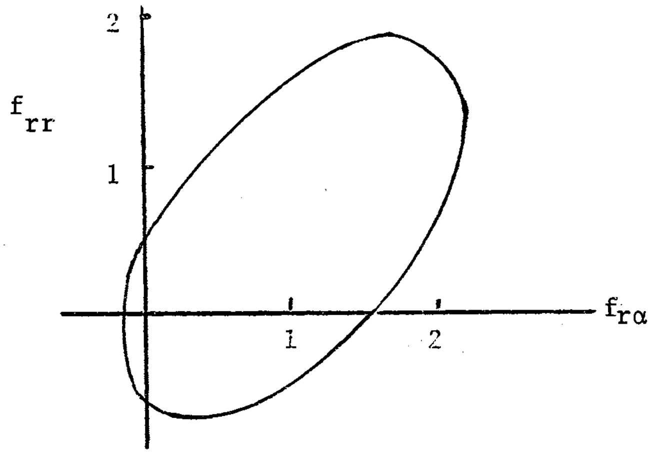


Figure 6. GVFF Calculations for OF_2, Allowed Solutions of f_{rr} as a Function of $f_{r\alpha}$.

concluded that f_{rr} for OF_2 is definitely positive. Less extensive force constant calculations have been completed in our laboratory and our results agree with those given above. Linnett and Hoare[22] have also stated that f_{rr} may measure effects other than the delocalization of electrons. Linnett and Heath[20] have explained that a large positive bond-bond interaction constant, f_{rr}, may be due to a non-bonded interaction. This fact was illustrated by the equation

$$f_r + f_{rr} = K + 2F \sin^2 \alpha/2 \quad . \qquad (11)$$

A large non-bonded force constant, F, tends to show up in the interaction constant, f_{rr}, and vice versa. This can be seen in the UBFF calculations on the XF_2 molecules presented in the next section.

UBFF Calculations on OF_2, NF_2, and CF_2

UBFF calculations on OF_2, NF_2 and CF_2 were performed in our laboratory. The potential energy expression (9) and the frequencies given in Table I were used to calculate K, H and F. These calculations were accomplished by means of a computer program described in several references.[17,19] The program was run on an IBM 7040 computer at Oklahoma State University. The results of the calculations are given in Table II. Two calculations were performed on OF_2, one assuming that F' is negligibly small, the other utilizing the assumption of a Lennard-Jones potential describing the non-bonded interaction. As expected, the two calculations are not significantly different even though the non-bonded interaction constant is quite large.

TABLE II

UREY-BRADLEY FORCE CONSTANTS OF OF_2, NF_2 AND CF_2

Force Constants	OF_2(F'=0)	NF_2(F'=0)	CF_2(F'=0)	OF_2(F'=-.1F)
K	3.15	3.60	4.42	3.37
H	-0.08	0.02	0.07	-0.32
F	3.14	4.51	6.01	2.81

Force Constants are in units of millidynes/angstrom.

Discussion of Results

A comparison of results between the two force field calculations illustrates the correspondence between the non-bonded force constant, F, and the bond-bond interaction constant, f_{rr}, as expressed in equation (11). The correspondence of a large non-bonded interaction constant as reflected in F and the large positive bond-bond interaction constant, f_{rr}, is clearly demonstrated. In the absence of other experimental data which might allow a calculation including both of these force constants in a potential energy function it would be very difficult to deduce which effect is producing large values for F and f_{rr}. This is not incongruous with the experimental results presented in Chapter I where either stabilizing non-bonded interactions or DBNB resonance could explain most of the data presented.

It appears as though the non-bonded force constants calculated for OF_2, NF_2 and CF_2 are measuring effects in addition to the non-bonded interaction, because their large values cannot be explained by assuming either a stabilizing or destabilizing non-bonded interaction. The X-F equilibrium bond distances in these molecules are between 1.3Å and 1.4Å which correspond to non-bonded distances in the range of 2.0Å to 2.2Å. It seems unreasonable to accept values of $F \geq K$ for these molecules in view of the distances listed above if the non-bonded interaction is stabilizing. Shimanouchi[24] lists values of non-bonded force constants between fluorines calculated for molecules using the UBFF potential energy function and compares these values with force constant values calculated assuming a destabilizing interaction and using a Lennard-Jones 6:12 potential such as is given in Equation (9a). Shimanouchi illustrates that relatively good agreement exists between the two sets of force constants for the molecules examined. However the non-bonded force constants for OF_2, NF_2 and CF_2 presented earlier in this chapter do not exhibit this agreement. For example, the F···F distances in OF_2 and CF_4 are approximately equal (2.14Å and 2.16Å) whereas the non-bonded force constant in OF_2 is about 2.5 times as large as this same force constant in CF_4 (F_{OF_2} = 3.14 ml/Å, F_{CF_4} = 1.24 ml/Å).[24] Hopefully, theoretical molecular orbital calculations treating non-bonded interactions and/or DBNB resonance might help clarify the situation to a large extent.

In this research project the significance of DBNB resonance has been studied by a configuration interaction calculation. A wave function of the form

$$\Psi = C_I\psi_I + C_{II}\psi_{II} + C_{III}\psi_{III} \tag{12}$$

was used to calculate the binding energy of OF_2. The wave function ψ_I describes a set of localized electrons in OF_2 while ψ_{II} and ψ_{III} describe a delocalization of electrons which would produce multiple bonding in this molecule. The variation of this binding energy as

OF_2 vibrates in its symmetric and its antisymmetric stretching modes was calculated. From these energy values and the size of the coefficients, C_{II} and C_{III}, in equation (12), deductions of the significance of multiple bonding can be made. The methods involved in the calculation and the results of this calculation are presented later in this thesis.

CHAPTER III

THE LCAO-MO-SCF CALCULATION

In order to carry out a quantum mechanical energy calculation to determine whether multiple bonding, as discussed in the previous chapters, is significant in XF_2 molecules, it is first necessary to obtain physically resonable wave functions for the molecules involved. A frequently utilized and reasonably successful approximation for molecular wave functions is the linear combination of atomic orbital (LCAO) method to build up molecular orbitals (MO). The method has previously met with particular success in the explanation of bonding phenomena and the mathematical apparatus needed to handle many electron problems has been well formulated. Because of these two facts, the LCAO-MO technique seems particularly well-suited for the present problem. It has thus been chosen to treat the OF_2, NF_2 and CF_2 molecules.

To determine the energy, E, of a time independent quantum mechanical system, an equation of the form

$$H\Psi = E\Psi \tag{13}$$

must be solved. This can be cast into the form

$$E = \frac{\int_{\text{all space}} \Psi^* H \Psi d\tau}{\int_{\text{all space}} \Psi^* \Psi d\tau} \tag{14}$$

where the asterisk indicates a complex conjugate quantity and $d\tau$ is the volume element for the integration over all space.

Both Equations (13) and (14) are virtually impossible to solve for systems of high complexity. Thus one usually resorts to the variation principle[25] to obtain approximate energies. Here one guesses a wave function, ψ, of proper symmetry and minimizes the expression

$$E_{VAR} = \frac{\int_{\text{all space}} \psi^* H \psi \, d\tau}{\int_{\text{all space}} \psi^* \psi \, d\tau} \tag{15}$$

with respect to parameters contained in ψ. The variation principle then guarantees the result to be an upper limit to the true energy, if the integrals are evaluated exactly.

The Four Electron Problem

OF_2, NF_2 and CF_2 have 26, 25 and 24 electrons, respectively. Treating such a large number of electrons explicitly, even within the framework of the variation technique, results in a very tedious quantum mechanical problem. For this reason it is desirable to use a technique which treats explicitly those electrons which are involved in chemical bonding, and to a large extent determine the chemical and physical properties of a molecule, while treating the "non-bonding" electrons implicitly in nonpolarizable cores about the nuclei. This type of separation has been employed extensively to unsaturated hydrocarbons and recently has been applied to sigma bonded systems by Pohl et al.[26] With this procedure one can reduce the XF_2 calculation to one involving four electrons. This approximation, in terms of wave functions, may be expressed as

$$\psi_{total} = [(\Sigma)(\Sigma')]$$

where Σ' denotes a four by four Slater determinant corresponding to the wave functions for the four bonding electrons and the brackets represent the proper antisymmetrization of the total wave function. Σ represents a Slater determinant containing orbitals representing the core electrons. By this approximation the effect of electrons occupying orbitals in the Σ part of the total wave function are introduced empirically into the calculation through the nonpolarizable cores about the nuclei.

The core for the four electron problem is shown in Figure 7 for the XF_2 molecule. Each fluorine core may be described by the electronic configuration, $1S^2\ 2S^2\ 2P_x^{\ 2}\ 2P_y^{\ 2}$. The carbon atom has a core configuration $1S^2\ 2S^2$ while electrons are added to the $2P_x$ orbital to describe the nitrogen and oxygen cores. The four bonding electrons may

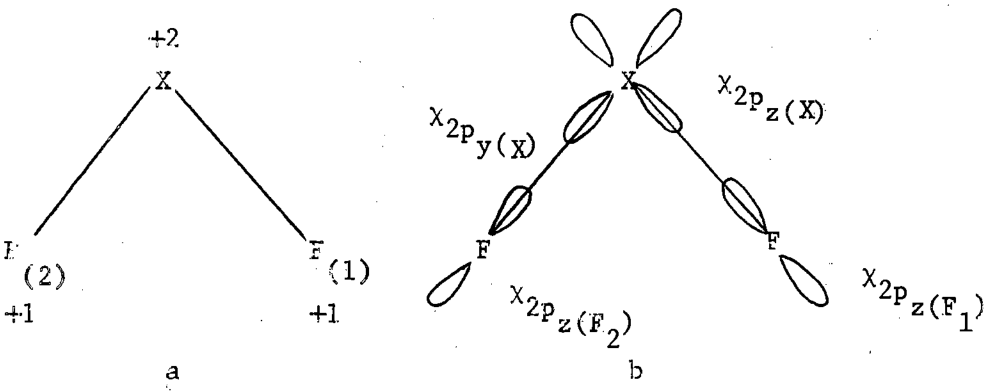


Figure 7. a) The cores of the XF_2 Molecule, b) The Atomic Orbital Basis Set for XF_2. Subscripts 1 and 2 Denote "Different" Fluorines.

then be described as occupying the $2p_y$ and $2p_z$ atomic orbitals on the X atom and the $2p_z$ atomic orbitals on the fluorines. This basis set of atomic orbitals is then used to form molecular orbitals for the XF_2 molecule.

The Hamiltonian operator for the four electron problem (in atomic units) may be written as

$$H_e(1,2,3,4) = \sum_{i=1}^{4} H_N(i) + \sum_{i<j=1}^{4} \frac{1}{r_{ij}} \tag{16}$$

where the summations are carried over all the electrons, r_{ij} represents the distance between the i^{th} and j^{th} electron, and

$$H_N(i) = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha=1}^{3} V_{\alpha i} \tag{17}$$

In Equation (17), α is a summation index for the three nuclei, $V_{\alpha i}$ represents the interaction of one of the three cores of XF_2 with the i^{th} electron and $-\frac{1}{2}\nabla_i^2$ represents the kinetic energy operator for the i^{th} electron. For the XF_2 four electron problem we may represent the Hamiltonian operator as

$$H = \sum_{i=1}^{4} \left(-\frac{1}{2}\nabla_i^2 - \sum_{\alpha=1}^{3} V_{\alpha i}\right) + \sum_{i<j=1}^{4} \frac{1}{r_{ij}} \tag{18}$$

The four electron wave function is written as a Slater determinant

$$\psi = \frac{1}{\sqrt{4!}} \begin{vmatrix} \lambda_1(1)\lambda_2(1)\lambda_3(1)\lambda_4(1) \\ \lambda_1(2)\lambda_2(2)\lambda_3(2)\lambda_4(2) \\ \lambda_1(3)\lambda_2(3)\lambda_3(3)\lambda_4(3) \\ \lambda_1(4)\lambda_2(4)\lambda_3(4)\lambda_4(4) \end{vmatrix} \tag{19}$$

where, as a first approximation, we shall take

$$\lambda_1 = \phi_1\alpha,\ \lambda_2 = \phi_1\beta,\ \lambda_3 = \phi_2\alpha \text{ and } \lambda_4 = \phi_2\beta.$$

The λ_i are spin orbitals made up of a spatial MO function, ϕ_i, and a spin function, α or β. The spin functions, α and β, correspond to an electron spin quantum number, S_z, of + 1/2 or - 1/2. Placing these spin orbitals in a Slater determinant insures the proper antisymmetrization of this wave function with respect to electron exchange. The molecular orbitals, ϕ_1 and ϕ_2, are taken to be linear combinations of the atomic orbitals illustrated in Figure 7 and are given by the equation

$$\phi_i = c_{i1}\chi_{2P_{z(0)}} + c_{i2}\chi_{2P_{z(F_1)}} + c_{i3}\chi_{2P_{y(0)}} + c_{i4}\chi_{2P_{z(F_2)}} \qquad (20)$$

The coefficients, $c_{i\nu}$, will be determined by a self-consistent field procedure to be discussed later in this chapter. Essentially these are the parameters which are varied in Equation (15) until the total energy for the XF_2 molecule is at a minimum. The atomic orbitals in Equation (20) are assumed to be Slater atomic orbitals.

A Slater atomic orbital[27] for atom X may be defined by the equation

$$\chi_x^{nl\lambda} = R_{nl}(r_x)\ Y_{l,\lambda}\ (\theta,\phi) \qquad (21)$$

where n, l, and λ denote the three spatial quantum numbers of the orbital. The $Y_{l,\lambda}$ (θ,ϕ) are the spherical harmonic functions while the radial part of the Slater orbital is given by

$$R_{nl}(r) = N_{nl}r^{n-l-\delta}\ e^{-\mu r} \qquad (22)$$

where N_{nl} is a normalization constant, $n-\delta$ is an effective quantum number and μ is a constant depending on the core being described. For orbitals with a principal quantum number, $n = 2$, δ is zero. The exponential coefficient, μ, may be expressed as $\mu = (Z-s)/n$ where Z is the nuclear charge of the nuclei and s is a screening constant for the electrons about the nuclei. This latter quantity may be determined from Slater's rules.[25] Values of μ for the atoms and ions of interest in this problem are listed in Table III.

TABLE III

SLATER EXPONENTIAL COEFFICIENTS

ATOM	C	C^+	N	N^+	O	O^+	F	F^{++}
	1.625	1.800	1.950	2.125	2.275	2.450	2.600	2.950

The Four Electron LCAO-MO-SCF Problem

The formalism for the application of the self-consistent field method to LCAO-MO type wave functions was first presented by Roothaan.[28] Essentially this method uses the variation principle in determining which set of LCAO coefficients, the $c_{i\nu}$, gives the minimum total energy for the molecule. In other words this technique finds the "best" LCAO-MO wave function for binding energy calculations. Pople[29] has given a set of working equations for Roothaan's method which have been employed in this calculation. The equations for the LCAO coefficients are given by

$$\sum_{\nu=1}^{4} F_{\mu\nu} c_{i\nu} = \varepsilon_i \sum_{\nu=1}^{4} S_{\mu\nu} c_{i\nu} . \qquad (23)$$

In equation (23) the Arabic letter indices are summed over the molecular orbitals, while the Greek letters correspond to the atomic orbitals. $S_{\mu\nu}$ represents the overlap between the ν^{th} and μ^{th} atomic orbitals, i.e.,

$$S_{\mu\nu} = \int \chi_\mu^* \chi_\nu d\tau = \langle \mu | \nu \rangle \ . \qquad (24)$$

$F_{\mu\nu}$ is defined as

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma=1}^{4} P_{\lambda\sigma} \left[\langle \mu\lambda | r_{12}^{-1} | \nu\sigma \rangle - \frac{1}{2} \langle \mu\lambda | r_{12}^{-1} | \sigma\nu \rangle \right] \qquad (25)$$

In this equation

$$H_{\mu\nu} = \int \chi_\mu^* \left(- \frac{1}{2} \nabla^2 - \sum_\alpha V_\alpha \right) \chi_\nu d\tau = \langle \mu | - \frac{1}{2} \nabla^2 - \sum_\alpha V_\alpha | \nu \rangle \ , \qquad (26)$$

$$\langle \mu\lambda | r_{12}^{-1} | \nu\sigma \rangle = \iint \chi_\mu^*(1) \chi_\lambda^*(2) r_{12}^{-1} \chi_\nu(1) \chi_\sigma(2) d\tau_1 d\tau_2 , \qquad (27)$$

and

$$P_{\lambda\sigma} = 2 \sum_i c_{i\lambda} c_{i\sigma} \ . \qquad (28)$$

In these equations $H_{\mu\nu}$ is the matrix element of the one electron Hamiltonian for motion of an electron in the field of the α^{th} core. The integral $\langle \mu\lambda | r_{12}^{-1} | \nu\sigma \rangle$ is a two electron integral, with $d\tau_1$ and $d\tau_2$ representing the volume elements for electrons numbered 1 and 2. In equation (28) $P_{\lambda\sigma}$ is a summation over various LCAO coefficients. The ε_i in equation (23) are the two lowest roots of the determinant

$$\left| F - \varepsilon S \right| = 0 \qquad (29)$$

where F and S are 4 x 4 matrices made up of $F_{\mu\nu}$ and $S_{\mu\nu}$ matrix elements for the XF_2 molecule. The secular equation corresponding to the above secular determinant is represented by

$$Fc = \varepsilon Sc. \qquad (30)$$

The 4 x 4 matrix c consists of four eigenvectors whose elements make up the LCAO coefficients for the various eigenvalues of Equation (29). That equation yields four eigenvalues corresponding to four molecular orbitals for XF_2. The four bonding electrons are placed in the two molecular orbitals corresponding to the two lowest eigenvalues of Equation (29). The total electronic energy using these two molecular orbitals is given by

$$\mathcal{E} = \frac{1}{2} \sum_{\mu\nu} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) . \qquad (31)$$

In solving this eigenvalue problem, elements of F and S are determined by use of equations (24) through (28). Then Equation (29) is solved for its eigenvalues. These eigenvalues are then substituted in Equation (30) from which the eigenvectors may be obtained. Equations (29) and (30) are complicated by the fact that the elements of F depend on the solutions of Equation (30), the $c_{i\nu}$. For this reason the solution of these two equations is determined by the following iterative procedure.

1) The zeroth set of coefficients are chosen in some manner, usually involving an "educated guess."

2) The elements of F are then obtained using Equation (25).

3) The elements of F and S are substituted into Equation (29) and the eigenvalues, ϵ_i, are obtained.

4) With these eigenvalues, the eigenvectors are obtained through Equation (30).

5) This set of coefficients, c_{ij}, are then used to determine new elements of F (Step 2) and the process is repeated until the LCAO coefficients become constant or self-consistent.

In addition to the aforementioned assumptions, three assumptions were used to simplify this iterative calculation. First, maximum orthogonality of the atomic orbital basis set is attained by constraining the XF_2 molecular angle at 90^o and using non-hybridized Slater orbitals on the X atom as shown in Figure 7. With this assumption, the only non-orthogonal atomic orbitals on adjacent atoms are those oriented directly toward one another along an X-F bond. In principle, the calculated energy should be minimized with respect to angle but in this problem we are mainly concerned with the binding energy and its variation when the X-F bonds are stretched and compressed.

Overlaps between atomic orbitals on nonadjacent atoms are assumed to be zero. This assumption is commonly made in molecular orbital calculations and here it implies that the overlap between $\chi_{2P_{z(F_1)}}$ and $\chi_{2P_{z(F_2)}}$ is zero. One can see that this overlap is considerably smaller than the overlap between $\chi_{2P_{z(X)}}$ and $\chi_{2P_{z(F_1)}}$ or $\chi_{2P_{y(X)}}$ and $\chi_{2P_{z(F_2)}}$ because the $F_1 \cdots F_2$ distance is larger than the X-F_1 bond length and because these two orbitals are not strongly directed towards each other.

The third assumption states that the XF_2 molecule contains only localized bonds. In other words

$$\phi_1 = c_{11}\chi_{2P_{z(X)}} + c_{12}\chi_{2P_{z(F_1)}} \qquad (32)$$

and

$$\phi_2 = c_{23}\chi_{2P_{y(x)}} + c_{24}\chi_{2P_{z(F_2)}} \quad . \tag{33}$$

Inspection of Equation (20) illustrates that C_{13}, C_{14}, C_{21} and C_{22} have been set equal to zero. Although this assumption is not rigorous if the electrons occupy delocalized molecular orbitals, we are mainly interested here in determining good localized molecular orbitals. The delocalization effects in the XF_2 molecules will be brought into the problem by means of a configuration interaction calculation described in the next chapter.

In Equation (18) provision has not been made for electrostatic repulsion between the nuclei or core-core repulsions. The term which when added to (18) forms the complete Hamiltonian for XF_2 is

$$\sum_{\alpha<\beta=1}^{3} \frac{Z_{\text{eff}(\alpha)}\, Z_{\text{eff}(\beta)}}{R_{\alpha\beta}} \tag{34}$$

where α and β are the summation indices for the nuclei, Z_α and Z_β are the effective nuclear charges of nuclei α and β and $R_{\alpha\beta}$ is the distance between the α^{th} and β^{th} nuclei. The total Hamiltonian may be expressed explicitly for the XF_2 molecule as the sum of Equations (18) and (34).

Determination of the Binding Energy

The binding energy, E_B, of an XF_2 molecule is defined as the change in energy of the reaction

$$X + 2F \longrightarrow XF_2 \quad .$$

where the reacting atoms are infinitely separated and each of these atoms is in its ground electronic state. This energy is calculated by considering the following processes. In the first step,

$$X + 2F \rightarrow X_v + 2F_v \text{ ,}$$

the three infinitely separated atoms are promoted to their hypothetical valence states,[30] the energy change for this process being $P^o_X + 2P^o_F$ where P represents the promotion energies of the various atoms from the ground state to the valence state.[31,32] The atoms are then ionized while in the valence state

$$X_v + 2F_v \rightarrow X^{++}_v + 2F^+_v + 4^-_e$$

the energy change being $I_{v(X)} + I_{v(X^+)} + 2I_{v(F)}$ where I_v denotes the valence state ionization potentials for species indicated in the subscripted parenthesis. The atoms are then brought from infinity to a proper molecular geometry of the XF_2 molecule. This hypothetical step occurs without any changes in the electronic configuration of the three ions and may be symbolized by the equation

$$X^{++}_v + 2F^+_v \rightarrow \overset{+}{F}_v \cdot \overset{++}{X}_v \cdot \overset{+}{F}_v$$

where ΔE for this process is simply the nuclear-nuclear repulsion energy, E_{nuc}, given by Equation (34). With the species in this geometrical configuration the four electrons are then placed in the lowest available unoccupied molecular orbitals

$$\overset{+}{F}_v \cdot \overset{++}{X}_v \cdot \overset{+}{F}_v + 4e^- \rightarrow F_v \cdot X_v \cdot F_v \rightarrow XF_2$$

The energy required for this last process is the electronic energy, $\mathcal{E}$, of Equation (31). For the overall process

$$X + 2F \rightarrow XF_2$$

the binding energy may thus be expressed as

$$E_B = P^o_X + 2P^o_F + I_{v(X)} + I_{v(X^+)} + 2I_{v(F)} + E_{nuc} + \mathcal{E} .$$

Semiempirical Integral Evaluations

In a semiempirical MO calculation of this type some scheme must be employed to evaluate the integrals. Two sets of integral approximations have been investigated in this project, these being identified as Set I and Set II. Both sets are an extension of the integral evaluations used by Pohl, et al.,[26] for the hydrogen halides.

For the semiempirical integral approximations of Set I, the $2P_z$ and $2P_y$ Slater wave functions for the X atom are assumed to have exponential parameters (μ) equal to those of the X^+ ion rather than the X atom. The $2P_z$ Slater wave function for fluorine contains a μ value of the fluorine atom.

To clarify the above assumption consider a fluorine atom in XF_2. All the electrons save one are considered to be in a core about fluorine. The remaining electron occupies a $2P_z$ orbital and is considered explicitly in the MO calculation. This electron should see about the same effective charge as a 2p electron on a free fluorine atom. The Slater orbital containing this electron should then be described by a Slater function with an exponential coefficient for the fluorine atom. The central atom, X, has all but two of its electrons in its core. These remaining electrons occupy the $2P_z$ and $2P_y$ orbitals on an X atom and are considered explicitly in this calculation. Considering either one of these electrons, it will see an effective charge of the X core which will approximately equal the effective charge seen by a 2p electron of an X^+ ion. Therefore the Slater wave function describing the atomic orbital containing this electron should have an exponential parameter corresponding to the X^+ ion.

The various integrals appearing in the MO calculation are now approximated as follows:

$$\left\langle Z(X) \middle| -\frac{1}{2}\nabla^2 - V_{X^+} \middle| Z(X) \right\rangle = \left\langle Z(X) \middle| -I_{X^+} \middle| Z(X) \right\rangle = -I_{X^+} \tag{35}$$

where $Z(X) = X_{2P_{z(X)}}$. Here the fact that $H\psi = E\psi$ for an electron about a nonpolarizable core has been employed.

Two center core integrals such as the integral in Equation (36) are evaluated using Pople's point charge approximation.[29]

$$\left\langle Z(F_1) \middle| V_{X^+} \middle| Z(F_1) \right\rangle = Z_{X^+}R^{-1}_{XF_1} = 2R^{-1}_{XF_1} \tag{36}$$

where Z_X is the charge of the core of atom X and $Z(F_1)$ represents the $2P_z$ Slater orbital on fluorine one.

The one center core integrals such as

$$\left\langle Z(X) \middle| V_{X^+} \middle| Z(X) \right\rangle \approx \left\langle Z(X) \middle| Z_{X^+}r^{-1} \middle| Z(X) \right\rangle = Z_{X^+}\left\langle Z(X) \middle| r^{-1} \middle| Z(X) \right\rangle \tag{37}$$

are evaluated analytically. In this equation r represents the distance between an electron in a $2P_Z$ orbital and the nucleus of the X atom. Upon substitution of the expression for a $2P_z$ Slater orbital, $\chi_{2P_{z(X)}} = (N_{X^+})^{\frac{1}{2}}\, r e^{-\mu_{X^+} r} \cos\theta$, into Equation (37) one finds that

$$\left\langle Z(X) \middle| r^{-1} \middle| Z(X) \right\rangle = \frac{\mu_{X^+}}{n} = \rho_{X^+} \qquad (38)$$

where n = 2 for a $2p_z$ orbital.

One center-two electron integrals such as

$$\left\langle Z(X)Z(X) \middle| r_{12}^{-1} \middle| Z(X)Z(X) \right\rangle = I_{X^+} + A_{X^+}, \qquad (39)$$

are evaluated using Pariser's approximation.[33]

Two center Coulomb integrals such as

$$\left\langle Z(X)Z(F_1) \middle| r_{12}^{-1} \middle| Z(X)Z(F_1) \right\rangle = R_{XF_1}^{-1} \qquad (40)$$

are evaluated by an interaction energy of point charges at the nuclear centers.[29]

For two center integrals of the type,

$$\left\langle Z(X)Z(X) \middle| r_{12}^{-1} \middle| Z(X)Z(F_1) \right\rangle ,$$

Mulliken's approximation[34] is used to reduce the integral to a sum of those listed above. This approximation is illustrated by the equation

$$\left\langle Z(X)Z(X) \middle| r_{12}^{-1} \middle| Z(X)Z(F_1) \right\rangle =$$

$$\frac{S_{Z(X)Z(F_1)}}{2} \left[\left\langle Z(X)Z(X) \middle| r_{12}^{-1} \middle| Z(X)Z(X) \right\rangle \right.$$

$$\left. + \left\langle Z(X)Z(F_1) \middle| r_{12}^{-1} \middle| Z(X)Z(F_1) \right\rangle \right] = \frac{S_{Z(X)Z(F_1)}}{2} \left[I_{X^+} + A_{X^+} + R_{XF_1}^{-1} \right]$$

$$(41)$$

In this equation $S_{Z(X)Z(F_1)}$ is the overlap integral of a $2p_z$ orbital on X and a $2P_z$ orbital on fluorine. Three center-two electron integrals and some two center-one electron integrals were simplified in the same manner.

One center exchange integrals such as $\langle Z(X)Z(X) | r_{12}^{-1} | Y(X)Y(X)\rangle$, where Y(X) represents a $2P_y$ Slater orbital on X, were evaluated using a method described by Rein and Harris.[35] This integral may be approximated by the expression

$$\langle Z(X)Z(X) | r_{12}^{-1} | Y(X)Y(X)\rangle_{\text{emp}} = \frac{\langle Z(X)Z(X) | r_{12}^{-1} | Y(X)Y(X)\rangle_{\text{num}}}{\langle Z(X)Y(X) | r_{12}^{-1} | Z(X)Y(X)\rangle_{\text{num}}} \langle Z(X)Y(X) | r_{12}^{-1} | Z(X)Y(x)\rangle_{\text{emp}} \tag{42}$$

where the subscripts "emp" and "num" indicate that the integrals have been determined empirically and numerically. An integration program written by Switendick and Carbato[36] numerically evaluates the integrals in Equation (42) for Slater orbitals. This program, written in Fortran II for the IBM 7090 computer, was obtained through the Quantum Chemistry Program Exchange at the University of Indiana (DI BC DIAT, #29). The ratio of the numerically evaluated integrals in Equation (42) was found to be independent of the Slater exponential coefficient, μ, and this equation may be expressed as

$$\langle Z(X)Z(X) | r_{12}^{-1} | Y(X)Y(X)\rangle_{\text{emp}} = 0.06040 \ \langle Z(X)Y(X) | r_{12}^{-1} | Z(X)Y(X)\rangle_{\text{emp}}$$

where X may be the C, C^+, N, N^+, O, or O^+ atoms and ions.

Table IV lists the different types of integrals arising in the MO calculation and the Set I semiempirical evaluations employed. These integrals were evaluated using procedures analogous to those presented in the above examples.

The semiempirical integral approximations of Set II will now be

TABLE IV

SEMIEMPIRICAL INTEGRAL EVALUATIONS - SET I

<u>One Electron Integrals</u>:

$$\langle z(X)|-\frac{1}{2}\nabla^2-V_{X+}|\,z(X)\rangle = \langle y(X)\,|-\frac{1}{2}\nabla^2-V_{X+}|\,y(X)\rangle = -\,I_{X+}$$

$$\langle z(F_1)|\,-\frac{1}{2}\nabla^2-V_{F_1}|z(F_1)\rangle = -\,I_F$$

$$\langle z(F_2)|\,-\frac{1}{2}\nabla^2-V_{F_2}|z(F_2)\rangle = -\,I_F$$

$$\langle z(X)|\,V_{F_1}|\,z(X)\rangle = \langle y(X)|\,V_{F_1}|\,y(X)\rangle = +\,R^{-1}_{XF_1}$$

$$\langle z(X)|\,V_{F_2}|\,z(X)\rangle = \langle y(X)|\,V_{F_2}|\,y(X)\rangle = +\,R^{-1}_{XF_2}$$

$$\langle z(F_1)|\,V_X|z(F_1)\rangle = +\,2R^{-1}_{XF_1}$$

$$\langle z(F_2)|\,V_X|z(F_2)\rangle = +\,2R^{-1}_{XF_2}$$

$$\langle z(F_1)|\,V_{F_2}|z(F_1)\rangle = \langle z(F_2)|\,V_{F_1}|z(F_2)\rangle = R^{-1}_{FF}$$

$$\langle z(X)|\,V_{X+}|z(X)\rangle = +\,2\rho_{X+}$$

$$\langle z(F_1)|\,V_{F_1}|z(F_1)\rangle = \langle z(F_2)|\,V_{F_2}|z(F_2)\rangle = \rho_F$$

<u>Two Electron Integrals</u>:

$$\langle y(X)y(X)|\,r^{-1}_{12}|y(X)y(X)\rangle = \langle z(X)z(X)|\,r^{-1}_{12}|z(X)z(X)\rangle = I_{X+} + A_{X+}$$

$$\langle z(X)y(X)|\,r^{-1}_{12}|z(X)y(X)\rangle = I_{X+} + A_{X+}$$

$$\langle z(F_1)z(F_1)|\,r^{-1}_{12}|z(F_1)z(F_1)\rangle = \langle y(F_1)y(F_1)|\,r^{-1}_{12}|y(F_1)y(F_1)\rangle = I_F + A_F$$

$$\langle z(X)z(X)|\,r^{-1}_{12}\,|y(X)y(X)\rangle = 0.06040\,(I_{X+} + A_{X+})$$

$$\langle z(X)z(F_2)|\,r^{-1}_{12}|z(X)z(F_2)\rangle = \langle y(X)z(F_2)|\,r^{-1}_{12}|y(X)z(F_2)\rangle = R^{-1}_{XF_2}$$

$$\langle z(X)z(F_1)|\,r^{-1}_{12}|z(X)z(F_1)\rangle = \langle y(X)z(F_1)|\,r^{-1}_{12}|y(X)z(F_1)\rangle = R^{-1}_{XF_1}$$

$$\langle z(F_1)z(F_2)|\,r^{-1}_{12}|z(F_1)z(F_2)\rangle = R^{-1}_{FF}$$

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examined. The exponential parameters of the Slater orbital expressions are simply those of the corresponding atoms, independent of the number of electrons from each atom which are treated explicitly in the problem.

The Slater orbitals are solutions to the central field problem where V(r), the potential, is given by (corresponding to the convention used in Equation (18))

$$V(r) = + \frac{(Z - s)e^2}{r} - \frac{n^*(n^* - 1)h^2}{8\pi^2 mr^2}$$

where Z is the nuclear charge of the atom, s is the Slater screening constant, n^* represents the "effective quantum number," h is Planck's constant, m is the mass of an electron and r is the distance between the electron and the nucleus. For the X atom and the X^+ ion (in atomic units)

$$V_X(r) - V_{X^+}(r) = + \frac{Z_X - s_X}{r} - \frac{Z_{X^+} - s_{X^+}}{r} = \frac{-.35}{r}$$

Using this relationship, the integral

$$\left\langle Z(X) \right| - \frac{1}{2}\nabla^2 - V_{X^+} \left| Z(X) \right\rangle = \left\langle Z(X) \right| - \frac{1}{2}\nabla^2 - V_X - \frac{.35}{r} \left| Z(X) \right\rangle$$

$$= \left\langle Z(X) \right| - \frac{1}{2}\nabla^2 - V_X \left| Z(X) \right\rangle - .35 \left\langle Z(X) \right| r^{-1} \left| Z(X) \right\rangle = -I_X - .35\rho_X$$

where the last two integrals are solved by procedures demonstrated in Equations (35) and (38). The balance of the integrals derived in this calculation, which are not of the form given in the last equation, are evaluated using the procedures demonstrated by Equations (36) through (42). A listing of the different types of integrals derived in this calculation and their evaluation using Set II approximations may be

TABLE V

SEMIEMPIRICAL INTEGRAL EVALUATIONS - SET II

One Electron Integrals:

$$\langle z(X)| -\frac{1}{2}\nabla^2 - V_{X+} |z(X)\rangle = \langle y(X)| -\frac{1}{2}\nabla^2 - V_{X+} |y(X)\rangle = -I_X - .35\rho_X$$

$$\langle z(F_1)| -\frac{1}{2}\nabla^2 - V_{F_1} |z(F_1)\rangle = \langle z(F_2)| -\frac{1}{2}\nabla^2 - V_{F_2} |z(F_2)\rangle = -I_F$$

$$\langle z(X)|V_{F_1}|z(X)\rangle = \langle y(X)|V_{F_1}|y(X)\rangle = R^{-1}_{XF_1}$$

$$\langle z(X)|V_{F_2}|z(X)\rangle = \langle y(X)|V_{F_2}|y(X)\rangle = R^{-1}_{XF_2}$$

$$\langle z(F_1)|V_X|z(F_1)\rangle = 2R^{-1}_{XF_1}$$

$$\langle z(F_2)|V_X|z(F_2)\rangle = 2R^{-1}_{XF_2}$$

$$\langle z(F_1)|V_X|z(F_1)\rangle = \langle z(F_2)|V_{F_1}|z(F_2)\rangle = R^{-1}_{FF}$$

$$\langle z(X)|V_{X+}|z(X)\rangle = -2\rho_X$$

$$\langle z(F_1)|V_{F_1}|z(F_1)\rangle = \langle z(F_2)|V_{F_2}|z(F_2)\rangle = \rho_F$$

Two Electron Integrals:

$$\langle y(X)y(X)|r^{-1}_{12}|y(X)y(X)\rangle = \langle z(X)z(X)|r^{-1}_{12}|z(X)z(X)\rangle = I_X + A_X$$

$$\langle z(X)y(X)|r^{-1}_{12}|z(X)y(X)\rangle = I_X + A_X$$

$$\langle z(F_1)z(F_1)|r^{-1}_{12}|z(F_1)z(F_1)\rangle = \langle y(F_1)y(F_1)|r^{-1}_{12}|y(F_1)y(F_1)\rangle = I_F + A_F$$

$$\langle z(X)z(X)|r^{-1}_{12}|y(X)y(X)\rangle = 0.06040\ (I_X + A_X)$$

$$\langle y(X)z(F_1)|r^{-1}_{12}|y(X)z(F_1)\rangle = \langle z(X)z(F_1)|r^{-1}_{12}|z(X)z(F_1)\rangle = R^{-1}_{XF_1}$$

$$\langle y(X)z(F_2)|r^{-1}_{12}|y(X)z(F_2)\rangle = \langle z(X)z(F_2)|r^{-1}_{12}|z(X)z(F_2)\rangle = R^{-1}_{XF_2}$$

$$\langle z(F_1)z(F_2)|r^{-1}_{12}|z(F_1)z(F_2)\rangle = R^{-1}_{FF}$$

TABLE VI

F-MATRIX ELEMENTS - SET I

$$\begin{aligned}F_{11} = {} & -I_{X+} - R^{-1}_{XF_1} - R^{-1}_{XF_2} + C^2_{11}[I_{X+} + A_{X+}] + 2C^2_{12}[R^{-1}_{XF_1} - 0.125\ S^2_{XF_1}(I_{X+} \\ & + A_{X+} + I_F + A_F + 2R^{-1}_{XF_1})] + 2C^2_{23}[I_{X+} + A_{X+} - .03020(I_{X+} + A_{X+})] \\ & + 2C^2_{24}R^{-1}_{XF_2} + C_{11}C_{12}S_{XF_1}(I_{X+} + A_{X+} + R^{-1}_{XF_1}) + 2C_{23}C_{24}S_{XF_2}(I_{X+} + A_{X+} \\ & + R^{-1}_{XF_2})\end{aligned}$$

$$\begin{aligned}F_{22} = {} & -I_F - 2R^{-1}_{XF_1} - R^{-1}_{FF} + 2C^2_{11}[R^{-1}_{XF_1} - 0.125\ S^2_{XF_1}(I_{X+} + A_{X+} + I_F + A_F \\ & + 2R^{-1}_{XF_1})] + C^2_{12}(I_F + A_F) + 2C^2_{23}R^{-1}_{XF_1} + 2C^2_{24}R^{-1}_{FF} + C_{11}C_{12}S_{XF_1}(I_F + A_F \\ & + R^{-1}_{XF_1}) + 2C_{23}C_{24}S_{XF_2}(R^{-1}_{XF_1} + R^{-1}_{FF})\end{aligned}$$

$$\begin{aligned}F_{33} = {} & -I_{X+} - R^{-1}_{XF_1} - R^{-1}_{XF_2} + 2C^2_{11}[I_{X+} + A_{X+} - 0.03020(I_{X+} + A_{X+})] \\ & + 2C^2_{12}R^{-1}_{XF_1} + C^2_{23}(I_{X+} + A_{X+}) + 2C^2_{24}[R^{-1}_{XF_2} - 0.125\ S^2_{XF_2}(I_{X+} + A_{X+} + I_F \\ & + A_F + 2R^{-1}_{XF_2})] + 2C_{11}C_{12}S_{XF_1}(I_{X+} + A_{X+} + R^{-1}_{XF_1})\end{aligned}$$

$$\begin{aligned}F_{44} = {} & -I_F - 2R^{-1}_{XF_2} - R^{-1}_{FF} + 2C^2_{11}R^{-1}_{XF_2} + 2C^2_{12}R^{-1}_{FF} + 2C^2_{23}[R^{-1}_{XF_2} \\ & - 0.125\ S^2_{XF_2}(I_{X+} + A_{X+} + I_F + A_F + 2R^{-1}_{XF_2})] + C^2_{24}(I_F + A_F) \\ & + 2C_{11}C_{12}S_{XF_1}(R^{-1}_{XF_2} + R^{-1}_{FF}) + C_{23}C_{24}S_{XF_2}(I_F + A_F + R_{XF_2})\end{aligned}$$

$$\begin{aligned}F_{12} = F_{21} = {} & 0.5\ S_{XF_1}(-I_F - I_{X+} - \rho_{X+} - 0.5\rho_F - 1.5R^{-1}_{XF_1} - R^{-1}_{XF_2} - R^{-1}_{FF}) \\ & + 0.5\ S_{XF_1}C^2_{11}(I_{X+} + A_{X+} + R^{-1}_{XF_1}) + 0.5\ C^2_{12}S_{XF_1}(I_F + A_F + R^{-1}_{XF_1}) \\ & + C^2_{23}S_{XF_1}(I_{X+} + A_{X+} + R^{-1}_{XF_1}) + C^2_{24}S_{XF_1}(R^{-1}_{XF_2} + R^{-1}_{FF}) \\ & + 0.75\ C_{11}C_{12}S^2_{XF_1}(I_{X+} + A_{X+} + I_F + A_F + 2R^{-1}_{XF_1}) - C_{11}C_{12}R^{-1}_{XF_1} \\ & + C_{23}C_{24}S_{XF_1}S_{XF_2}(I_{X+} + A_{X+} + R^{-1}_{XF_1} + R^{-1}_{XF_2} + R^{-1}_{FF})\end{aligned}$$

TABLE VI (Continued)

$$F_{34} = F_{43} = 0.5\, S_{XF_2}(- I_F - I_{X+} - \rho_{X+} - R^{-1}_{XF_1} - 1.5\, R^{-1}_{XF_2} - R^{-1}_{FF} - 0.5\rho_F)$$

$$+ C^2_{11} S_{XF_2}(I_{X+} + A_{X+} + R^{-1}_{XF_2}) + C^2_{12} S_{XF_2}(R^{-1}_{XF_1} + R^{-1}_{FF}) + 0.5\, C^2_{23} S_{XF_2}(I_{X+}$$

$$+ A_{X+} + R^{-1}_{XF_2}) + 0.5\, C^2_{24} S_{XF_2}(I_F + A_F + R^{-1}_{XF_2}) + C_{11}C_{12}S_{XF_1}S_{XF_2}(I_{X+}$$

$$+ A_{X+} + R^{-1}_{XF_1} + R^{-1}_{XF_2} + R^{-1}_{FF}) + 0.75\, C_{23}C_{24}S^2_{XF_2}(I_{X+} + A_{X+} + 2R^{-1}_{XF_2} + I_F$$

$$+ A_F) - C_{23}C_{24}R^{-1}_{XF_2}$$

$$F_{13} = F_{31} = 0$$

$$F_{14} = F_{41} = 0$$

$$F_{23} = F_{32} = 0$$

$$F_{24} = F_{42} = 0$$

TABLE VII

F-MATRIX ELEMENTS - SET II

$$\begin{aligned} F_{11} = {} & -I_X - .35\rho_X - R^{-1}_{XF_1} - R^{-1}_{XF_2} + C^2_{11}(I_X + A_X) + 2C^2_{12}\left[R^{-1}_{XF_1} - \frac{S^2_{XF_1}}{8}(I_X \right. \\ & \left. + A_X + I_F + A_F + 2R^{-1}_{XF_1})\right] + 2C^2_{23}\left[I_X + A_X - 0.03020(I_X + A_X)\right] \\ & + 2C^2_{24}R^{-1}_{XF_2} + C_{11}C_{12}S_{XF_1}(I_X + A_X + R^{-1}_{XF_1}) + 2C_{23}C_{24}S_{XF_2}(I_X + A_X \\ & + R^{-1}_{XF_2}) \end{aligned}$$

$$\begin{aligned} F_{22} = {} & -I_F - 2R^{-1}_{XF_1} - R^{-1}_{FF} + 2C^2_{11}\left[R^{-1}_{XF_1} - \frac{S^2_{XF_1}}{8}(I_X + A_X + I_F + A_F + 2R^{-1}_{XF_1})\right] \\ & + C^2_{12}(I_F + A_F) + 2C^2_{23}R^{-1}_{XF_1} + 2C^2_{24}R^{-1}_{FF} + C_{11}C_{12}S_{XF_1}(I_F + A_F + R^{-1}_{XF_1}) \\ & 2C_{23}C_{24}(R^{-1}_{XF_1} + R^{-1}_{FF}) \end{aligned}$$

$$\begin{aligned} F_{33} = {} & -I_X - .35\rho_X - R^{-1}_{XF_1} - R^{-1}_{XF_2} + 2C^2_{11}\left[I_X + A_X - 0.03020(I_X + A_X)\right] \\ & + 2C^2_{12}R^{-1}_{XF_1} + C^2_{23}(I_X + A_X) + 2C^2_{24}\left[R^{-1}_{XF_2} - \frac{S^2_{XF_2}}{8}(I_X + A_X + I_F + A_F \right. \\ & \left. + 2R^{-1}_{XF_2})\right] + 2C_{11}C_{12}S_{XF_1}(I_X + A_X + R^{-1}_{XF_1}) + C_{23}C_{24}S_{XF_2}(I_X + A_X \\ & + R^{-1}_{XF_2}) \end{aligned}$$

$$\begin{aligned} F_{44} = {} & -I_F - 2R^{-1}_{XF_2} - R^{-1}_{FF} + 2C^2_{11}R^{-1}_{XF_2} + 2C^2_{12}R^{-1}_{FF} + 2C^2_{23}\left[R^{-1}_{XF_2} - \frac{S^2_{XF_2}}{8}(I_X \right. \\ & \left. + A_X + I_F + A_F + 2R^{-1}_{XF_2})\right] + C^2_{24}(I_F + A_F) + 2C_{11}C_{12}S_{XF_1}(R^{-1}_{XF_2} + R^{-1}_{FF}) \\ & + C_{23}C_{24}S_{XF_2}(I_F + A_F + R^{-1}_{XF_2}) \end{aligned}$$

$$\begin{aligned} F_{12} = F_{21} = {} & 0.5S_{XF_1}(- I_F - I_X - 1.35\rho_X - 0.5\rho_F - 1.5R_{XF_1} - R_{XF_2} - R^{-1}_{FF}) \\ & + 0.5\ C^2_{11}S_{XF_1}(I_X + A_X + R^{-1}_{XF_1}) + 0.5\ C^2_{12}S_{XF_1}(I_F + A_F + R^{-1}_{XF_1}) \\ & + C^2_{23}S_{XF_1}(I_X + A_X + R^{-1}_{XF_1}) + C^2_{24}S_{XF_1}(R^{-1}_{XF_2} + R^{-1}_{FF}) + 0.75\ C_{11}C_{12}S^2_{XF_1} \\ & (I_X + A_X + I_F + A_F + 2R^{-1}_{XF_1}) - C_{11}C_{12}R^{-1}_{XF_1} + C_{23}C_{24}S_{XF_1}S_{XF_2}(I_X \\ & + A_X + R^{-1}_{XF_1} + R^{-1}_{XF_2} + R^{-1}_{FF}) \end{aligned}$$

TABLE VII (Continued)

$$
\begin{aligned}
F_{34} = F_{43} = {} & 0.5\ S_{XF_2}(-\ I_F - I_X - 1.35\rho_X - .5\rho_F - R^{-1}_{XF_1} - 1.5\ R^{-1}_{XF_2} - R^{-1}_{FF}) \\
& + C^2_{11}S_{XF_2}(I_X + A_X + R^{-1}_{XF_2}) + C^2_{12}S_{XF_2}(R^{-1}_{XF_1} + R^{-1}_{FF}) + 0.5\ C^2_{23}S_{XF_2}(I_X \\
& + A_X + R^{-1}_{XF_2}) + 0.5\ C^2_{24}S_{XF_2}(I_F + A_F + R^{-1}_{XF_2}) + C_{11}C_{12}S_{XF_1}S_{XF_2}(I_X \\
& + A_X + R^{-1}_{XF_1} + R^{-1}_{XF_2} + R^{-1}_{FF}) + 0.75\ C_{23}C_{24}S^2_{XF_2}(I_X + A_X + I_F + A_F \\
& + 2.0\ R^{-1}_{XF_2}) - C_{23}C_{24}R^{-1}_{XF_2}
\end{aligned}
$$

$F_{13} = F_{31} = 0$

$F_{14} = F_{41} = 0$

$F_{23} = F_{32} = 0$

$F_{24} = F_{42} = 0$

found on Table V. With either set of semiempirical integral evaluations the F matrix elements, as expressed by Equation (25), may be determined. These elements for an XF_2 molecule are listed in Tables VI and VII. The former table corresponds to Set I integral approximations while the latter table corresponds to those of Set II.

The numerical values for the valence state ionization potentials and electron affinities used in these calculations are given in Table VIII.

TABLE VIII

VALENCE STATE IONIZATION POTENTIALS AND ELECTRON AFFINITIES*

$I_F = 0.7672$	$I_C = 0.4020$	$A_N = -0.0310$
$I_{F^{++}} = 2.2515$	$I_{C^+} = 0.8926$	$A_{N^+} = -0.5127$
$I_O = 0.6354$	$A_F = -0.1287$	$A_C = -0.0281$
$I_{O^+} = 1.2543$	$A_{F^{++}} = -1.3504$	$A_{C^+} = -0.4020$
$I_N = 0.5127$	$A_O = -0.07403$	
$I_{N^+} = 1.0658$	$A_{O^+} = -0.6354$	

*The valence state values given above were obtained from ground state ionization potentials and electron affinities and from promotion energies which have been published by Hinze and Jaffe in references (31) and (32) and from an Air Force report which may be obtained from Professor Jaffe.

Evaluation of Overlap Integrals

Numerical values of overlap integrals for Slater orbitals were obtained from a paper by Mulliken et.al.[37] The overlap integral between $2P_z$ orbitals on two centers, and X atom and a fluorine atom, directed toward each other may be expressed as a function dependent on the distance between the two centers and on the Slater exponential parameters of the two nuclei involved. In Mulliken's paper this overlap integral is expressed as a function of p and t where

$$p = \frac{1}{2}(\mu_F + \mu_X)r \quad \text{and} \quad t = \frac{\mu_F - \mu_X}{\mu_F + \mu_X}$$

and where r is the distance between the nuclei in atomic units.

Mulliken lists tables of values for overlap integrals corresponding to various values of p and t. (Each table depends on the quantum numbers of the two Slater orbitals involved.) A simple graphical interpolation was utilized to obtain values for overlap integrals which are not listed.

Core-Core Repulsions

Herman and Skillman[38] have determined the Hartree-Fock potentials for all the atoms of interest in the XF_2 problems. Values of effective nuclear charges, Z_{eff}, for the various cores were obtained from these potentials. Effective nuclear charges are needed for the fluorine atom and for the oxygen, nitrogen and carbon singly charged ions. Values of Z_{eff} for these ions were obtained by adding 1 atomic unit to the effective nuclear charges of the oxygen, nitrogen and carbon atoms. Values of Z_{eff} as a function of distance are given in Figure 8 for the carbon, nitrogen, oxygen and fluorine atoms.

Numerical Method

A computer program was written in Fortran IV to handle the tedious computations demanded by this calculation. A description of the program and a Fortran listing of the program are given in Appendix A. Two

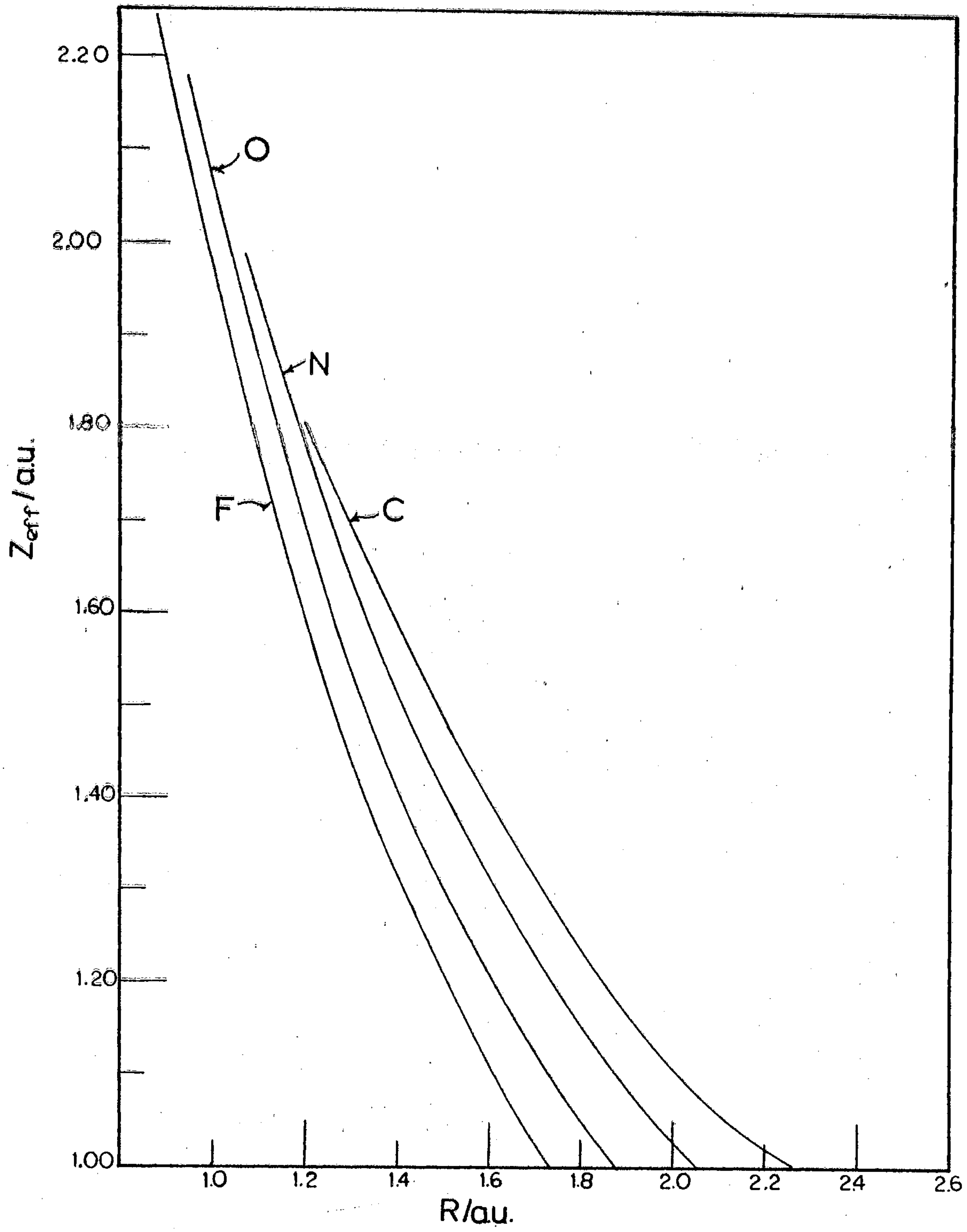


Figure 8. The Effective Nuclear Charges for Core-Core Repulsion Terms.

main points are mentioned here. First, the solution of the secular equation

$$Fc = \varepsilon Sc \tag{30}$$

is obtained in a straightforward manner. The overlap matrix S is diagonalized and the secular equation is rearranged to form

$$F'c' = \varepsilon Ec'$$

where E is the identity matrix and F' and c' differ from F and c. Then the F' matrix is diagonalized and the eigenvalues and eigenvectors of Equation (30) are obtained.

Secondly, each LCAO coefficient is tested for self-consistency by an equation of the form

$$c_{i\nu}^{i+1} - c_{i\nu}^{i} \leqslant 0.0001 \tag{43}$$

The superscripts i and i+1 merely indicate that the coefficient being considered has values obtained from successive iterations. This test was applied to each LCAO coefficient, all of which must satisfy Equation (43) before the set is accepted and used to calculate binding energies. The program was tested for correctness by calculating binding energies of the FCl molecule as a function of bond distance. This calculation has been previously carried out by Pohl and Raff.[39] They solved for LCAO coefficients using a grid technique rather than using the matrix diagonalization method. The results of both calculations were identical indicating that the subroutines employed in this problem to obtain the eigenvalues and eigenvectors are correct.

Results and Discussion

For symmetric, nonlinear, triatomic molecules the study of the variation of energy as one changes the two bond lengths may be accomplished in two ways. The two bonds may be extended or compressed from equilibrium by the same amounts which would approximate the symmetric stretching mode of the molecule. Actually the expression of the symmetric stretching normal coordinate as a function of internal coordinates indicates that the angle varies as the bond lengths change but this is neglected in these calculations. Secondly, displacing the nuclei of XF_2 in its antisymmetric stretching mode permits a study of the variation in energy as one bond is compressed and the other bond is extended from equilibrium by the same amount. This mode is a pure stretching mode with no change in the molecular angle. The calculations discussed in the remaining part of this chapter correspond to the symmetric stretching mode. For these calculations, molecular symmetry allows Equations (32) and (33) for the two bonding molecular orbitals to be expressed as

$$\phi_1 = c_X \chi_{2P_{z(X)}} + c_F \chi_{2P_{z(F_1)}}$$

$$\phi_2 = c_X \chi_{2P_{y(X)}} + c_F \chi_{2P_{z(F_2)}}$$

where $c_X = c_{11} = c_{23}$ and $c_F = c_{12} = c_{24}$.

The procedure explained thus far differs from Huckel theory[40] in that no calibration scheme has been employed in describing the XF_2 series. As a result one cannot expect quantitative predictions of binding energies which are as accurate as those one might obtain if the calculations were judiciously calibrated.

One can introduce such a calibration into this type of MO treatment through the Wolfsberg-Helmholtz parameter,[26] the value of which is theoretically equal to one. In references (26) and (39) values of this parameter are determined such that the calculation of certain physical properties (binding energy, dipole moment, etc.) are in optimum agreement with the experimental data for a series of molecules. Such a technique could be employed here and would undoubtedly improve the agreement between the calculated and experimental binding energies.

Binding energy values as a function of bond distance, using the Set I integral approximations, are shown in Figure 9 for OF_2, NF_2 and CF_2. Table IX contains a listing of these binding energies at various bond distances. Table X contains a listing of the LCAO coefficients obtained in these SCF calculations. Table XI illustrates how the calculated values of equilibrium binding energies and bond lengths compare with the corresponding experimental values. The calculated binding energies are much too large, the ratio of the calculated to experimental energies being 3.1, 1.9 and 1.4 for OF_2, NF_2 and CF_2 respectively. The trend of these calculated binding energies as one compares the series OF_2, NF_2 and CF_2 is not in agreement with experiment as the calculated binding energy of OF_2 is larger than this quantity for NF_2.

The calculated equilibrium bond lengths for these molecules are much shorter than the corresponding experimental quantities. This result was not unexpected since the hydrogen halide and interhalogen calculations show this same general phenomenon. The calculated equilibrium bond lengths of the XF_2 molecules do not vary by more than 0.1 Å which is in agreement with experimental observations.

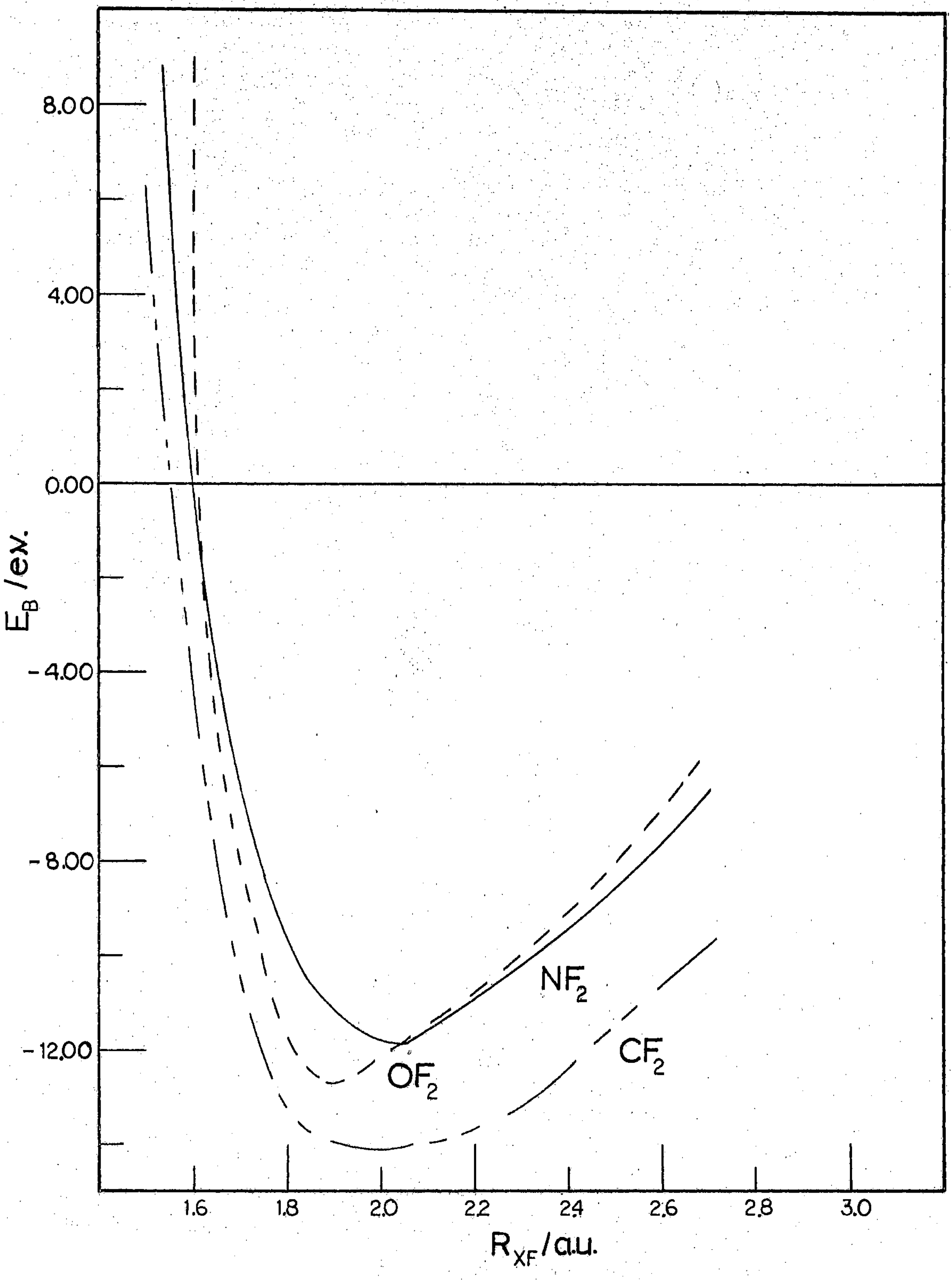


Figure 9. The Binding Energy Curves for OF_2, NF_2 and CF_2 - Set I.

TABLE IX

BINDING ENERGY VALUES FOR OF_2, NF_2 and CF_2* - SET I

R_{xf}(a.u.)	R(Å)	E_B (OF_2) e.v.	E_B (NF_2) e.v.	E_B (CF_2) e.v.
1.50	0.794	-12.62		- 6.04
1.60	0.846	- 2.10	- 8.88	3.45
1.70	0.899	6.87	6.65	10.65
1.80	0.952	11.64	9.62	13.53
1.90	1.005	12.74	10.80	13.98
2.00	1.058	12.19	11.85	14.05
2.10	1.111	11.57	11.61	14.01
2.20	1.164	10.82	10.93	13.74
2.30	1.217	9.98	10.19	13.29
2.40	1.270	8.99	9.35	12.36
2.50	1.323	7.92	8.52	11.50
2.60	1.375	--	7.69	10.68
2.70	1.428	--	--	9.90

*In this and the following tables and in the discussions concerning binding energies in the body of the text, the convention of listing and discussing the negative values of the binding energies ($-E_B$ as defined on page 30) is used.

TABLE X

LCAO-MO-SCF COEFFICIENTS FOR OF_2, NF_2 AND CF_2 - SET I

	OF_2		NF_2		CF_2	
R_{XF}(a.u.)	C_O	C_F	C_N	C_F	C_C	C_F
1.50	.1746	.9365			-.02173	1.0031
1.60	.2964	.8708	.07579	.9775	-.00803	1.0015
1.70	.4078	.7911	.1459	.9483	.01623	.9963
1.80	.4637	.7469	.2226	.9102	.05089	.9861
1.90	.4941	.7231	.2935	.8693	.09350	.9713
2.00	.5134	.7099	.3473	.8359	.1417	.9517
2.10	.5273	.7022	.3863	.8110	.1899	.9299
2.20	.5384	.6987	.4150	.7927	.2346	.9080
2.30	.5479	.6976	.4362	.7811	.2728	.8885
2.40	.5565	.6986	.4526	.7747	.3040	.8727
2.50	.5646	.7009	.4663	.7705	.3294	.8606
2.60			.4780	.7678	.3506	.8510
2.70					.3685	.8438

TABLE XI

EQUILIBRIUM BINDING ENERGIES AND BOND LENGTHS

	XF Bond Distances (Å)			XF_2 Binding Energies (e.V.)		
	Exptl.	Set I	Set II	Exptl.	Set I	Set II
OF_2	1.38[6]	1.00	0.96	3.9[41]	12.74	6.33
NF_2	1.37[7]	1.07	1.02	6.2[42]	11.90	8.47
CF_2	1.32[8]	1.07	0.99	≈10[43]	14.08	13.56

Figure 10 shows the binding energy-bond distance curves for these three molecules as calculated using the Set II integral approximations. Table XII lists numerical values of binding energies at various X-F bond lengths. Table XIII lists the LCAO coefficients obtained at these same distances. Table XI compares the calculated and experimental values for the Set II calculations. The calculated binding energies are much closer to the experimental energies than the corresponding Set I calculations. The calculated values are again too large, deviating from the experimental values by 59%, 37% and 36% for OF_2, NF_2 and CF_2, respectively. The trend in the calculated binding energies agrees quite well with the experimental trend. The calculated values for the equilibrium bond lengths are again too small.

The calculated binding energies for molecules containing fluorine are anomalously large when compared with the calculated energies of non-fluoride molecules. Pohl and Raff[39] have calculated a binding energy for the fluorine molecule of 3.90 e.V. while the experimental energy, although not exactly determined, has an upper limit of 2.5 e.V. The equilibrium binding energies for Cl_2, Br_2 and I_2 were approximately

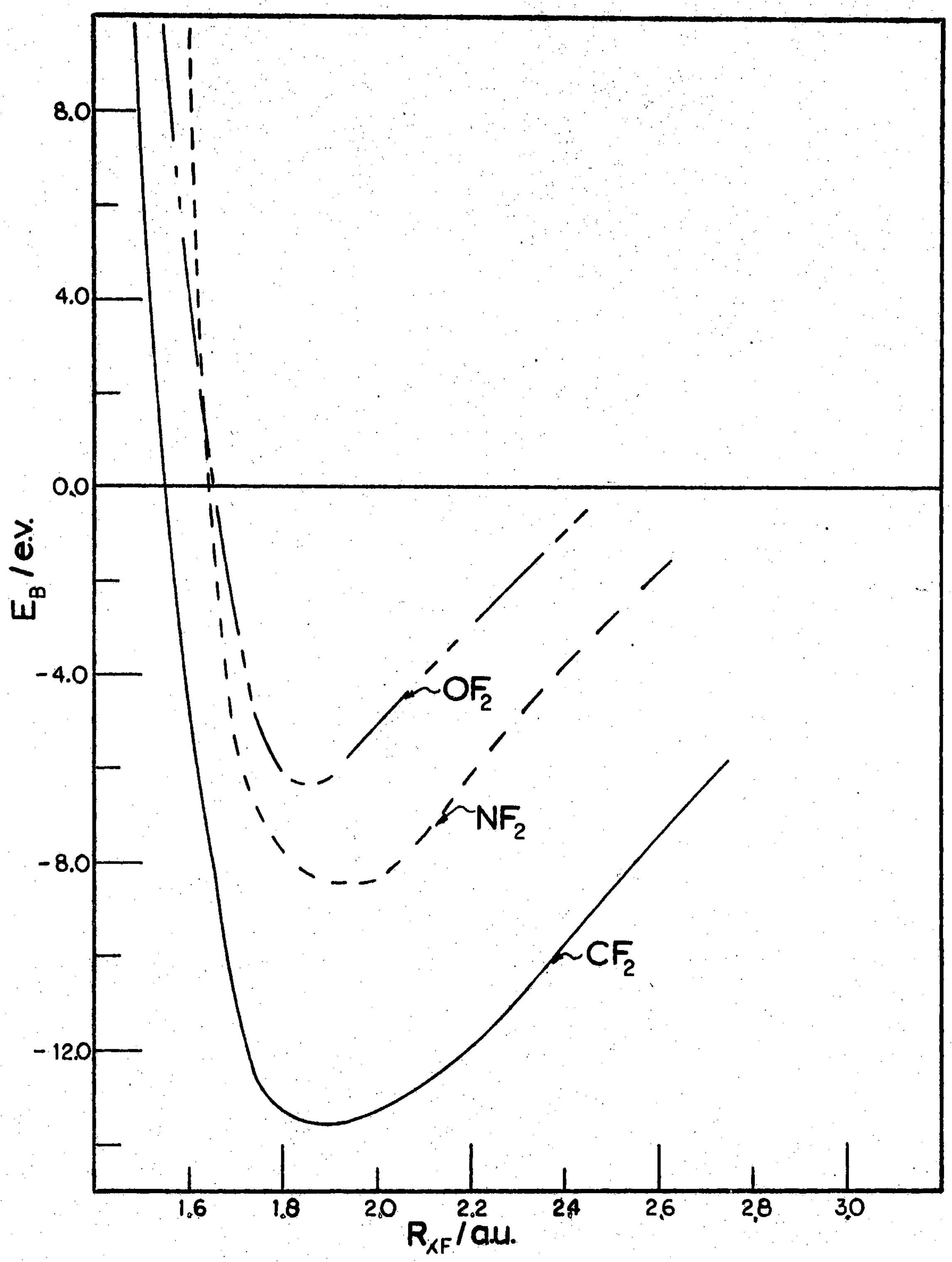


Figure 10. The Binding Energy Curves for OF_2, NF_2 and CF_2 - Set II.

TABLE XII

BINDING ENERGY VALUES FOR OF_2, NF_2 AND CF_2 - SET II.

R_{XF}(a.u.)	R_{XF}(Å)	E_B (OF_2) e.v.	E_B (NF_2) e.v.	E_B (CF_2) e.V.
1.50	0.794	−13.75	--	− 5.91
1.60	0.846	− 4.52	−11.83	3.59
1.70	0.899	2.65	5.77	10.71
1.80	0.952	6.06	7.88	13.41
1.90	1.005	6.22	8.46	13.56
2.00	1.058	5.06	8.38	13.22
2.10	1.111	4.04	7.42	12.71
2.20	1.164	3.04	6.15	11.94
2.30	1.217	2.03	5.00	11.02
2.40	1.270	0.96	3.89	9.68
2.50	1.323	− .15	2.86	8.48
2.60	1.375	--	1.87	7.39
2.70	1.428	--	--	6.38

TABLE XIII

LCAO-MO-SCF COEFFICIENTS FOR OF_2, NF_2 and CF_2 - SET II

	OF_2		NF_2		CF_2	
R_{XF}	C_o	C_f	C_N	C_F	C_C	C_F
1.50	.03891	.9883			-.04066	1.0054
1.60	.09327	.9682	-.00382	1.0010	-.03825	1.0065
1.70	.1634	.9354	.02847	.9915	-.03063	1.0064
1.80	.2297	.9009	.06802	.9774	-.01548	1.0037
1.90	.2856	.8697	.1122	.9595	.00509	.9986
2.00	.3295	.8449	.1562	.9404	.02977	.9915
2.10	.3630	.8264	.1976	.9213	.05720	.9824
2.20	.3885	.8140	.2351	.9034	.08602	.9723
2.30	.4086	.8058	.2662	.8891	.1147	.9617
2.40	.4248	.8015	.2910	.8793	.1419	.9516
2.50	.4384	.7997	.3123	.8714	.1668	.9426
2.60			.3306	.8653	.1896	.9345
2.70					.2102	.9275

.7 - .9 e.V. smaller than their experimental values. The calculated binding energies of HF, HCl, HBr and HI are all smaller than their experimental binding energies.[26] However, the calculated values for HCl, HBr and HI deviate from the experimental values by a constant fraction, 58%, whereas the calculated value for HF is 93% of its experimental value. Both the above data and the results of the XF_2 calculations seem to indicate that the extremely high ionization potential and electron affinity of the fluorine atom result in these unusually large calculated energy values.

Table XIV lists the LCAO coefficients for OF_2, NF_2, CF_2 and ClF[39] close to their calculated equilibrium bond lengths. The trend of these LCAO coefficients through the CF_2, NF_2 and OF_2 series is correct for both calculations. Both sets of calculations result in molecular orbitals which have LCAO coefficients indicating an extraordinarily high electron density on the fluorine atom of these XF_2 molecules. The Set I LCAO coefficients, exhibit this phenomenon to a lesser degree than the Set II coefficients. The electronegativity difference of the nuclei of the N-F and Cl-F bonds are about the same although the LCAO coefficients of the N-F molecular orbitals in each calculation indicate a much larger attraction of electrons for the fluorine atom than do the LCAO coefficients for the Cl-F molecular orbital. It appears as though these difluoride calculations may over-emphasize the repulsion of the two X electrons forcing the LCAO coefficient for fluorine to take an unusually large value when the electronic energy is minimized. Of course c_X would then be small due to the overlap condition. The greater variation in these XF_2 LCAO coefficients as a function of internuclear distance compared to this variation in the diatomic LCAO coefficients is not incongruous with the above explanation.

TABLE XIV

EQUILIBRIUM LCAO-MO-SCF COEFFICIENTS

	Set I		Set II	
Molecule	C_X	C_F	C_X	C_F
OF_2	.4941	.7231	.2856	.8697
NF_2	.3473	.8359	.1122	.9595
CF_2	.1417	.9517	.0051	.9986
	C_{CI}	C_F		
CIF	.4988	.7437		

The results of these four electron LCAO-MO-SCF calculations are also used to provide a basis of attack on the eight electron configuration interaction calculations, in which the significance of double bonding in OF_2 is investigated. This problem is discussed in the next chapter.

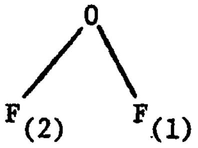
CHAPTER IV

THE CONFIGURATION INTERACTION CALCULATION

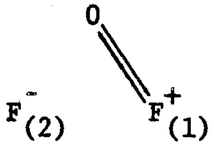
The significance of double bond-no bond resonance in OF_2 was investigated by means of a configuration interaction (CI) calculation[40] which is described in this chapter. A CI calculation is essentially the application of the linear variation method to a wave function which is approximated as a linear combination of Slater determinants. The CI wave function for OF_2 is approximated as

$$\psi = C_I D_I + C_{II} D_{II} + C_{III} D_{III} \tag{44}$$

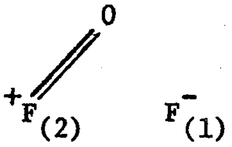
where the coefficients C_I, C_{II} and C_{III} are chosen such that the energy of OF_2 is minimized. The Slater determinants D_I, D_{II} and D_{III} correspond to the resonance structures



I



II



III

I, II and III respectively. The magnitude of the coefficients, C_{II} and C_{III}, with respect to C_I gives a measure of the significance of the D_{II} and D_{III} structures. The added stability calculated for OF_2 using the wave function described by Equation (44) compared with a calculation using $\psi = D_I$ alone, gives a measure of the effect of determinants D_{II}

and D_{III} on the molecular energy of OF_2.

The OF_2 molecule was chosen as the subject of the configuration interaction calculation because the most important form of π-bonding should occur through the DBNB resonance structures shown above. However multiple bonding may occur in NF_2 and CF_2 through use of a vacant or half-filled 2P orbital on carbon or nitrogen and a filled 2P orbital on a fluorine atom in addition to multiple bonding through DBNB resonance.

The Eight Electron Problem

Resonance structure I can be related to structure II in the following way. The two electrons in O-$F_{(2)}$ bond in structure I are localized on the $F_{(2)}$ atom forming an F^- ion in structure II. A localized pair of electrons on $F_{(1)}$ in structure I may be thought of as forming a π-bond in structure II using the vacated atomic orbital on oxygen. In resonance structure III, a localized pair of electrons on $F_{(2)}$ forms a π-bond with oxygen. Eight electrons are needed to describe these three resonance structures of OF_2 simultaneously in a configuration interaction wave function. Therefore eight electrons will be considered explicitly in this calculation while the effect of the remaining 18 electrons are introduced into the problem through nonpolarizable cores about the nuclei. The cores of OF_2 used in this calculation are represented schematically in Figure 11. The electronic configurations of the various cores in this CI calculation are the same as in the SCF problem except that a pair of electrons on each fluorine are considered explicitly in this eight electron problem whereas these electrons were part of the non-polarizable fluorine cores in the four electron SCF problem.

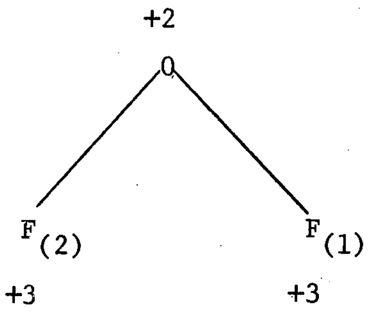


Figure 11. The Cores of OF_2 for the CI Calculation.

The eight electron Hamiltonian may be expressed as

$$H = \sum_{i=1}^{8} \left(-\frac{1}{2}\nabla_i^2 - \sum_{\alpha=1}^{3} V_{\alpha i}\right) + \sum_{i<j=1}^{8} \frac{1}{r_{ij}} + \sum_{\alpha<\beta=1}^{3} \frac{Z_{eff(\alpha)} Z_{eff(\beta)}}{R_{\alpha\beta}} \tag{45}$$

where the symbols have been defined in Chapter III and the $V_{\alpha i}$ represent the potentials of an electron about the O, $F_{(1)}$ and $F_{(2)}$ cores.

The wave function in Equation (44) is a linear combination of three 8 x 8 Slater determinants, each determinant having a form similar to D_I as expressed in Equation (46).

$$D_I = \frac{1}{\sqrt{8!}} \begin{vmatrix} \lambda_1(1)\lambda_2(1)\lambda_3(1)\lambda_4(1)\lambda_5(1)\lambda_6(1)\lambda_7(1)\lambda_8(1) \\ \lambda_1(2)\lambda_2(2)\lambda_3(2)\lambda_4(2)\lambda_5(2)\lambda_6(2)\lambda_7(2)\lambda_8(2) \\ \lambda_1(3)\lambda_2(3)\lambda_3(3)\lambda_4(3)\lambda_5(3)\lambda_6(3)\lambda_7(3)\lambda_8(3) \\ \lambda_1(4)\lambda_2(4)\lambda_3(4)\lambda_4(4)\lambda_5(4)\lambda_6(4)\lambda_7(4)\lambda_8(4) \\ \lambda_1(5)\lambda_2(5)\lambda_3(5)\lambda_4(5)\lambda_5(5)\lambda_6(5)\lambda_7(5)\lambda_8(5) \\ \lambda_1(6)\lambda_2(6)\lambda_3(6)\lambda_4(6)\lambda_5(6)\lambda_6(6)\lambda_7(6)\lambda_8(6) \\ \lambda_1(7)\lambda_2(7)\lambda_3(7)\lambda_4(7)\lambda_5(7)\lambda_6(7)\lambda_7(7)\lambda_8(7) \\ \lambda_1(8)\lambda_2(8)\lambda_3(8)\lambda_4(8)\lambda_5(8)\lambda_6(8)\lambda_7(8)\lambda_8(8) \end{vmatrix} \qquad (46)$$

where the spin orbitals, λ_i, are approximated as the product of a molecular orbital, ϕ_i, and a spin orbital, α or β, by the equations

$$\lambda_i = \phi_{\frac{i+1}{2}} \alpha \qquad \text{for odd values of i}$$

and

$$\lambda_i = \phi_{i/2} \beta \qquad \text{for even values of i.}$$

The basis set functions, ϕ_i, have been expressed in essentially two ways by using either an in-plane or an out-of-plane basis set of Slater atomic orbitals. These alternatives are represented schematically in Figure 12. The atomic orbitals and molecular orbitals used to build up each determinant, for both the in-plane and the out-of-plane cases are given in Table XV. For each basis set, π-bonding in OF_2 may occur through overlaps of the $2P_{y(0)}$ and $2P_{y(F_1)}$ Slater orbitals and the $2P_{z(0)}$ and $2P_{y(F_2)}$ Slater orbitals.

The σ- bonds in OF_2 have been described by normalized molecular orbitals of the form

$$\phi_2 = \left[\chi_{2P_{z(0)}} + \chi_{2P_{z(F_1)}}\right] \frac{1}{\sqrt{2 + 2S_{OF_{1(\sigma)}}}} \qquad (47)$$

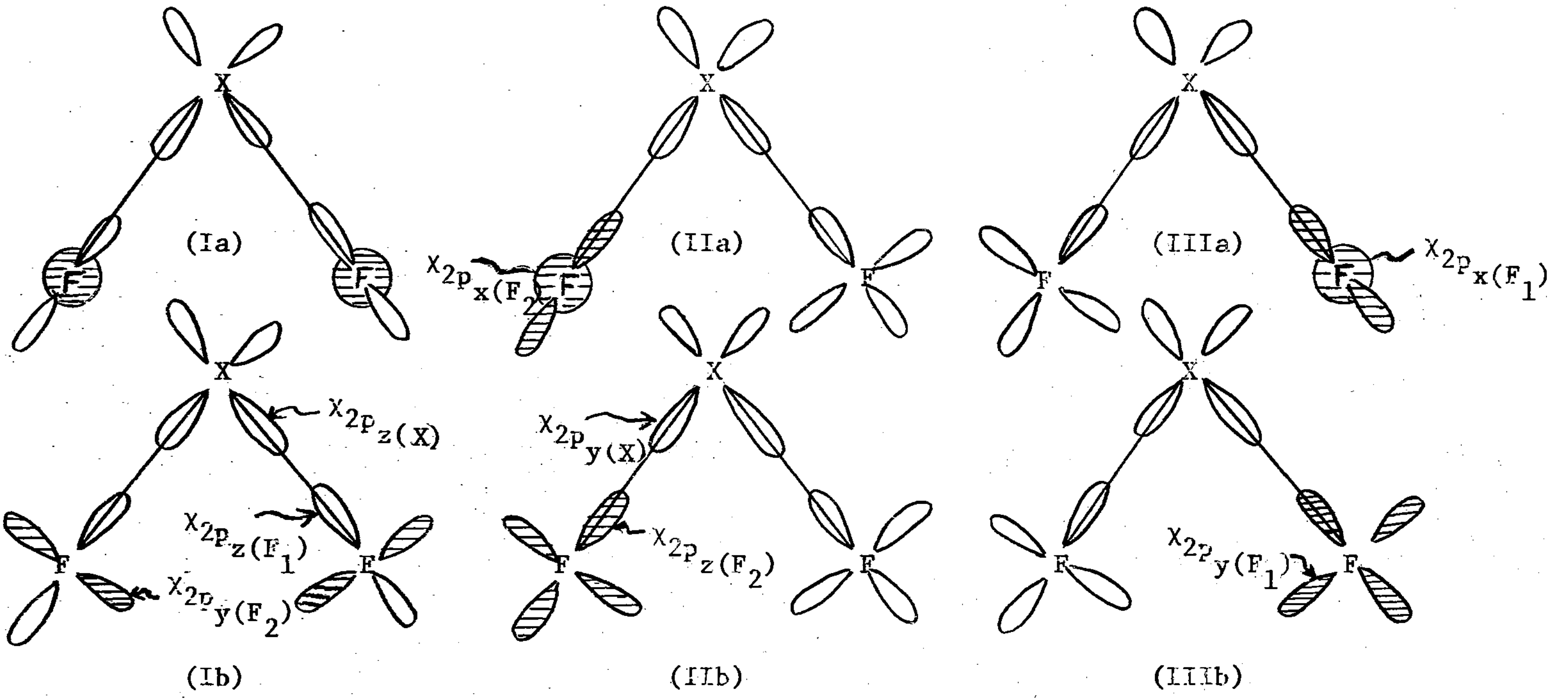


Figure 12. Atomic Orbital Basis Sets for the CI Calculation. (The Roman numerals in parenthesis correspond to the Slater determinats in equation (1), a- corresponds to the out-of-plane A.O. basis set and b corresponds to the in-plane basis set. The shaded orbitals contain two electrons while the other orbitals, which contain one electron, are used to form molecular orbitals.)

TABLE XV

ATOMIC AND MOLECULAR ORBITALS FOR THE CONFIGURATION INTERACTION PROBLEM

Atomic and molecular orbitals for the out-of-plane basis set:*

D_I:	D_{II}:	D_{III}:
$\phi_1 = X(F_2)$	$\phi_1 = X(F_2)$	$\phi_7 = N_4[Z(O) + y(F_2)]$
$\phi_2 = N_1[Z(O) + Z(F_1)]$	$\phi_2 = N_1[Z(O) + Z(F_1)]$	$\phi_8 = Z(F_1)$
$\phi_3 = N_2[y(O) + Z(F_2)]$	$\phi_5 = N_3[y(O) + y(F_1)]$	$\phi_3 = N_2[y(O) + Z(F_2)]$
$\phi_4 = X(F_1)$	$\phi_6 = Z(F_2)$	$\phi_4 = X(F_1)$

Atomic and molecular orbitals for the in-plane basis set:*

D_I:	D_{II}:	D_{III}:
$\phi_1 = y(F_2)$	$\phi_1 = y(F_2)$	$\phi_3 = N_2[y(O) + Z(F_2)]$
$\phi_2 = N_1[Z(O) + Z(F_1)]$	$\phi_2 = N_1[Z(O) + Z(F_1)]$	$\phi_4 = y(F_1)$
$\phi_3 = N_2[y(O) + Z(F_2)]$	$\phi_5 = N_3[y(O) + y(F_1)]$	$\phi_7 = N_4[Z(O) + y(F_2)]$
$\phi_4 = y(F_1)$	$\phi_6 = Z(F_2)$	$\phi_8 = Z(F_1)$

where:

$$N_1 = \frac{1}{\sqrt{2 + 2S_{OF_1(\sigma)}}} \quad \text{where } S_{OF_1(\sigma)} = S_{Z(O)Z(F_1)}$$

$$N_2 = \frac{1}{\sqrt{2 + 2S_{OF_2(\sigma)}}} \quad \text{where } S_{OF_2(\sigma)} = S_{y(O)Z(F_2)}$$

$$N_3 = \frac{1}{\sqrt{2 + 2S_{OF_1(\pi)}}} \quad \text{where } S_{OF_1(\pi)} = S_{y(O)y(F_1)}$$

$$N_4 = \frac{1}{\sqrt{2 + 2S_{OF_2(\pi)}}} \quad \text{where } S_{OF_2(\pi)} = S_{Z(O)y(F_2)}$$

---

*The above formulae have been expressed using the shorthand notation for Slater orbitals employed in Chapter III.

$$\phi_3 = \left[\chi_{2P_{y(0)}} + \chi_{2P_{z(F_2)}} \right] \frac{1}{\sqrt{2 + 2S_{OF_{2(o)}}}} \qquad (48)$$

Equations (47) and (48) are special cases of Equations (32) and (33) where $c_0 = c_F$. This equality of LCAO coefficients implies that the O-F bond is completely covalent. The LCAO-MO-SCF calculations for OF_2 presented in Chapter III resulted in orbital coefficients which indicated a greater ionic character for the O-F bond than would be expected on the basis of the electronegativities of the oxygen and the fluorine atoms. It seems reasonable to expect that constraining the LCAO coefficients as indicated in Equations (47) and (48) would tend to balance those effects in the calculation which tend to over-emphasize the ionic character of the O-F bond.

The π-molecular orbitals are also assumed covalent as

$$\phi_5 = \frac{1}{\sqrt{2 + 2S_{OF_1(\pi)}}} \left[\chi_{2P_{y(0)}} + \chi_{2P_{y(F_1)}} \right] \qquad (49)$$

$$\phi_7 = \frac{1}{\sqrt{2 + 2S_{OF_2(\pi)}}} \left[\chi_{2P_{z(0)}} + \chi_{2P_{y(F_2)}} \right] \qquad (50)$$

Two additional assumptions, similar to approximations given in Chapter III, are used to simplify these CI calculations. First, the OF_2 molecular angle is set at 90° rather than the experimentally determined value of 101.5°. Secondly, the overlap between atomic oribtals on nonadjacent atoms (the two fluorines) are assumed zero. The comments made in Chapter III concerning these assumptions also apply to this CI calculation.

Mathematical Formalism

A mathematical formalism for CI calculations has been worked out and is presented in the reference by Parr.[40] The energy corresponding to the approximate wave function given in Equation (44) may be determined by the solution of the secular determinant

$$\begin{vmatrix} H_{11} - \varepsilon S_{11} & H_{12} - \varepsilon S_{12} & H_{13} - \varepsilon S_{13} \\ H_{21} - \varepsilon S_{21} & H_{22} - \varepsilon S_{22} & H_{23} - \varepsilon S_{23} \\ H_{31} - \varepsilon S_{31} & H_{32} - \varepsilon S_{32} & H_{33} - \varepsilon S_{33} \end{vmatrix} = 0 \qquad (51)$$

where ε represents the electronic energy plus the nuclear repulsion energy of the molecule and

$$H_{ij} = \int D_i \, H \, D_j \, d\tau \qquad (52)$$

$$S_{ij} = \int D_i \, D_j \, d\tau \qquad (53)$$

where the integration in Equations (52) and (53) are carried out over all space and $d\tau = d\tau_1 d\tau_2 \cdots d\tau_8$. The subscripts of the various volume elements refer to the volume elements for each electron of the eight electron problem. Equation (51) may be expressed as

$$\left| H - \varepsilon S \right| = 0 \qquad (54)$$

where H and S are 3 x 3 symmetric matrices containing the H_{ij} and S_{ij} elements and ε represents the three roots of this secular determinant.

The CI coefficients, C_I, C_{II} and C_{III}, may be determined by solving for the eigenvectors of the secular equation

$$HC = \varepsilon SC. \qquad (55)$$

These eigenvectors can be obtained in a straightforward manner by solving the set of simultaneous equations

$$C_{11}(H_{11}-\varepsilon S_{11}) + C_{12}(H_{12}-\varepsilon S_{12}) + C_{13}(H_{13}-\varepsilon S_{13}) = 0 \quad (56)$$

$$C_{21}(H_{21}-\varepsilon S_{21}) + C_{22}(H_{22}-\varepsilon S_{22}) + C_{23}(H_{23}-\varepsilon S_{23}) = 0 \quad (57)$$

$$C_{31}(H_{31}-\varepsilon S_{31}) + C_{32}(H_{32}-\varepsilon S_{32}) + C_{33}(H_{33}-\varepsilon S_{33}) = 0. \quad (58)$$

Numerical values for H_{ij} and S_{ij} are substituted in Equations (56) through (58) along with the lowest root of the three eigenvalues of Equation (54). The CI coefficients corresponding to this lowest configuration interaction energy state, C_I, C_{II} and C_{III}, of Equation (44), may then be determined from these three equations.

The solutions of Equations (52) and (53) are straightforward but contain a large number of terms. Each 8 x 8 determinant is a sum of 64 terms, each term containing as factors expressions for the molecular and atomic orbitals occupied by the eight electrons. If the spin orbitals used in the calculation are orthonormal,

$$\int \lambda_i \lambda_j d\tau = \delta_{ij} , \quad (59)$$

where $\delta_{ij} = 0$ if $i \neq j$ and $\delta_{ij} = 1$ if $i = j$, then the equations given by Parr[1] can be used as most of the terms of Equations (52) and (53) integrate to zero.

In the OF_2 calculation the spin orbitals do not make up an orthonormal set. Rather than orthogonalize these spin orbitals and use the equations given by Parr,[40] Equations (52) and (53) were expanded and each term was examined individually to determine its value. This procedure was greatly simplified by use of a theorem mentioned by Roothaan.[28]

$$\frac{1}{N!}\int\left[\sum_{P}(-1)^{P}\prod_{i=1}^{8}\lambda_{i}(i)\right] H\left[\sum_{P}(-1)^{P}\prod_{i=1}^{8}\lambda_{i}^{'}(i)\right] d\tau_{1}\cdots d\tau_{8} =$$

$$\int\left[\lambda_{1}(1)\lambda_{2}(2)\cdots\lambda_{8}(8)\right] H\left[\sum_{P}(-1)^{P}\prod_{i=1}^{8}\lambda_{i}^{'}(i)\right] d\tau_{1}\cdots d\tau_{8} \qquad (60)$$

where $\sum\limits_{P}$ indicates a sum over all possible permutations, and $(-1)^{P}$ is +1 if the permutation is even and $(-1)^{P}$ is -1 if the permuation is odd. This theorem also holds for the overlap integral where H in Equation (60) may be taken as equal to one.

Semiempirical Integral Approximations

The semiempirical procedures used to evaluate the integrals resulting from expansion of the H_{ij} matrix elements are essentially the same as those employed in the LCAO-MO-SCF calculations discussed in Chapter III. Semiempirical integral values using the Set I integral approximations for the in-plane atomic orbital basis set of OF_2 are given in Table XVI. No table is included containing these values for the out-of-plane AO basis set as these are very similar, and in many cases identical, to those listed in Table XVI.

Core-Core Repulsion Terms

The core-core repulsions for this eight electron problem were obtained using the procedure explained in Chapter III. Figure 8 gives the values for Z_{eff} for the oxygen and fluorine atoms. Two atomic units were added to Z_{eff} for fluorine and one atomic unit was added to

TABLE XVI

SEMIEMPIRICAL INTEGRAL VALUES - SET I

One Electron Integrals:

$$\langle y(F_2) | -\frac{1}{2}\nabla^2 - V_{F_2+2} | y(F_2)\rangle = \langle z(F_2) | -\frac{1}{2}\nabla^2 - V_{F_2+2} | z(F_2)\rangle$$

$$= -I_{F}++$$

$$\langle y(F_1) | -\frac{1}{2}\nabla^2 - V_{F_1+1} | y(F_1)\rangle = \langle z(F_1) | -\frac{1}{2}\nabla^2 - V_{F_1+2} | z(F_1)\rangle$$

$$= -I_{F}++$$

$$\langle y(0) | V_{0}+ | y(0)\rangle = \langle z(0) | V_{0}+ | z(0)\rangle = +2\rho_{0+}$$

$$\langle y(F_2) | V_{0}+ | y(F_2)\rangle = \langle z(F_2) | V_{0}+ | z(F_2)\rangle = +2R_{OF_2}^{-1}$$

$$\langle y(F_1) | V_{0}+ | y(F_1)\rangle = \langle z(F_1) | V_{0}+ | z(F_1)\rangle = +2R_{OF_1}^{-1}$$

$$\langle y(F_2) | V_{F_1+2} | y(F_2)\rangle = \langle z(F_2) | V_{F_1+2} | z(F_2)\rangle = +3R_{FF}^{-1}$$

$$\langle y(F_1) | V_{F_2+2} | y(F_1)\rangle = \langle z(F_1) | V_{F_2+2} | z(F_1)\rangle = +3R_{FF}^{-1}$$

$$\langle z(0) | -\frac{1}{2}\nabla^2 + V_{0}+ | z(0)\rangle = \langle y(0) | -\frac{1}{2}\nabla^2 + V_{0}+ | y(0)\rangle = -I_{0+}$$

$$\langle z(0) | V_{F_1+2} | z(0)\rangle = \langle y(0) | V_{F_1+2} | y(0)\rangle = +3R_{OF_1}^{-1}$$

$$\langle z(0) | V_{F_2+2} | z(0)\rangle = \langle y(0) | V_{F_2+2} | y(0)\rangle = +3R_{OF_2}^{-1}$$

$$\langle y(F_2) | V_{F_2+2} | y(F_2)\rangle = \langle z(F_2) | V_{F_2+2} | z(F_2)\rangle = 3\rho_{F+2}$$

$$\langle z(F_1) | V_{F_1+2} | z(F_1)\rangle = \langle y(F_1) | V_{F_1+2} | y(F_1)\rangle = 3\rho_{F+2}$$

TABLE XVI (Continued)

Two Electron Integrals:

$$\langle Z(F_1)Z(F_1)|r_{12}^{-1}|Z(F_1)Z(F_1)\rangle = \langle y(F_1)y(F_1)|r_{12}^{-1}|y(F_1)y(F_1)\rangle = I_{F+2}$$
$$+ A_{F+2}$$

$$\langle Z(F_2)Z(F_2)|r_{12}^{-1}|Z(F_2)Z(F_2)\rangle = \langle y(F_2)y(F_2)|r_{12}^{-1}|y(F_2)y(F_2)\rangle = I_{F+2}$$
$$+ A_{F+2}$$

$$\langle Z(F_2)y(F_2)|r_{12}^{-1}|Z(F_2)y(F_2)\rangle = \langle y(F_1)Z(F_1)|r_{12}^{-1}|y(F_1)Z(F_1)\rangle = I_{F+2}$$
$$+ A_{F+2}$$

$$\langle Z(0)Z(F_1)|r_{12}^{-1}|Z(0)Z(F_1)\rangle = \langle y(0)Z(F_1)|r_{12}^{-1}|y(0)Z(F_1)\rangle = R_{OF_1}^{-1}$$

$$\langle Z(0)y(F_1)|r_{12}^{-1}|Z(0)y(F_1)\rangle = \langle y(0)y(F_1)|r_{12}^{-1}|y(0)y(F_1)\rangle = R_{OF_1}^{-1}$$

$$\langle Z(0)y(F_2)|r_{12}^{-1}|Z(0)y(F_2)\rangle = \langle Z(0)Z(F_2)|r_{12}^{-1}|Z(0)Z(F_2)\rangle = R_{OF_2}^{-1}$$

$$\langle y(0)y(F_2)|r_{12}^{-1}|y(0)y(F_2)\rangle = \langle y(0)Z(F_2)|r_{12}^{-1}|y(0)Z(F_2)\rangle = R_{OF_2}^{-1}$$

$$\langle y(F_2)Z(F_1)|r_{12}^{-1}|y(F_2)Z(F_1)\rangle = \langle Z(F_2)y(F_1)|r_{12}^{-1}|Z(F_2)y(F_1)\rangle = R_{FF}^{-1}$$

$$\langle Z(0)Z(0)|r_{12}^{-1}|Z(0)Z(0)\rangle = \langle y(0)y(0)|r_{12}^{-1}|y(0)y(0)\rangle = I_{0^+} + A_{0^+}$$

$$\langle Z(0)y(0)|r_{12}^{-1}|Z(0)y(0)\rangle = I_{0^+} + A_{0^+}$$

$$\langle Z(0)y(0)|r_{12}^{-1}|y(0)Z(0)\rangle = 0.06040\ (I_{0^+} + A_{0^+})$$

$$\langle Z(F_1)y(F_1)|r_{12}^{-1}|y(F_1)Z(F_1)\rangle = 0.06040\ (I_{F+2} + A_{F+2})$$

$$\langle Z(F_2)y(F_2)|r_{12}^{-1}|y(F_2)Z(F_2)\rangle = 0.06040\ (I_{F+2} + A_{F+2})$$

Z_{eff} for oxygen to compensate for the fact that the cores of oxygen and fluorine have formal charges of +2 and +3 in this calculation.

Calculation of Binding Energy

The method used to calculate the binding energy corresponding to the process

$$0 + 2F \longrightarrow OF_2$$

is analogous to the procedure described in Chapter III. The processes involved, with their energy changes in parenthesis, are given below:

$$0 + 2F \longrightarrow O_V + 2F_V \qquad (P^o_O + 2P^o_F)$$

$$O_V + 2F_V \longrightarrow O_V^{+2} + 2F_V^{+3} \qquad (2I_{V(F)} + 2I_{V(F^+)} + 2I_{V(F^{+2})}$$

$$+ I_{V(O)} + I_{V(O^+)})$$

$$O_V^{+2} + 2F_V^{+3} \longrightarrow F_V^{+3} \cdot O_V^{+3} \cdot F_V^{+3} \qquad (E_{nuc})$$

$$F_V^{+3} \cdot O_V^{+2} \cdot F_V^{+3} + 8_e^- \longrightarrow OF_2 \qquad (\mathcal{E})$$

The binding energy, E_B, is then given by

$$E_B = P^o_O + 2P^o_F + 2I_{V(F)} + 2I_{V(F^+)} + 2I_{V(F^{++})} + I_{V(O)} + I_{V(O^+)} +$$
$$E_{nuc} + \mathcal{E}$$

The symbols and processes given above have been described in Chapter III.

Overlap Integrals

Numerical values for the overlap integrals containing Slater orbitals were obtained from Mulliken's paper[37] as described in

Chapter III.

Results

The eight electron calculations, as described earlier in this chapter, were attempted using the Set II integral approximations. The results of these calculations (for both the out-of-plane and the in-plane AO basis sets) were unsatisfactory in that they predicted an unstable OF_2 molecule with respect to the separated atoms.

The calculations using the Set I integral approximations predicted very reasonable values for the binding energy of the OF_2 molecule. Figure 13 illustrates the binding energy versus bond distance curves for the symmetric stretch of OF_2 for both the in-plane and the out-of-plane AO basis sets. Figure 14 shows the analogous curves for the antisymmetric stretching mode of OF_2. The calculated equilibrium binding energies, 5.683 e.V. for the out-of-plane set and 4.015 e.V. for the in-plane set, agree quite well with the experimental binding energy of 3.9 e.V. The calculated equilibrium bond distances for the out-of-plane and the in-plane basis sets are 1.03 Å and 1.09 Å respectively. These bond lengths are considerably smaller than the experimentally determined value of 1.38 Å.

Tables XVII and XVIII contain data for the CI calculation using the out-of-plane AO basis set. Table XVII lists values of the binding energy for OF_2 at various internuclear distances corresponding to the symmetric and antisymmetric stretch. $E_{B(I)}$ corresponds to the binding energy calculated using the wave function

$$\psi' = D_I \tag{61}$$

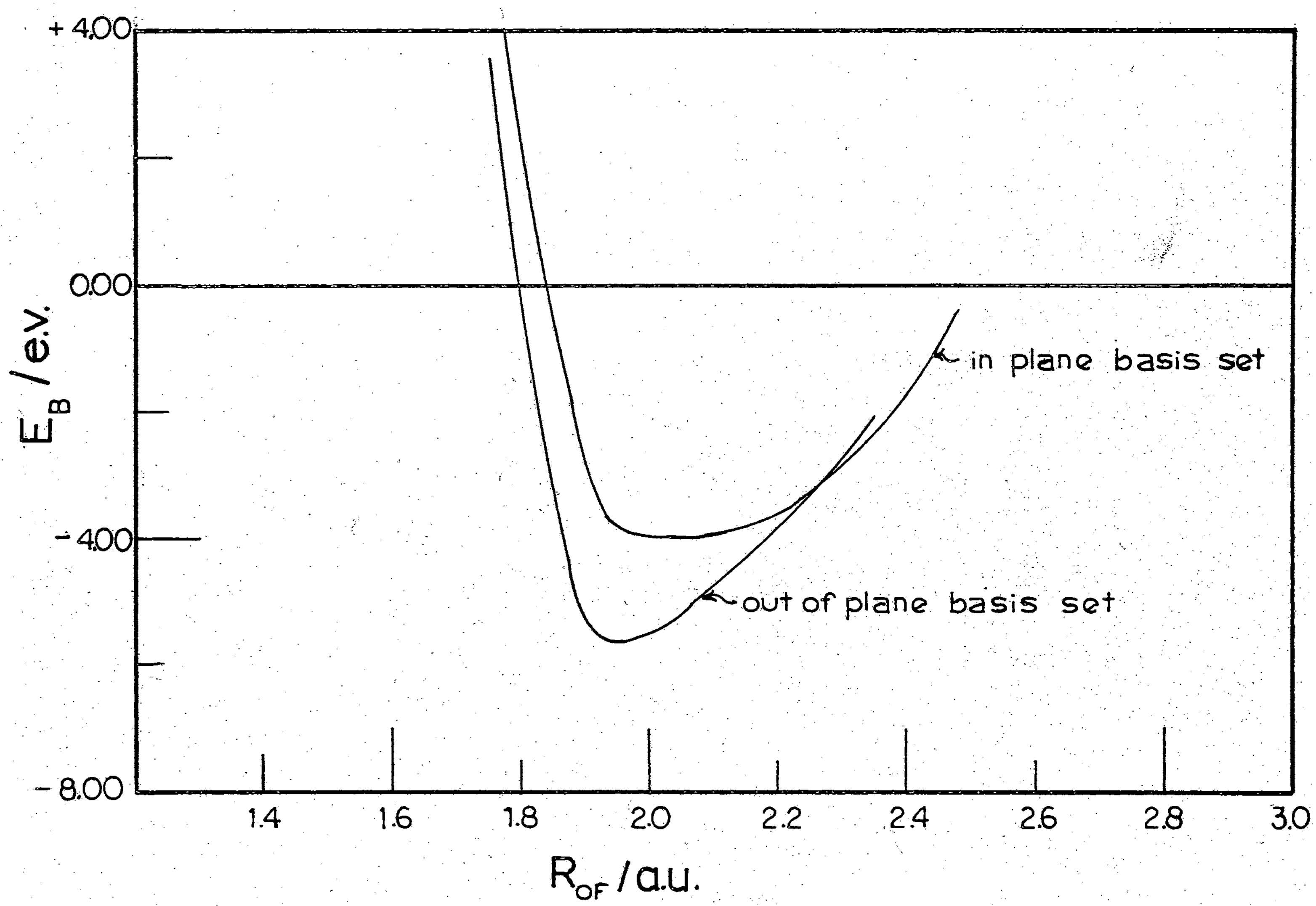


Figure 13. The Configuration Interaction Binding Curves for OF_2 - Symmetric Stretch.

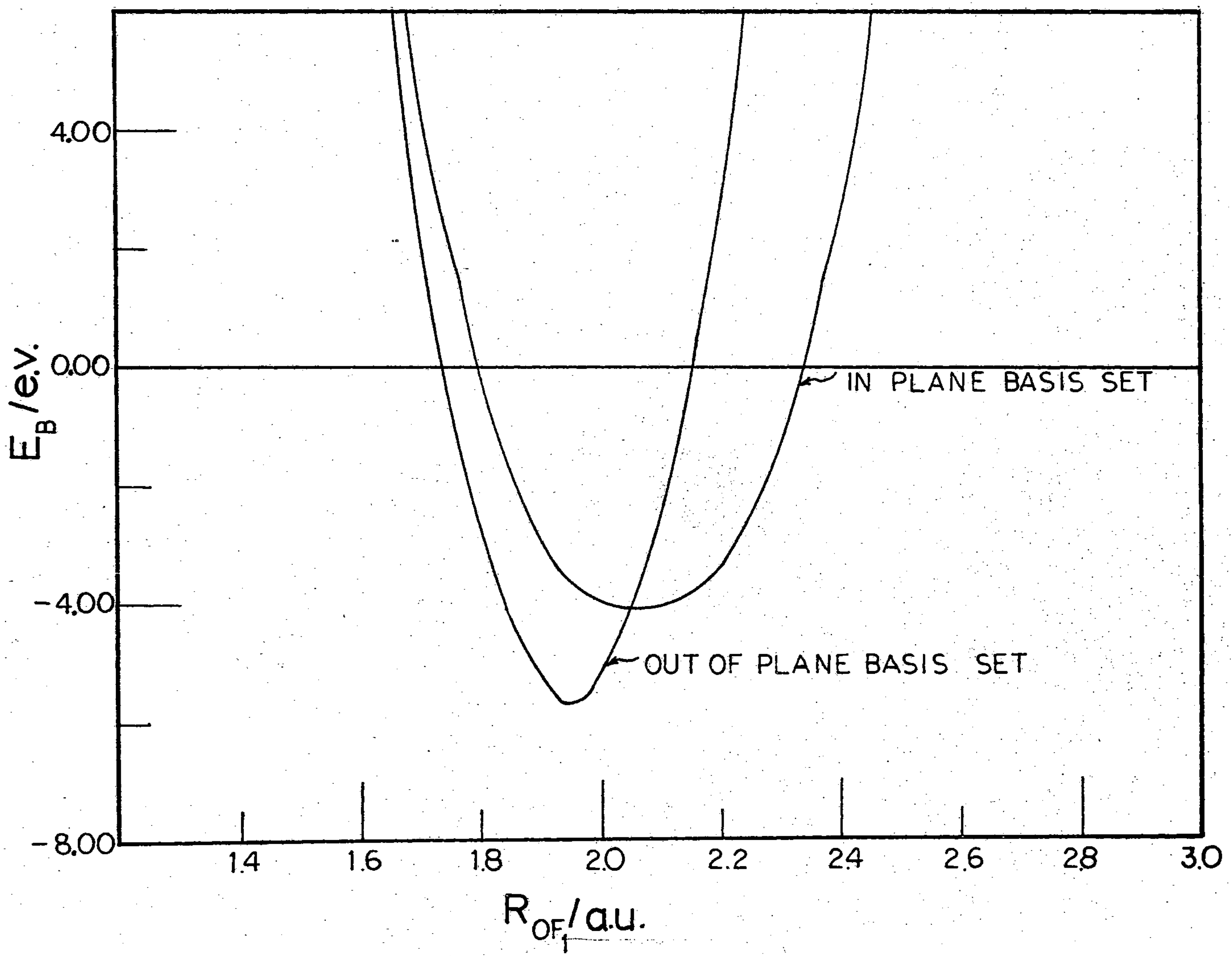


Figure 14. The Configuration Interaction Binding Energy Curves for OF_2 - Antisymmetric Stretch.

TABLE XVII

BINDING ENERGIES -- OUT-OF-PLANE ATOMIC ORBITAL BASIS SET

R_{OF}(a.u.)	$E_{B(I)}$(e.V.)	$E_{B(CI)}$(e.V.)
Symmetric Stretch:		
1.55	-34.602	-34.594
1.65	-18.183	-18.175
1.75	-3.543	-3.535
1.85	3.005	3.013
1.95	5.675	5.683
2.05	5.210	5.218
2.15	4.470	4.479
2.25	3.443	3.451
2.35	2.094	2.102

R_{OF_1}(a.u.)	R_{OF_2}(a.u.)	$E_{B(I)}$(e.V.)	$E_{B(CI)}$(e.V.)
Antisymmetric Stretch:			
1.55	2.35	-16.253	-16.245
1.65	2.25	-7.369	-7.361
1.75	2.15	0.465	0.473
1.85	2.05	4.109	4.117
1.95	1.95	5.675	5.683
2.05	1.85	4.109	4.117
2.15	1.75	0.465	0.473
2.25	1.65	-7.369	-7.361
2.35	1.55	-16.253	-16.245

TABLE XVIII

CONFIGURATION INTERACTION COEFFICIENTS -- OUT-OF-PLANE ATOMIC ORBITAL BASIS SET

R_{OF}(a.u.)	C_I	C_{II}	C_{III}
Symmetric Stretch:			
1.55	.9999	-.01164	-.01164
1.65	.9999	-.01037	-.01037
1.75	.9999	-.009673	-.009673
1.85	.9999	-.009403	-.009403
1.95	.9999	-.009428	-.009428
2.05	.9999	-.009561	-.009561
2.15	.9999	-.009813	-.009813
2.25	.9999	-.01017	-.01017
2.35	.9999	-.01065	-.01065

R_{OF_1}(a.u.)	R_{OF_2}(a.u.)	C_I	C_{II}	C_{III}
Antisymmetric Stretch:				
1.55	2.35	.9999	-.01252	-.009889
1.65	2.25	.9999	-.01133	-.009378
1.75	2.15	.9999	-.01047	-.009127
1.85	2.05	.9999	-.009842	-.009148
1.95	1.95	.9999	-.009428	-.009428
2.05	1.85	.9999	-.009148	-.009842
2.15	1.75	.9999	-.009127	-.01047
2.25	1.65	.9999	-.009378	-.01133
2.35	1.55	.9999	-.009889	-.01252

which corresponds to a resonance structure for OF_2 with no provision for multiple bonding. $E_{B(CI)}$ denotes the configuration interaction binding energy of OF_2 which corresponds to the wave function given by Equation (44). Table XVIII lists the configuration interaction coefficients corresponding to the values of $E_{B(CI)}$ given in Table XVII.

Tables XIX through XXII contain data for calculations utilizing the in-plane AO basis set. Tablex XIX and XX contain values of $E_{B(I)}$ and $E_{B(CI)}$ for the symmetric and antisymmetric configurations respectively. Tables XXI and XXII list the configuration interaction coefficients for the symmetric and antisymmetric stretching geometries of OF_2.

TABLE XIX

BINDING ENERGIES -- IN-PLANE ATOMIC ORBITAL BASIS SET -- SYMMETRIC STRETCH

R_{OF}(a.u.)	$E_{B(I)}$	$E_{B(CI)}$
1.57	−39.483	−37.308
1.67	−19.070	−17.865
1.77	−5.169	−4.544
1.87	1.191	1.460
1.97	3.810	3.932
2.07	3.996	4.015
2.17	3.750	3.755
2.27	3.043	3.065
2.37	2.012	2.091
2.47	0.606	0.748
2.57	−0.767	−0.563

TABLE XX

BINDING ENERGIES -- IN-PLANE ATOMIC ORBITAL BASIS SET -- ANTISYMMETRIC STRETCH

R_{OF_1} (a.u.)	R_{OF_2} (a.u.)	$E_{B(I)}$ e.V.	$E_{B(CI)}$ e.V.
1.57	2.57	−20.307	−19.717
1.67	2.47	− 9.376	− 9.052
1.77	2.37	− 1.667	− 1.447
1.87	2.27	2.077	2.167
1.97	2.17	3.76857	3.80664
1.98	2.16	3.79494	3.82893
1.99	2.15	3.85368	3.88413
2.00	2.14	3.91405	3.94124
2.01	2.13	3.92193	3.94776
2.02	2.12	3.92873	3.95320
2.03	2.11	3.93607	3.95864
2.04	2.10	3.97632	3.99807
2.05	2.09	3.98012	4.00133
2.06	2.08	3.98203	4.00242
2.07	2.07	3.99589	4.01520
2.08	2.06	3.98203	4.00242
2.09	2.05	3.98012	4.00133
2.10	2.04	3.97632	3.99807
2.11	2.03	3.93607	3.95864
2.12	2.02	3.92873	3.95320
2.13	2.01	3.92193	3.94776
2.14	2.00	3.91405	3.94124

TABLE XX (Continued)

R_{OF_1} (a.u.)	R_{OF_2} (a.u.)	$E_{B(I)}$ e.V.	$E_{B(CI)}$ e.V.
2.15	1.99	3.85368	3.88413
2.16	1.98	3.79494	3.82893
2.17	1.97	3.76857	3.80664
2.27	1.87	2.077	2.167
2.37	1.77	-1.667	- 1.447
2.47	1.67	-9.376	- 9.052
2.57	1.57	-20.307	-19.717

TABLE XXI

CONFIGURATION INTERACTION COEFFICIENTS -- IN-PLANE ATOMIC ORBITAL BASIS SET -- SYMMETRIC STRETCH

R_{OF}	C_I	C_{II}	C_{III}
1.57	.7550	.2848	.2848
1.67	.8498	.2017	.2017
1.77	.9134	.1370	.1370
1.87	.9556	.08764	.08764
1.97	.9816	.05341	.05341
2.07	1.0031	.02110	.02110
2.17	1.0177	-.003830	-.003830
2.27	1.0278	-.02392	-.02392
2.37	1.0358	-.04169	-.04169
2.47	1.0408	-.05461	-.05461
2.57	1.0452	-.06691	-.06691

TABLE XXII

CONFIGURATION INTERACTION COEFFICIENTS -- IN-PLANE ATOMIC ORBITAL BASIS SET -- ANTISYMMETRIC STRETCH

R_{OF_1}	R_{OF_2}	C_I	C_{II}	C_{III}
1.57	2.57	.9433	.2098	-.02874
1.67	2.47	.9715	.1472	-.02373
1.77	2.37	.9881	.1012	-.01806
1.87	2.27	.9977	.06566	-.007951
1.97	2.17	1.0005	.04379	.005770
1.99	2.15	1.0013	.03848	.008730
2.01	2.13	1.0025	.03308	.01082
2.03	2.11	1.0027	.02939	.01404
2.05	2.09	1.0022	.02582	.01889
2.07	2.07	1.0031	.02110	.02110
2.09	2.05	1.0022	.01889	.02582
2.11	2.03	1.0027	.01404	.02939
2.13	2.01	1.0025	.01082	.03308
2.15	1.99	1.0013	.008730	.03848
2.17	1.97	1.0005	.005770	.04379
2.27	1.87	.9977	-.007951	.06566
2.37	1.77	.9881	-.01806	.1012
2.47	1.67	.9715	-.02373	.1472
2.57	1.57	.9433	-.02874	.2098

Tables XVII, XIX and XX illustrate that $E_{B(I)} < E_{B(CI)}$ for all the geometrical configurations calculated. This is to be expected since the wave function in Equation (61) is a special case of the more general configuration interaction wave function. This latter wave function should be a better approximation to the "true" wave function than the single determinant wave function, ψ'. In Chapter V the significance of this increase in binding energy upon introducing D_{II} and D_{III} into the OF_2 wave function will be examined.

The CI coefficients listed in Table XVIII illustrate that C_I is much greater than C_{II} and C_{III} for all the geometrical configurations listed. This is reflected energetically in the fact that the configuration interaction energy is never more than 0.01 e.V. larger than $E_{B(I)}$.

For the in-plane basis set the determinants D_{II} and D_{III} are more important in Equation (44) than they are for the out-of-plane basis set. For the geometrical configuration where both bonds are about 0.25 Å shorter than the calculated equilibrium bond lengths, the ratio, $C_{II}/C_I = C_{III}/C_I = 0.37$. As the bonds are stretched toward equilibrium this ratio becomes smaller, as one might anticipate. As D_{II} and D_{III} become less important in the CI wave function, the absolute magnitude of the difference, $E_{B(CI)}-E_{B(I)}$ becomes smaller.

For the antisymmetric stretching mode where for example, the $O\text{-}F_{(1)}$ bond is compressed and the $O\text{-}F_{(2)}$ bond is stretched from equilibrium by the same amount, $C_{II} > C_{III}$; the more one distorts the molecule from equilibrium in this manner, the more important DBNB resonance structure II becomes relative to resonance structures I and III. When the $O\text{-}F_{(1)}$ bond is about 0.25 Å shorter than the calculated equilibrium bond length the ratio of $C_{II}/C_I = 0.22$. In Chapter V the significance of these CI coefficients, which are a measure of the extent of DBNB resonance in OF_2, is discussed.

CHAPTER V

DISCUSSION OF RESULTS

The data obtained from the molecular orbital calculations in Chapter IV are analyzed in this chapter to determine whether the model employed to describe DBNB resonance can explain the frequency inversion one observes in OF_2. This frequency inversion appears to be the most striking physical manifestation of DBNB resonance (and/or non-bonded interaction) in the OF_2 molecule.

The fundamental frequencies of OF_2 are related to the general valence force constants through the equations:[10]

$$\lambda_1 + \lambda_2 = \left(1 + \frac{2m_F}{m_o} \cos^2 \frac{\alpha}{2}\right) \frac{f_r + f_{rr}}{m_F} + 2\left(1 + \frac{2m_F}{m_o} \sin^2 \frac{\alpha}{2}\right) \frac{f_\alpha}{m_F r^2} \tag{62}$$

$$\lambda_1 \lambda_2 = 2\left(1 + \frac{2m_F}{m_o}\right) \frac{f_r + f_{rr}}{m_F^2} \frac{f_\alpha}{r^2} \tag{63}$$

$$\lambda_3 = \left(1 + \frac{2m_F}{m_o} \sin^2 \frac{\alpha}{2}\right) \frac{f_r - f_{rr}}{m_F} \tag{64}$$

These equations are derived by solving the vibrational problem using the potential energy function given in Equation (7). Equations (62) and (63) have been simplified by setting the bond-angle interaction constant, $f_{r\alpha}$, at zero, although Equation (64) is exact within the harmonic oscillator approximation. The variables α and r represent the equilibrium molecular angle and bond length for OF_2 while m_o and m_F indicate the masses of the oxygen and fluorine atoms respectively. The force constant notation has been defined in Chapter II. The vibrational frequencies, ν_i, are related to the λ_i by the equation

$$\lambda_i = 4\pi^2\nu_i^2 \qquad (65)$$

Inspection of Equations (62) through (64) indicate that a positive bond-bond interaction constant, f_{rr}, would tend to lower the value of the antisymmetric stretching frequency, ν_3 , while it would tend to increase ν_1, the symmetric stretching frequency. A delocalization of electrons in OF_2, such as DBNB resonance, would manifest itself in a positive bond-bond interaction constant which, if large enough, would cause ν_1 to have a larger value than ν_3. In molecules where f_{rr} is nearly zero, such as H_2O, this frequency inversion is not observed. The next several paragraphs indicate how a value for this bond-bond interaction constant is obtained from the energy data of the MO calculations presented in Chapter IV. This value is then compared with the interaction constant determined experimentally from the fundamental frequencies of OF_2.

In Chapter IV the results of two MO calculations are given for both AO basis sets presented. Those energy values corresponding to the single determinantal wave function, denoted by $E_{B(I)}$, approximate energy values for an OF_2 molecule in which the binding electrons are localized in their respective bonds. Delocalization effects are explicitly entered into the calculation through the determinants D_{II} and D_{III}

in the CI wave function. Binding energies corresponding to the CI wave function were denoted by $E_{B(CI)}$ in Chapter IV. The bond-bond interaction force constant for OF_2 may be determined by considering the change in binding energy of OF_2 as the molecule is displaced from equilibrium. The quantities $\Delta E_{B(I)}$ and $\Delta E_{B(CI)}$ are defined by Equations (66) and (67),

$$\Delta E_{B(I)} = E^{o}_{B(I)} - E_{B(I)} \tag{66}$$

and

$$\Delta E_{B(CI)} = E^{o}_{B(CI)} - E_{B(CI)} \tag{67}$$

where $E^{o}_{B(I)}$ and $E^{o}_{B(CI)}$ are the single configuration and the CI energies for the equilibrium geometry of OF_2. Figure 15 illustrates a schematic drawing of the quantities $\Delta E_{B(I)}$ and $\Delta E_{B(CI)}$ as a function of the antisymmetric stretching normal coordinate, Q_3.

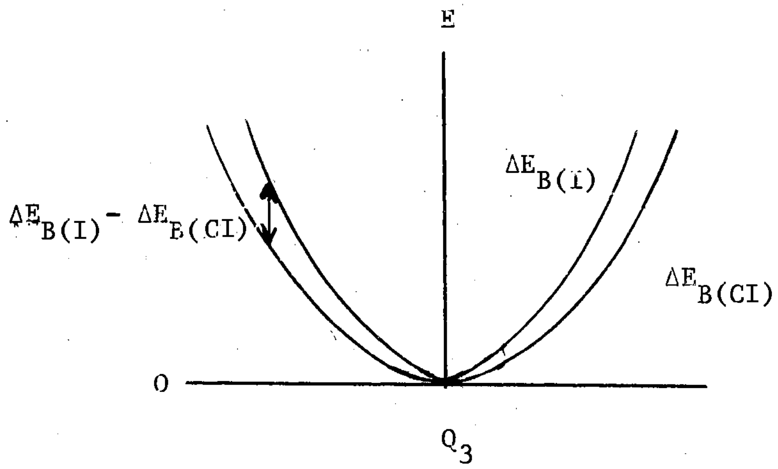


Figure 15. Schematic Drawing of the Quantities $\Delta E_{B(I)}$ and $\Delta E_{B(CI)}$ as a Function of the Normal Coordinate, Q_3.

The change in the potential energy of OF_2 as the molecule vibrates in its antisymmetric stretching mode may be expressed as

$$\Delta V = \frac{1}{2} f_r(\Delta r_1^2 + \Delta r_2^2) + f_{rr} \Delta r_1 \Delta r_2 \quad . \qquad (68)$$

For this normal mode $\Delta r = \Delta r_1 = -\Delta r_2$ and Equation (68) may be simplified to

$$\Delta V = f_r \Delta r^2 - f_{rr} \Delta r^2 \; . \qquad (69)$$

The quantities $\Delta E_{B(I)}$ and $\Delta E_{B(CI)}$, which measure this change in energy for the calculations using the wave functions given in Chapter IV may be expressed as

$$\Delta E_{B(I)} = f_r'\Delta r^2 - f_{rr}' \Delta r^2 \qquad (70)$$

and

$$\Delta E_{B(CI)} = f_r \Delta r^2 - f_{rr} \Delta r^2 \qquad (71)$$

The quantities f_r' and f_{rr}' represent force constants for energy calculations in which no provision has been included for delocalization of electrons. The force constants f_r and f_{rr} correspond to energy calculations in which electron delocalization effects, in the form of DBNB resonance, have been provided for in addition to the localized effects illustrated by the quantities in Equation (70).

The difference

$$\Delta E_{B(I)} - \Delta E_{B(CI)} = (f_r' - f_r)\Delta r^2 + (f_{rr} - f_{rr}')\Delta r^2 \qquad (72)$$

is illustrated in Figure 15. The equality of f_r and f_r' is not guaranteed because the addition of determinants D_{II} and D_{III} to the wave function described by D_I results in added stability calculated for OF_2.

This stability may be reflected in stronger O-F bonds so that one may state that $f'_r \leq f_r$ or

$$f'_r - f_r = \Delta f_r \leq 0$$

Rearranging Equation (72) results in the equation

$$\frac{\Delta E_{B(I)} - \Delta E_{B(CI)}}{\Delta r^2} - \Delta f_r = f_{rr} - f'_{rr} \tag{73}$$

The first term on the left-hand side of this equation is positive so that one may write the expression

$$\frac{\Delta E_{B(I)} - \Delta E_{B(CI)}}{\Delta r^2} \leq f_{rr} - f'_{rr} = f_d \tag{74}$$

For convenience the difference, $f_{rr} - f'_{rr}$, is denoted by f_d.

The quantity, f'_{rr}, measures the interaction constant essentially of a σ- bonded system containing localized electrons. The constant, f_{rr}, measures contributions to the interaction constant from DBNB resonance as well as from the localized system of electrons. Theoretically the quantity, f_d, would be the contribution to the bond-bond interaction constant due to electron delocalization of the DBNB resonance type. Theoretical values of f_d as determined from the data presented in Chapter IV using the term on the left-hand side of expression (74) are given in Table XXIII along with the displacements from equilibrium at which these quantities were calculated. The displacements chosen are large enough such that the difference, $\Delta E_{B(I)} - \Delta E_{B(CI)}$, was significant, and are small enough such that they correspond roughly to the size of the displacements expected for an O-F bond in the Q_3 coordinate.

TABLE XXIII

THEORETICAL VALUES FOR f_d

r(Å)	$f_d \times 10^{-5}$ dynes/cm
In Plane Atomic Orbital Basis Set:	
0.02116	1.166
0.02645	1.181
0.03174	1.036
0.03703	0.920
0.04232	0.996
0.04761	1.037
0.05290	1.073
Out-of-Plane Atomic Orbital Basis Set:	
0.0529	0.000

For the out-of-plane basis set, only one value is entered in Table XXIII, but it is representative of all the points calculated. These calculations predict a value of zero for f_d, resulting from the fact that the difference $E_{B(I)} - E_{B(CI)}$ is constant for all the antisymmetric geometries calculated for OF_2.

The values listed for the in-plane calculation predict a value of 1.058×10^5 dyne/cm for the quantity, f_d, this value being an average of those listed in Table XXIII. Thus the model employed in this calculation of the binding energy for OF_2 predicts a large positive contribution to the bond-bond interaction constant as a result of DBNB resonance. Such a contribution could partially explain why a positive bond-bond interaction constant, which Linnett and Hoare[22] state as a characteristic of triatomic molecules with delocalized electrons, is calculated for OF_2 from the frequency data.

Use of expression (74), coupled with a reasonable estimate of f'_{rr}, allows a calculation of the interaction constant, f_{rr}, which can be compared with experimental data. If $f'_{rr} \geqslant 0$ expression (74) may be written as

$$\frac{\Delta E_{B(I)} - \Delta E_{B(CI)}}{\Delta r^2} \leqslant f_{rr} \qquad (75)$$

If this is the case, the values listed for f_d in Table XXIII should provide a reasonable estimate of a lower limit for the bond-bond interaction constant. If $f'_{rr} < 0$ it is unlikely that it will have a large absolute magnitude judging from the results of force constant calculations for essentially σ-bonded triatomic molecules. Table XXIV list some of these molecules and their corresponding interaction constants. It seems unlikely that f'_{rr} would have a value larger in absolute magnitude than any listed in Table XXIV. If this is the case, expression (75) should be approximately correct.

TABLE XXIV

BOND-BOND INTERACTION CONSTANTS FOR SEVERAL TRIATOMIC MOLECULES

Molecule	H_2O	H_2S	H_2S_e	H_gCl_2	H_gBr_2	HgI_2
f'_{rr}	-.201	-.219	-.249	-.058	-.0905	-.0912

Values taken from reference (22). (Constants in dynes/cm x 10^{-5}.)

The possible experimental values for f_{rr} of OF_2, calculated by Duchesne and Burnelle,[23] have been presented in Figure 6 as a function of $f_{r\alpha}$, the bond-angle interaction constant. Assuming that the equality in expression (75) is approximately correct our calculated value of f_{rr}, 1.058×10^5 dyne/cm, represents allowed solutions of 0.35×10^5 and 2.2×10^5 dyne/cm for $f_{r\alpha}/r$. Duchesne and Burnelle list representative values of f_{rr} and $f_{r\alpha}/r$ of 1.1×10^5 and 0.38×10^5 dyne/cm for OF_2, although they state no reason for this choice over other possible solutions. This excellent agreement, in view of the approximations heretofore made and the fact that the experimental f_{rr} also includes contributions from the non-bonded interaction between the fluorines to some extent, is probably fortuitous, but the reasonableness of the theoretical quantity, f_d, is clearly demonstrated.

Linnett and Hoare[22] have demonstrated that a large non-bonded interaction between the fluorines in OF_2 can result in a major contribution to the large positive experimental value for f_{rr} in OF_2. Equation (11) illustrates this correspondence between F and f_{rr}. Assuming a potential energy function containing both F and f_{rr}, these authors conclude that the non-bonded interaction in OF_2 cannot completely explain the large positive f_{rr}. For example, assuming that $F = 2 \times 10^5$ dyne/cm, which seems reasonable compared to other fluorine molecules in which DBNB resonance is not expected to be as significant as in OF_2, a set of force constant solutions with reasonable values for f_r, f_α and $f_{r\alpha}$ could exhibit a value of f_{rr}, of $+ 0.6 \times 10^5$ dyne/cm, which should measure essentially bond-bond interaction.

The model employed here indicates that a solution with f_{rr} of this magnitude and sign may be explained by significant DBNB resonance in OF_2. When sufficient data becomes available to determine all the force constants of the GVFF, modified by a proper non-bonded interaction, a more definite conclusion about the significance of f_{rr} may be drawn.

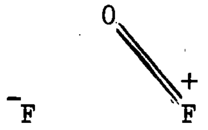
The assumption that OF_2 contains only localized electrons, in the light of these calculations, seems premature. Therefore the correlation described by Linnett and Hoare,[22] between the algebraic sign of f_{rr} and the electronic configuration of a triatomic molecule, is not necessarily violated by the specific example of OF_2 as originally inferred in reference (23).

The positive contribution to f_{rr} due to DBNB resonance, f_d as determined by these calculations, would decrease the frequency of the antisymmetric stretch by approximately 480 cm^{-1}, according to equation (64). Inspection of equations (62) and (63) indicate that the frequency of the symmetric stretching mode would be increased by a comparable amount. Such frequency increments could easily account for the frequency inversion observed in OF_2.

One of the most interesting aspects of this study is the apparently acute sensitivity of the interaction constant, f_{rr}, to a small change in the trial wave function. For the data used to calculate the difference between f_{rr} and f'_{rr}, the largest value of the variation coefficients, C_{II} and C_{III}, is 0.04379 at a bond displacement of 0.0529 Å. Resonance structures, such as those of the DBNB type, which may appear unimportant in the determination of molecular properties, such as binding energies, bond force constants, etc., may not be insignificant as far as their effect on the bond-bond interaction constant.

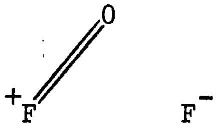
The above analysis may be extended to NF_2 and CF_2. In these molecules a filled fluorine AO and either a vacant or half-filled orbital on carbon or nitrogen may participate in significant π-bonding. This would be reflected in positive contributions to f_{rr} in addition to those effects mentioned for OF_2.

The binding energy curves which approximate the symmetric stretch are more difficult to interpret. First, the symmetric stretching mode as determined from normal coordinate analysis contains a considerable amount of angular displacement as the bond lengths are varied. Secondly, the analysis used to calculate f_d for the antisymmetric stretch is complicated by the presence of f_α, f'_α, f_r in the potential energy function for the symmetric stretch. If such effects are ignored, the resultant calculations of f_d are discouraging. At the bond displacement of -0.0529 Å, this quantity is -5.3×10^5 dyne/cm and at +0.0529, $f_d = +1.4 \times 10^5$ dyne/cm. This latter value agrees reasonably well with the results of the antisymmetric stretching calculations, but the former value deviates badly and even possesses a negative sign. The negative sign for f_d results from a relatively large contribution of determinants, D_{II} and D_{III}, to the CI wave function which would lead to a large positive difference, $\Delta E_{B(I)} - \Delta E_{B(CI)}$, for the symmetric stretch. Such a difference would result in a large negative value for f_d. D_{II} and D_{III} represent resonance structures



II

and



III

.

The molecular angle has been constrained at 90°; this angle cannot become larger as the bonds are compressed. This would result in an abnormally high core-core repulsion between the fluorines. The introduction of determinants D_{II} and D_{III}, multiplied by adjustable parameters may allow the effect of this abnormally high repulsion term, which in reality is decreased by a wider angle at short bond distances, to be compensated for by a relatively large contribution of structures II and III to the CI wave function. This would explain why the values of f_d, calculated for the symmetric stretching geometries, deviate less from the antisymmetric stretching values as the bond length is increased.

The model predicts an increase in thermodynamic stability of OF_2 of 0.445 kcal/mole due to the inclusion of D_{II} and D_{III} into the CI wave function. This value was calculated from the difference $E^o_{B(CI)} - E^o_{B(I)}$, these quantities representing equilibrium binding energies as determined in Chapter IV. Since two DBNB resonance structures may be drawn for OF_2, this corresponds to a resonance energy of 0.223 kcal/mole for each possible DBNB resonance structure. No experimental data is available for DBNB resonance structures involving oxygen and fluorine. Hine[4] estimates a value of 3.2 kcal/mole resonance energy for each DBNB resonance structure in carbon-fluorine compounds. The calculation of this value assumes that all this resonance energy is due to DBNB resonance with no contribution from the non-bonded interaction between the fluorines. From the above data, it appears as though our calculated value for the resonance energy is considerably smaller than the value which might be expected experimentally.

Summary

1. The binding energies calculated for OF_2, NF_2 and CF_2 using the semiempirical LCAO-MO-SCF procedure, described in Chapter III, are larger than their corresponding experimental values. This appears to be the result of the relatively high ionization potential and electron

affinity of the fluorine atom employed in the semiempirical evaluation of the integrals which determine the binding energies of these molecules.

2. The Set II integral approximations, coupled with the assumption of completely covalent O-F bonds in OF_2, lead to equilibrium binding energies of 5.683 e.V. and 4.015 e.V. for the out-of-plane and in-plane AO basis sets, respectively. These CI binding energies agree reasonably well with the experimental energy of 3.9 e.V.

3. The model employed in this calculation predicts a bond-bond interaction constant of approximately 1×10^5 dyne/cm. This calculated value explains the large positive bond-bond interaction constant calculated from the fundamental frequencies of OF_2.

4. This calculation indicates that the OF_2 molecule obeys the correlation of Linnett and Hoare between the sign of the bond-bond interaction constant and the electronic configuration of the triatomic molecule.

5. The calculation indicates that DBNB resonance, while having a relatively small effect on the equilibrium binding energy, plays a large role in determining the value of the bond-bond interaction constant.

6. A resonance energy of 0.223 kcal/mole for each possible DBNB resonance structure was determined for OF_2. This appears to be inconsistent with Hine's conclusion, as f_{rr} is less for CF_4 than for OF_2.

Suggestions for Future Work

1. Extend the LCAO-MO-SCF calculations for the XF_2 molecules by utilizing other possible sets of integral approximations and by

minimizing the energy of these molecules with respect to the molecular angle. Possibly a study of the effect of the Wolfsberg-Helmholtz parameter on the calculated molecular properties of these molecules would be of value.

2. A study of the CI wave function and the calculated binding energies of OF_2 as a function of molecular angle for the symmetric stretching mode, coupled with calculations similar to those presented above for the symmetric stretch, may illustrate the proper dependence of $E_{B(I)}$ and $E_{B(CI)}$ for symmetric stretching geometries on the positive bond-bond interaction constant.

3. A configuration interaction calculation to determine the extent of bonding between the fluorines in XF_2 molecules would appear to be helpful in classifying the nature of the interaction between these atoms.

4. Theoretical investigations of the alkaline earth dihalides, with emphasis on non-bonded interaction and/or multiple bonding would be particularly interesting as several of these molecules are nonlinear.

5. As data becomes available on more triatomic dihalide molecules, such as CCl_2 and NBr_2, calculations of the type described in this thesis may be employed to determine values for the bond-bond interaction constant. A comparison of these values with experimental data would be helpful in deducing the importance of DBNB resonance in these molecules. Also LCAO-MO-SCF calculations would be useful in determining the best set of semiempirical integral evaluations to be employed in treating these molecules.

6. Vibronic coupling of the DBNB resonance type in OF_2 may be investigated by measuring the experimental band intensities of the

fundamental frequencies for OF_2. By comparing the intensities of the symmetric and antisymmetric stretching modes an estimate of the extent of vibronic coupling in OF_2 may be obtained.

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APPENDIX A

The LCAO-MO-SCF problem for an XF_2 molecule using the procedure described in Chapter III demands solution of the determinant

$$\left| F - \varepsilon S \right| = 0 \qquad (29)$$

where F and S are 4 x 4 symmetric matrices and ε represents the eigenvalues of this equation. A well-known matrix diagonalization routine[44] written in Fortran IV and employed in this project successfully determines the eigenvalues and eigenvectors corresponding to the secular determinant

$$\left| F' - \varepsilon E \right| = 0 \qquad (76)$$

where F' can be a 4 x 4 symmetric matrix and E is the identity matrix. The procedure for deriving Equation (76) from (29) is described below. Since F is a symmetric matrix the equations

$$S_D = C_1^{-1} S C_1 \qquad (77)$$

or

$$S = C_1 S_D C_1^{-1} \qquad (78)$$

may be written where S_D is a diagonal matrix. Substituting Equation (78) into (29) yields

$$\left| F - \varepsilon C_1 S_D C_1^{-1} \right| = 0 \qquad (79)$$

Pre- and post-multiplying this equation by C_1^{-1} and C_1 respectively results in the determinant

$$\left| C_1^{-1} FC_1 - \varepsilon S_D \right| = 0 \qquad (80)$$

This same procedure may be applied to S_D in order to transform it into the identity matrix. This procedure yields the determinant

$$\left| C_2^{-1} C_1^{-1} FC_1 C_2 - \varepsilon E \right| = 0$$

which is identical to Equation (76) where

$$F' = C_2^{-1} C_1^{-1} FC_1 C_2$$

A Fortran IV listing of the computer program used in these LCAO-MO-SCF calculations is presented at the end of this Appendix. This program contains four subroutines, COEF, EVAL, DIAGP, and HDIAG, in addition to the main program. The main program specifies the input variables and the geometry of the molecule in addition to calculating the binding energy of the XF_2 molecule. The subroutine COEF specifies the initial guess for the LCAO coefficients and tests the successive sets of coefficients for self-consistency. Subroutine EVAL evaluates the elements of the F and S matrices as given by Equations (24) and (25). The steps presented earlier in the derivation in this Appendix is essentially used in the subroutine DIAG to prepare matrix Equation (29) for subroutine HDIAG. This latter subroutine determines the eigenvalues and eigenvectors of an equation similar to (76) by a modified Jacobi method.[44]

```
C  READ IN DATA FOR CALCULATION
      DIMENSION H(4,4),F(4,4),S(4,4),C(4,4)
      COMMON PF,PO,AF,AO,RHOF,RHOO,NN,N,ROF1,ROF2,RFF,SOF1,SOF2,ZEFO,
     1ZEFF,C,F,H,S
C  SYMMETRIC STRETCH
  711 READ(5,10)PF,PO,AF,AO,RHOF,RHOO,CONST
   10 FORMAT(7F10.4)
      READ(5,11)NN
   11 FORMAT(I3)
      READ(5,14)N
   14 FORMAT(I2)
      READ(5,12)ROF1
   12 FORMAT(F10.4)
      DR=0.10
      DO 15 I=1,N
      DO 15 J=1,N
   15 H(I,J)=0.0
      DO 16 I=1,N
      DO 16 J=1,N
   16 F(I,J)=0.0
      DO 17 I=1,N
      DO 17 J=1,N
   17 S(1,J)=0.0
      DO 18 I=1,N
      DO 18 J=1,N
   18 C(I,J)=0.0
      DO 50 J=1,NN
      ROF2=ROF1
      RFF=SQRT(ROF1*ROF1+ROF2*ROF2)
   13 FORMAT(4F10.4)
      READ(5,13)SOF1,SOF2,ZEFO,ZEFF
      CALL COEF
C CALCULATE ELECTRONIC ENERGY
      C(2,3)=C(1,1)
      C(2,4)=C(1,2)
      EE=C(1,1)*C(1,1)*(H(1,1)+F(1,1))+C(1,2)*C(1,2)*(H(2,2)+F(2,2))+C(2
     1,3)*C(2,3)*(H(3,3)+F(3,3))+C(2,4)*C(2,4)*(H(4,4)+F(4,4))+2.0*C(1,1
     2)*C(1,2)*(H(1,2)+F(1,2))+2.0*C(2,3)*C(2,4)*(H(3,4)+F(3,4))
C CALCULATE ENERGY CONTRIBUTION FROM NUCLEAR REPULSIONS
      ENUC=2.0*ZEFO*ZEFF*(1.0/ROF1)+(1.0/RFF)
C CALCULATE BINDING ENERGY
      EBIND=EE+ENUC+CONST
      BINDE=EBIND*27.19224
  202 FORMAT(1X,30H SLATER EXPONENTIAL PARAMETERS,10X,6H RHOO=,F10.5,5X,
     16H RHOF=,F10.5/1X,22H IONIZATION POTENTIALS,10X,4H PO=,F10.5,5X,4H
     2 PF=,F10.5/20H ELECTRON AFFINITIES,10X,4H AO=,F10.5,5X,4H AF=,F10.
     35/)
  204 FORMAT(1X,20H NUCLEAR SEPARATIONS,5X,10HROF1=ROF2=,F10.5,/1X,13H C
     1OEFFICIENTS,5X,4H CO=,F10.5,5X,4H CF=,F10.5/1X,16H ELECTRON ENERGY
     2,10X,4H EE=,F15.9)
      WRITE(6,202)RHOO,RHOF,PO,PF,AO,AF
      WRITE(6,204)ROF1,C(1,1),C(1,2),EE
  205 FORMAT(///17H  BINDING ENERGY=,E15.8///)
      WRITE(6,205)BINDE
   50 ROF1=ROF1+DR
      READ(5,11)M
      IF(M-0)712,711,712
  712 CONTINUE
      STOP
```

```
      END
C SUBROUTINE COEF
      SUBROUTINE COEF
C THIS SUBROUTINE GIVES THE FIRST GUESS FOR THE LCAO COEFFICIENTS AND
C SEARCHES FOR SELF-CONSISTENCY.
      DIMENSION H(4,4),F(4,4),S(4,4),C(4,4)
      COMMON PF,PO,AF,AO,RHOF,RHOO,NN,N,ROF1,ROF2,RFF,SOF1,SOF2,ZEFO,
     1ZEFF,C,F,H,S
      C(4,4)=0.7
      C(3,4)=-C(4,4)*SOF1+SQRT(C(4,4)*C(4,4)*SOF1*SOF1+1.0-C(4,4)*C(4,4)
     1)
   77 ZZ12=C(4,4)
      ZZ11=C(3,4)
  116 FORMAT(14H ZZ11 AND ZZ12)
      WRITE(6,116)
      WRITE(6,115)ZZ11,ZZ12
  115 FORMAT(2F10.4)
      CALL EVAL(C,H,F,S)
      ZNN=C(3,4)*C(3,4)+2.0*C(3,4)*C(4,4)*SOF1+C(4,4)*C(4,4)
      SZNN=SQRT(ZNN)
      C(3,4)=C(3,4)/SZNN
      C(4,4)=C(4,4)/SZNN
      IF (ABS(C(3,4)-ZZ11) .GT. .0001) GO TO 77
      IF (ABS(C(4,4)-ZZ12) .GT. .0001) GO TO 77
      C(1,1)=C(3,4)
      C(1,2)=C(4,4)
      RETURN
      END
C  SUBROUTINE EVAL
      SUBROUTINE EVAL(C,H,F,S)
      DIMENSION C(4,4),H(4,4),F(4,4),S(4,4)
      COMMON PF,PO,AF,AO,RHOF,RHOO,NN,N,ROF1,ROF2,RFF,SOF1,SOF2,ZEFO,
     1ZEFF
      C11=C(3,4)
      C12=C(4,4)
      C23=C(3,4)
      C24=C(4,4)
C EVALUATE H(I,J) TERMS
      H(1,1)=-PO-.35*RHOO-1.0/ROF1-1.0/ROF2
      H(2,2)=-PF-2.0/ROF1-1.0/RFF
      H(3,3)=H(1,1)
      H(4,4)=-PF-2.0/ROF2-1.0/RFF
      H(1,2)=0.5*SOF1*(-PF-PO-1.35*RHOO-0.5*RHOF-1.5/ROF1-1.0/ROF2-1.0/R
     1FF)
      H(2,1)=H(1,2)
      H(1,3)=0.0
      H(3,1)=H(1,3)
      H(1,4)=0.0
      H(4,1)=0.0
      H(2,3)=0.0
      H(3,2)=0.0
      H(2,4)=0.0
      H(4,2)=0.0
      H(3,4)=0.5*SOF2*(-PF-PO-1.35*RHOO-0.5*RHOF-1./ROF1-1.5/ROF2-1.0/RF
     1F)
      H(4,3)=H(3,4)
C EVALUATE ELEMENTS OF F-MATRIX.
      F(1,1)=H(1,1)+C11*C11*(PO+AO)+2.0*C12*C12*(1.0/ROF1-((SOF1*SOF1)/8
     1.0)*(PO+AO+PF+AF+2.0/ROF1))+2.0*C23*C23*(PO+AO-((.0604/2.0)*(PO+AO
```

```
     2)))+2.0*C24*C24*(1.0/ROF2)+C11*C12*SOF1*(PO+AO+1.0/ROF1)+2.0*C23*C
     324*SOF2*(PO+AO+1.0/ROF2)
      F(2,2)=H(2,2)+2.0*C11*C11*(1.0/ROF1-((SOF1*SOF1)/8.0)*(PO+AO+PF+AF
     1+2.0/ROF1))+C12*C12*(PF+AF)+2.0*C23*C23*(1.0/ROF1)+2.0*C24*C24*(1.
     20/RFF)+C11*C12*SOF1*(PF+AF+1.0/ROF1)+2.0*C23*C24*SOF2*(1.0/ROF1+1.
     30/RFF)
      F(3,3)=H(3,3)+2.0*C11*C11*(PO+AO-((.06040/2.0)*(PO+AO)))+2.0*C12*C
     112*(1.0/ROF1)+C23*C23*(PO+AO)+2.0*C24*C24*(1.0/ROF2-((SOF2*SOF2)/8
     2.0)*(PO+AO+PF+AF+2.0/ROF2))+2.0*C11*C12*SOF1*(PO+AO+1.0/ROF1)+C23*
     3C24*SOF2*(PO+AO+1.0/ROF2)
      F(4,4)=H(4,4)+2.0*C11*C11*(1.0/ROF2)+2.0*C12*C12*(1.0/RFF)+2.0*C23
     1*C23*(1.0/ROF2-((SOF2*SOF2)/8.0)*(PO+AO+PF+AF+2.0/ROF2))+C24*C24*(
     2PF+AF)+2.0*C11*C12*SOF1*(1.0/ROF2+1.0/RFF)+C23*C24*SOF2*(PF+AF+1.0
     3/ROF2)
      F(1,2)=H(1,2)+C11*C11*0.5*SOF1*(PO+AO+1.0/ROF1)+0.5*C12*C12*SOF1*(
     1PF+AF+1.0/ROF1)+C23*C23*SOF1*(PO+AO+1.0/ROF1)+C24*C24*SOF1*(1.0/RO
     2F2+1.0/RFF)+0.75*C11*C12*SOF1*SOF1*(PO+AO+PF+AF+2.0/ROF1)-C11*C12*
     3(1./ROF1)+C23*C24*SOF1*SOF2*(PO+AO+1.0/ROF1+1.00/ROF2+1.0/RFF)
      F(2,1)=F(1,2)
      F(1,3)=0.0
      F(3,1)=F(1,3)
      F(1,4)=0.0
      F(4,1)=F(1,4)
      F(2,3)=0.0
      F(3,2)=F(2,3)
      F(3,4)=H(3,4)+C11*C11*SOF2*(PO+AO+(1.0/ROF2))+C12*C12*SOF2*((1.0/R
     1OF1)+(1.0/RFF))+0.5*C23*C23*SOF2*(PO+AO+(1.0/ROF2))+0.5*C24*C24*SO
     2F2*(PF+AF+(1.0/ROF2))+C11*C12*SOF1*SOF2*(PO+AO+(1.0/ROF1)+(1.0/ROF
     32)+(1.0/RFF))+0.75*C23*C24*SOF2*SOF2*(PO+AO+PF+AF+2.0/ROF2)-C23*C2
     44*(1.0/ROF2)
      F(4,3)=F(3,4)
      F(2,4)=0.0
      F(4,2)=0.0
C EVALUATE ELEMENTS OF THE OVERLAP MATRIX.
      S(1,1)=1.0
      S(2,2)=1.0
      S(3,3)=1.0
      S(4,4)=1.0
      S(1,2)=SOF1
      S(1,3)=0.0
      S(1,4)=0.0
      S(2,3)=0.0
      S(2,4)=0.0
      S(3,4)=SOF2
      S(2,1)=S(1,2)
      S(3,1)=S(1,3)
      S(4,1)=S(1,4)
      S(3,2)=S(2,3)
      S(4,2)=S(2,4)
      S(4,3)=S(3,4)
      CALL DIAGP(S,F,C)
      RETURN
      END
C SUBROUTINE DIAGP
C THIS SUBROUTINE PREPARES DATA FOR SUBROUTINE HDIAG.
C FIRST DIAGONALIZE S MATRIX,THEN THE RESULTING F PRIME MATRIX.
      SUBROUTINE DIAGP(S,F,C)
      DIMENSION S(4,4),F(4,4),C(4,4),A(4,4),B(4,4),T(4,4)
      COMMON PF,PO,AF,AO,RHOF,RHOO,NN,N,ROF1,ROF2,RFF,SOF1,SOF2,ZEFO,
```

```
     1ZEFF
      DO 777 I=1,N
      DO 777 J=1,N
  777 T(I,J)=0.0
      DO 109 I=1,N
      DO 109 J=1,N
  109 A(I,J)=S(I,J)
      CALL HDIAG(A,N,0,T,NR)
      DO 110 I=1,N
      TEMP=1.0/SQRT(A(I,I))
      DO 110 J=1,N
  110 T(J,I)=T(J,I)*TEMP
      DO 120 I=1,N
      DO 120 J=1,N
  120 A(I,J)=F(I,J)
C PREPARE NEW MATRIX TO BE DIAGONALIZED,SHS-1
      DO 130 I=1,N
      DO 130 J=1,N
      C(I,J)=0.0
      DO 130 K=1,N
  130 C(I,J)=C(I,J)+T(K,I)*A(K,J)
      DO 140 I=1,N
      DO 140 J=1,N
      A(I,J)=0.0
      DO 140 K=1,N
  140 A(I,J)=A(I,J)+C(I,K)*T(K,J)
      CALL HDIAG(A,N,0,B,NR)
      DO 150 I=1,N
      DO 150 J=1,N
      C(I,J)=0.0
      DO 150 K=1,N
  150 C(I,J)=C(I,J)+T(I,K)*B(K,J)
      K=0
      K=K+9
      K1=K-8
      IF(N .LT. K)K=N
 2002 FORMAT(//33H EIGENVALUES IN DECREASING ORDER(,I2,3H TO,I3,1H)/)
 2003 FORMAT(1H0,9E13.6)
 2004 FORMAT(55H EIGENVECTORS IN COLUMNS UNDER CORRESPONDING EIGENVALUE/
     1)
      WRITE(6,2002)K1,K
      WRITE(6,2003)(A(J,J),J=K1,K)
      WRITE(6,2004)
      DO 30 I=1,N
   30 WRITE(6,2003)(C(I,J),J=K1,K)
      RETURN
      END
      SUBROUTINE  HDIAG (H,N,IEGEN,U,NR)
C     SUBROUTINE HDIAG.
C
C     PROGRAMED BY F. J. CARBATO AND M.MERWIN OF THE MIT
C     COMPUTATION CENTER.
C
C          THIS SUBROUTINE COMPUTES THE EIGENVALUES AND EIGENVECTORS
C     OF A REAL SYMMETRIC MATRIX, H, OF ORDER N ( WHERE N MUST BE LESS
C     THAN 51), AND PLACES THE EIGENVALUES IN THE DIAGONAL ELEMENTS OF
C     THE MATRIX H, AND PLACES THE EIGENVECTORS (NORMALIZED ) IN THE
C     COLUMNS OF THE MATRIX U. IEGEN IS SET AS 1 IF ONLY EIGENVALUES
C     ARE DESIRED,AND IS SET TO 0 WHEN VECTORS ARE REQUIRED. NR CON-
```

```
C       TAINS THE NUMBER OF ROTATIONS DONE.
C
C       H, N, IENGEN, U, AND NR OF THE ARGUMENT LIST ARE DUMMY VARIABLES
C       AND MAY BE NAMED DIFFERENTLY IN THE CALLING OF THE SUBROUTINE.
C
C       SUBROUTINE PLACES COMPUTER IN THE FLOATING TRAP MODE
C       THE SUBROUTINE OPERATES ONLY ON THE ELEMENTS OF H THAT ARE TO THE
C               RIGHT OF THE MAIN DIAGONAL. THUS, ONLY A TRIANGULAR
C               SECTION NEED BE STORED IN THE ARRAY H.
        DIMENSION H(4,4),U(4,4),X(4),IQ(4)
      2 FORMAT(14H MAX OFF DIAG=,F14.7,3HNR=,I3)
   2001 FORMAT(1X,8E15.8)
   2002 FORMAT(18H ORTHOGONAL MATRIX)
   2003 FORMAT(15H ROTATED MATRIX)
        IF(IEGEN.NE.0) GO TO 15
     10 DO 14 I=1,N
        DO 14 J=1,N
        IF(I-J.NE.0) GO TO 12
     11 U(I,J)=1.0
        GO TO 14
     12 U(I,J)=0.0
     14 CONTINUE
     15 NR = 0
        IF(N-1.LE.0)  GO TO 1000
C       SCAN FOR LARGEST OFF-DIAGONAL ELEMENT IN EACH ROW
C       X(I) CONTAINS LARGEST ELEMENT IN ITH ROW
C       IQ(I) HOLDS SECOND SUBSCRIPT DEFINING POSITION OF ELEMENT
     17 NMI1=N-1
        DO 30 I=1,NMI1
        X(I) = 0.0
        IPL1=I+1
        DO 30 J=IPL1,N
        IF(X(I)-ABS(H(I,J)).GT. 0.0) GO TO 30
     20 X(I)=ABS(H(I,J))
        IQ(I)=J
     30 CONTINUE
C       SET INDICATOR FOR SHUT-OFF.RAP=2**-27,NR=NO. OF ROTATIONS
        RAP=7.450580596E-9
        HDTEST=1.0E38
C       FIND MAXIMUM OF X(I) S FOR PIVOT ELEMENT AND
C       TEST FOR END OF PROBLEM
     40 DO 70 I=1,NMI1
        IF(I-1.LE.0) GO TO 60
        IF(XMAX-X(I).GE.0.0) GO TO 70
     60 XMAX=X(I)
        IPIV=I
        JPIV=IQ(I)
     70 CONTINUE
C       IS MAX. X(I) EQUAL TO ZERO, IF LESS THAN HDTEST, REVISE HDTEST
        IF(XMAX.LE.0.0) GO TO 1002
     80 IF(HDTEST.LE.0.0) GO TO 90
     85 IF(XMAX-HDTEST.GT.0.0) GO TO 148
     90 HDIMIN = ABS( H(1,1) )
        DO 110 I=2,N
        IF(HDIMIN- ABS( H(I,I) ).LE. 0.0) GO TO 110
    100 HDIMIN=ABS( H(I,I) )
    110 CONTINUE
        HDTEST = HDIMIN*RAP
C       RETURN IF MAX.H(I,J)LESS THAN(2**-27)ABS(H(K,K)-MIN)
```

```
      IF(HDTEST-XMAX.GE.0.0)GO TO 1002
  148 NR = NR+1
C COMPUTE TANGENT, SINE AND COSINE,H(I,I),H(J,J)
  150 TANG=SIGN(2.0,(H(IPIV,IPIV)-H(JPIV,JPIV)))*H(IPIV,JPIV)/(ABS(H(I
     1PIV,IPIV)-H(JPIV,JPIV))+SQRT((H(IPIV,IPIV)-H(JPIV,JPIV))**2+4.0*H
     2(IPIV,JPIV)**2))
      COSINE=1.0/SQRT(1.0+TANG**2)
      SINE=TANG*COSINE
      HII=H(IPIV,IPIV)
      H(IPIV,IPIV)=COSINE**2*(HII+TANG*(2.*H(IPIV,JPIV)+TANG*H(JPIV,
     1JPIV)))
      H(JPIV,JPIV)=COSINE**2*(H(JPIV,JPIV)-TANG*(2.*H(IPIV,JPIV)-TANG*H
     1II))
      H(IPIV,JPIV)=0.0
C     PSEUDO RANK THE EIGENVALUES
C     ADJUST SINE AND COS FOR COMPUTATION OF H(IK) AND U(IK)
      IF(H(IPIV,IPIV)-H(JPIV,JPIV).GE.0.0) GO TO 153
  152 HTEMP = H(IPIV,IPIV)
      H(IPIV,IPIV) = H(JPIV,JPIV)
      H(JPIV,JPIV) = HTEMP
C     RECOMPUTE SINE AND COS
      HTEMP = SIGN(1.0, -SINE) * COSINE
      COSINE = ABS (SINE)
      SINE = HTEMP
  153 CONTINUE
C     INSPECT THE IQS BETWEEN I+1 AND N-1 TO DETERMINE
C     WHETHER A NEW MAXIMUM VALUE SHOULD BE COMPUTED SINCE
C     THE PRESENT MAXIMUM IS IN THE I OR J ROW.
      DO 350 I = 1,NMI1
      IF(I-IPIV.EQ.0) GO TO 350
      IF(I-IPIV.LT. 0 ) GO TO 210
  200 IF(I-JPIV.EQ. 0 ) GO TO 350
  210 IF(IQ(I)-IPIV.EQ. 0) GO TO 240
  230 IF(IQ(I)-JPIV.NE. 0 ) GO TO 350
  240 K = IQ(I)
  250 HTEMP = H(I,K)
      H(I,K) = 0.0
      IPL1 = I+1
      X(I) = 0.0
C     SEARCH IN DEPLETED ROW FOR NEW MAXIMUM
      DO 320 J = IPL1,N
      IF( X(I)-ABS( H(I,J) ).GT. 0.0) GO TO 320
  300 X(I) = ABS(H(I,J))
      IQ(I) = J
  320 CONTINUE
      H(I,K) = HTEMP
  350 CONTINUE
      X(IPIV) = 0.0
      X(JPIV) = 0.0
C     CHANGE THE OTHER ELEMENTS OF H
      DO 530 I = 1,N
      IF(I-IPIV.EQ. 0 ) GO TO 530
      IF(I-IPIV.GT. 0 ) GO TO 420
  370 HTEMP = H(I,IPIV)
      H(I,IPIV) = COSINE*HTEMP + SINE*H(I,JPIV)
      IF( X(I) - ABS( H(I,IPIV) ).GE. 0.0 ) GO TO 390
  380 X(I) = ABS( H(I,IPIV) )
      IQ(I) = IPIV
  390 H(I,JPIV) = -SINE*HTEMP + COSINE*H(I,JPIV)
```

```
      IF( X(I) - ABS( H(I,JPIV) ).GE. 0.0 ) GO TO 530
  400 X(I) = ABS( H(I,JPIV) )
      IQ(I) = JPIV
      GO TO 530
  420 IF( I-JPIV.EQ. 0 ) GO TO 530
      IF(I-JPIV.GT. 0 ) GO TO 480
  430 HTEMP = H(IPIV,I)
      H(IPIV,I) = COSINE*HTEMP + SINE*H(I,JPIV)
      IF( X(IPIV) - ABS( H(IPIV,I) ).GE. 0.0 ) GO TO 450
  440 X(IPIV) = ABS( H(IPIV,I) )
      IQ(IPIV) = I
  450 H(I,JPIV) = -SINE*HTEMP + COSINE*H(I,JPIV)
      IF( X(I) - ABS( H(I,JPIV) ).GE. 0.0 ) GO TO 530
      IF( X(I) - ABS( H(I,JPIV) ).LT. 0.0 ) GO TO 400
  480 HTEMP = H(IPIV,I)
      H(IPIV,I) = COSINE*HTEMP + SINE*H(JPIV,I)
      IF( X(IPIV) - ABS( H(IPIV,I) ).GE. 0.0 ) GO TO 500
  490 X(IPIV) = ABS( H(IPIV,I) )
      IQ(IPIV) = I
  500 H(JPIV,I) = -SINE*HTEMP + COSINE*H(JPIV,I)
      IF( X(JPIV) - ABS( H(JPIV,I) ).GE.0.0) GO TO 530
  510 X(JPIV) = ABS( H(JPIV,I) )
      IQ(JPIV) = I
  530 CONTINUE
C     TEST FOR COMPUTATION OF EIGENVECTORS
      IF(IEGEN.NE.0) GO TO 40
  540 DO 550 I = 1,N
      HTEMP = U(I,IPIV)
      U(I,IPIV) = COSINE*HTEMP + SINE*U(I,JPIV)
  550 U(I,JPIV) = -SINE*HTEMP+COSINE*U(I,JPIV)
      GO TO 40
 1002 WRITE(6,2)XMAX,NR
 1000 RETURN
      END
```

APPENDIX B

Six short computer programs, employed in the CI problem, are included in this appendix. The first four programs calculate the H_{ij} matrix elements for the in-plane AO basis set. These matrix elements are substituted into Equation (51) to obtain the eigenvalues and eigenvectors for the CI problem. The four matrix elements needed are H_{11}, H_{22}, H_{12} and H_{23}. For symmetric stretching geometries the balance of the elements in Equation (51) are related to these four by the equations

$$H_{12} = H_{21} = H_{13} = H_{31}\ , \qquad H_{23} = H_{32}$$

and $H_{22} = H_{33}$. For antisymmetric stretching geometries

$$H_{12} = H_{21}\ ,\quad H_{13} = H_{31} \quad \text{and} \quad H_{23} = H_{32}.$$

The matrix element H_{12} described by the geometry

$$R_{OF_1} = R^{o}_{OF} + \Delta R \quad \text{and} \quad R_{OF_2} = R^{o}_{OF} - \Delta R$$

is equivalent to the matrix element H_{13} described by the geometry

$$R_{OF_1} = R^{o}_{OF} - \Delta R \quad \text{and} \quad R_{OF_2} = R^{o}_{OF} + \Delta R.$$

In these equations R^{o}_{OF} indicates the calculated equilibrium bond length in OF_2 and ΔR denotes a displacement of the O-F bond from equilibrium. The elements H_{22} and H_{33} may be related in a manner similar to the relationship between H_{12} and H_{13}.

The two remaining programs calculate H_{11} and H_{22} for the out-of-plane AO basis set. The balance of the matrix elements in this problem were simple enough to determine using a desk calculator.

```
C THIS PROGRAM COMPUTES THE MATRIX ELEMENTS,H11 AND S11, IN PLANE AO BASIS SET.
 1234 FORMAT(8F10.4)
   12 FORMAT(I3)
   13 FORMAT(F10.4)
   14 FORMAT(6F10.4)
   16 FORMAT(1H1,5X,4HROF1,10X,4HROF2,10X,5HSOF1S,9X,5HSOF2S,9X,5HSOF1P,
     19X,5HSOF2P,14X,2HEE///)
      DR=0.01
      WRITE(6,16)
      READ(5,14)PF2,PO1,AF2,AO1,RHOF2,RHOO1
      READ(5,13)ROF1
      READ(5,12)N
      DO 30 J=1,N
      READ(5,1234)SOF1S,SOF2S,SOF1P,SOF2P,ZEFO1,ZEFF1,ZEFO2,ZEFF2
      ROF2=4.000-ROF1
      RFF=SQRT(ROF1*ROF1+ROF2*ROF2)
      RT1S=SQRT(2.0+2.0*SOF1S)
      RT2S=SQRT(2.0+2.0*SOF2S)
      S12=SOF2P/RT1S
      S34=SOF1P/RT2S
      H11=-PF2-2.0/ROF2-3.0/RFF
      H33=0.5*(1.0/(1.0+SOF1S))*(-PO1-PF2-5.0/ROF1-3.0/ROF2-3.0/RFF+SOF1
     1S*(-PF2-PO1-RHOO1-1.5*RHOF2-2.5/ROF1-3.0/ROF2-3.0/RFF))
      H55=0.5*(1.0/(1.0+SOF2S))*(-PO1-PF2-3.0/ROF1-5.0/ROF2-3.0/RFF+SOF2
     1S*(-PF2-PO1-RHOO1-1.5*RHOF2-3.0/ROF1-2.5/ROF2-3.0/RFF))
      H77=-PF2-2.0/ROF1-3.0/RFF
      H13=(SOF2P/RT1S)*(-PO1-1.5*RHOF2-1.5/ROF1-1.5/ROF2-1.5/RFF)
      H31=(SOF2P/RT1S)*(-PF2-RHOO1-1.0/ROF2-1.5/ROF1-1.5/RFF)
      H57=(SOF1P/RT2S)*(-PF2-RHOO1-1.0/ROF1-1.5/ROF2-1.5/RFF)
      H75=(SOF1P/RT2S)*(-PO1-1.5*RHOF2-1.5/ROF2-1.5/ROF1-1.5/RFF)
      Z1212=PF2+AF2
      Z1414=0.5*(1.0/ROF2+1.0/RFF)
      Z3434=0.25*(PO1+AO1+PF2+AF2+2.0/ROF1)
      Z1214=(0.5*SOF2P)*(1.0/RT1S)*(PF2+AF2+1.0/ROF2)
      Z1434=(SOF2P/(4.0* RT1S ))*(PO1+AO1+1.0/ROF1+1.0/ROF2+1.0/RFF)
      Z1234=((SOF2P*SOF2P)/(8.0*(1.0+SOF1S)))*(PF2+AF2+PO1+AO1+2.0/ROF2)
      Z1515=0.5*(PF2+AF2+1.0/ROF2)
      Z1717=1.0/RFF
      Z1771=0.0
      Z3535=0.25*(PO1+AO1+1.0/ROF1+1.0/ROF2+1.0/RFF)
      Z3553=0.25*(1.0/((1.0+SOF1S)*(1.0+SOF2S)))*(0.06040*(PO1+AO1))
      Z3838=0.5*(PF2+AF2+1.0/ROF1)
      Z3773=0.5*(1.0/(1.0+SOF1S))*(0.0640*(PF2+AF2))
      Z1551=0.5*(1.0/(1.0+SOF2S))*(0.06040*(PF2+AF2))
      Z1535=(SOF2P/(4.0*RT1S))*(PF2+AF2+PO1+AO1+2.0/ROF2)
      Z1553=0.0
      Z1737=(SOF2P/(2.0*RT1S))*(1.0/ROF1+1.0/RFF)
      Z1773=0.0
      Z1517=((.5*SOF1P)/(RT2S))*(1.0/ROF2+1.0/RFF)
      Z1571=0.0
      Z3537=((0.25*SOF1P)/(RT2S))*(PF2+AF2+PO1+AO1+2.0/ROF1)
      Z3573=0.0
      Z1537=((SOF2P*SOF1P*0.25)/(RT1S*RT2S))*(PO1+AO1+1.0/ROF1+1.0/ROF2+
     11.0/RFF)
      Z1573=0.0
      Z2864=0.0
      Z5656=0.25*(PO1+AO1+PF2+AF2+2.0/ROF2)
```

```
      Z5858=0.5*(1.0/ROF1+1.0/RFF)
      Z7878=PF2+AF2
      Z5676=(SOF1P/(4.0* RT2S ))*(PO1+AO1+1.0/ROF1+1.0/ROF2+1.0/RFF)
      Z5878=(SOF1P/(2.0*RT2S))*(PF2+AF2+1.0/ROF1)
      Z5678=((SOF1P*SOF1P)/(8.0*(1.0+SOF2S)))*(PF2+AF2+PO1+AO1+2.0/ROF1)
      Z5757=0.5*(1.0/ROF1+1.0/RFF)
      Z5775=Z5678
      Z1331=Z1234
      SZ12=1.0-S12*S12
      SZ34=1.0-S34*S34
      SS11=SZ12*SZ12*SZ34*SZ34
      E1=SZ12*SZ34*SZ34*(2.0*H11+2.0*H33)-S12*SZ12*SZ34*SZ34*(2.0*H13+2.
     10*H31)+SZ34*SZ12*SZ12*(2.0*H55+2.0*H77)-S34*SZ34*SZ12*SZ12*(2.0*H5
     27+2.0*H75)
      E2=SZ34*SZ34*(Z1212+2.0*Z1414+Z3434)-S12*SZ34*SZ34*(4.0*Z1214+4.0*
     1Z1434)+S12*S12*SZ34*SZ34*4.0*Z1234+SZ34*SZ34*SZ12*(2.0*Z1414-2.0*Z
     21331)+SZ12*SZ34*(4.0*Z1515+4.0*Z1717-2.0*Z1771+4.0*Z3535-2.0*Z3553
     3+4.0*Z3838-2.0*Z3773-2.0*Z1551)
      E3=-S12*SZ34*SZ12*(8.0*Z1535-4.0*Z1553+8.0*Z1737-4.0*Z1773)-S34*SZ
     134*SZ12*(8.0*Z1517-4.0*Z1571+8.0*Z3537-4.0*Z3573)+S12*S34*SZ12*SZ3
     24*(16.0*Z1537-4.0*Z1573-4.0*Z2864)+SZ12*SZ12*(Z5656+2.0*Z5858+Z787
     38)-S34*SZ12*SZ12*(4.0*Z5676+4.0*Z5878)+S34*S34*SZ12*SZ12*(4.0*Z567
     48)+SZ12*SZ12*SZ34*(2.0*Z5757-2.0*Z5775)
      EE=E1+E2+E3
      ENUC=ZEFO1*ZEFF1*(1.0/ROF1)+ZEFO2*ZEFF2*(1.0/ROF2)+(9.0/RFF)
      HH11=(EE+SS11*ENUC)
   15 FORMAT(F10.5,5X,F10.5,F14.5,F13.5,F14.4,F14.4,8X,F14.8//)
      WRITE(6,15)ROF1,ROF2,SOF1S,SOF2S,SOF1P,SOF2P,EE
   20 FORMAT(6H SS11=,F12.8,6H HH11=,F12.8//)
      WRITE(6,20)SS11,HH11
   30 ROF1=ROF1+DR
      CONTINUE
      STOP
      END
```

```
C THIS PROGRAM COMPUTES THE MATRIX ELEMENTS,H22 AND S22, IN PLANE AO BASIS SET.
 1234 FORMAT(8F10.4)
   12 FORMAT(I3)
   13 FORMAT(F10.4)
   14 FORMAT(6F10.4)
   16 FORMAT(1H1,5X,4HROF1,10X,4HROF2,10X,5HSOF1S,9X,5HSOF2S,9X,5HSOF1P,
     19X,5HSOF2P,9X,4HSS22,15X,2HEE///)
      DR=0.01
      WRITE(6,16)
      READ(5,14)PF2,PO1,AF2,AO1,RHOF2,RHOO1
      READ(5,13)ROF1
      READ(5,12)N
      DO 30 J=1,N
      READ(5,1234)SOF1S,SOF2S,SOF1P,SOF2P,ZEFO1,ZEFF1,ZEFO2,ZEFF2
      ROF2=4.000-ROF1
      RFF=SQRT(ROF1*ROF1+ROF2*ROF2)
      RT1S=SQRT(2.0+2.0*SOF1S)
      RT2S=SQRT(2.0+2.0*SOF2S)
      RT1P=SQRT(2.0+2.0*SOF1P)
      RT2P=SQRT(2.0+2.0*SOF2P)
```

```
 S12=SOF2P/RT1S
 S56=SOF2S/RT1P
 SS22=((1.0-S12**2)**2)*((1.0-S56**2)**2)
 H11=-PF2-2.0/ROF2-3.0/RFF
 H22=(1.0/(RT1S*RT1S))*(-PO1-PF2-5.0/ROF1-3.0/ROF2-3.0/RFF+SOF1S*(-
1PF2-PO1-RHOO1-1.5*RHOF2-2.5/ROF1-3.0/ROF2-3.0/RFF))
 H12=(SOF2P/RT1S)*(-PO1-1.5*RHOF2-1.5/ROF1-1.5/ROF2-1.5/RFF)
 H21=(SOF2P/RT1S)*(-PF2-RHOO1-1.0/ROF2-1.5/ROF1-1.5/RFF)
 H55=(1.0/(RT1P*RT1P))*(-PF2-PO1-5.0/ROF1-3.0/ROF2-3.0/RFF+SOF1P*(-
1PF2-PO1-RHOO1-1.5*RHOF2-2.5/ROF1-3.0/ROF2-3.0/RFF))
 H66=-PF2-2.0/ROF2-3.0/RFF
 H56=(SOF2S/RT1P)*(-PF2-RHOO1-1.5/ROF1-1.0/ROF2-1.5/RFF)
 H65=(SOF2S/RT1P)*(-PO1-1.5*RHOF2-1.5/ROF1-1.5/ROF2-1.5/RFF)
 Z1111=PF2+AF2
 Z1212=0.5*(1.0/ROF2+1.0/RFF)
 Z2222=0.25*(PO1+AO1+PF2+AF2+2.0/ROF1)
 Z1121=(0.5*(SOF2P/RT1S))*(PF2+AF2+1.0/ROF2)
 Z1222=(0.25*(SOF2P/RT1S))*(PO1+AO1+1.0/ROF1+1.0/ROF2+1.0/RFF)
 Z1122=(0.125*SOF2P*SOF2P*(1.0/(1.0+SOF1S)))*(PF2+AF2+PO1+AO1+2.0/R
1OF2)
 Z1212=0.5*(1.0/ROF2+1.0/RFF)
 Z1221=Z1122
 Z1515=0.5*(1.0/ROF2+1.0/RFF)
 Z1551=0.0
 Z1616=PF2+AF2
 Z1661=0.06040*(PF2+AF2)
 Z2525=0.25*(PO1+AO1+PF2+AF2+2.0/ROF1)
 Z2552=0.25*(1.0/((1.0+SOF1S)*(1.0+SOF1P)))*0.06040*(PO1+AO1+PF2+AF
12)
 Z2626=0.5*(1.0/ROF2+1.0/RFF)
 Z2662=0.0
 Z1525=(SOF2P/(4.0*RT1S))*(PO1+AO1+1.0/ROF1+1.0/ROF2+1.0/RFF)
 Z1552=0.0
 Z1626=(SOF2P/(2.0*RT1S))*(PF2+AF2+1.0/ROF2)
 Z1662=0.0
 Z1516=(SOF2S/(2.0*RT1P))*(PF2+AF2+1.0/ROF2)
 Z1651=0.0
 Z2526=(SOF2S/(4.0*RT1P))*(PO1+AO1+1.0/ROF2+1.0/ROF1+1.0/RFF)
 Z2652=0.0
 Z2516=((SOF2P*SOF2S)/(4.0*RT1S*RT1P))*(PO1+AO1+PF2+AF2+2.0/ROF2)
 Z2651=0.0
 Z2561=0.0
 Z5555=0.25*(PO1+AO1+PF2+AF2+2.0/ROF1)
 Z5656=0.5*(1.0/ROF2+1.0/RFF)
 Z6666=PF2+AF2
 Z5565=(SOF2S/(4.0*RT1P))*(PO1+AO1+1.0/ROF1+1.0/ROF2+1.0/RFF)
 Z5666=(SOF2S/(2.0*RT1P))*(PF2+AF2+1.0/ROF2)
 Z5566=((SOF2S*SOF2S)/(4.0*RT1P*RT1P))*(PO1+AO1+PF2+AF2+2.0/ROF2)
 Z5665=Z5566
 EE1=(2.0*H11+2.0*H22)*(1.0-S12**2)*(1.0-S56**2)**2+(2.0*H12+2.0*H2
11)*(-S12)*(1.0-S12**2)*(1.0-S56**2)**2+(2.0*H55+2.0*H66)*(1.0-S56*
2*2)*(1.0-S12**2)**2+(2.0*H56+2.0*H65)*(-S56)*(1.0-S56**2)*(1.0-S12
3**2)**2
 EE2=(Z1111+2.0*Z1212+Z2222)*(1.0-S56**2)**2+(4.0*Z1121+4.0*Z1222)*
1(-S12)*(1.-S56**2)**2+4.0*Z1122*S12*S12*(1.-S56**2)**2+(2.0*Z1212-
22.0*Z1221)*(1.0-S12**2)*(1.0-S56**2)**2+(4.0*Z1515-2.0*Z1551+4.0*Z
31616-2.0*Z1661+4.0*Z2525-2.0*Z2552+4.0*Z2626-2.0*Z2662)*(1.0-S12**
42)*(1.0-S56**2)+(8.0*Z1525-4.0*Z1552+8.0*Z1626-4.0*Z1662)*(-S12)*(
51.0-S56**2)*(1.0-S12**2)
```

```
      EE3=(8.0*Z1516-4.0*Z1651+8.0*Z2526-4.0*Z2652)*(-S56)*(1.0-S12**2)*
     1(1.0-S56**2)+(16.0*Z2516-4.0*Z2651-4.0*Z2561)*S12*S56*(1.0-S12**2)
     2*(1.0-S56**2)+(Z5555+2.0*Z5656+Z6666)*(1.0-S12**2)**2+(4.0*Z5565+4
     3.0*Z5666)*(-S56)*(1.0-S12**2)**2+4.0*Z5566*S56*S56*(1.0-S12**2)**2
     4+(2.0*Z5656-2.0*Z5665)*(1.0-S12**2)*(1.0-S12**2)*(1.0-S56**2)
      EE=EE1+EE2+EE3
      ENUC=ZEFO1*ZEFF1*(1.0/ROF1)+ZEFO2*ZEFF2*(1.0/ROF2)+(9.0/RFF)
      HH22=(EE+SS22*ENUC)
   15 FORMAT(F10.5,5X,F10.5,F14.5,F13.5,F14.5,F14.5,F14.5,8X,F14.8//)
      WRITE(6,15)ROF1,ROF2,SOF1S,SOF2S,SOF1P,SOF2P,SS22,EE
   20 FORMAT(6H SS22=,F12.8,6H HH22=,F12.8//)
      WRITE(6,20)SS22,HH22
   30 ROF1=ROF1+DR
      CONTINUE
      STOP
      END
```

```
C THIS PROGRAM COMPUTES THE MATRIX ELEMENTS,H12 AND S12, IN PLANE AO BASIS SET.
 1234 FORMAT(8F10.4)
   12 FORMAT(I3)
   13 FORMAT(F10.4)
   14 FORMAT(6F10.4)
   16 FORMAT(1H1,5X,4HROF1,10X,4HROF2,10X,5HSOF1S,9X,5HSOF2S,9X,5HSOF1P,
     19X,5HSOF2P,14X,2HEE///)
      DR=0.01
      WRITE(6,16)
      READ(5,14)PF2,PO1,AF2,AO1,RHOF2,RHOO1
      READ(5,13)ROF1
      READ(5,12)N
      DO 30 J=1,N
      READ(5,1234)SOF1S,SOF2S,SOF1P,SOF2P,ZEFO1,ZEFF1,ZEFO2,ZEFF2
      ROF2=4.000-ROF1
      RFF=SQRT(ROF1*ROF1+ROF2*ROF2)
      RT1S=SQRT(2.0+2.0*SOF1S)
      RT1P=SQRT(2.0+2.0*SOF1P)
      RT2S=SQRT(2.0+2.0*SOF2S)
      RT2P=SQRT(2.0+2.0*SOF2P)
      S12=SOF2P/RT1S
      S35=(1.0+SOF1P+SOF2S)/(RT2S*RT1P)
      S36=(1.0+SOF2S)/RT2S
      S45=(1.0+SOF1P)/RT1P
      SS12=S36*S36*S45*S45*(1.0-S12*S12)*(1.0-S12*S12)
      H11=-PF2-(2.0/ROF2)-(3.00/RFF)
      H13=(SOF2P/RT1S)*(-PO1-(1.5*RHOF2)-(1.5/ROF1)-(1.5/ROF2)-(1.5/RFF)
     1)
      H33=(1.0/(RT1S*RT1S))*(-PO1-PF2-(5.0/ROF1)-(3.0/ROF2)-(3.0/RFF)+SO
     1F1S*(-PF2-PO1-RHOO1-(1.5*RHOF2)-(2.5/ROF1)-(3.0/ROF2)-(3.0/RFF)))
      H31=(SOF2P/RT1S)*(-PF2-RHOO1-(1.0/ROF2)-(1.5/ROF1)-(1.5/RFF))
      H511=(1.0/RT2S)*(-PF2-(2.0/ROF2)-(3.0/RFF)+SOF2S*(-PF2-RHOO1-(1.0/
     1ROF2)-(1.5/ROF1)-(1.5/RFF)))
      H711=0.0
      H79=(1.0/RT1P)*(-PF2-(2.0/ROF1)-(3.0/RFF)+SOF1P*(-PO1-(1.5*RHOF2)-
     1(1.5/ROF1)-(1.5/ROF2)-(1.5/RFF)))
      H115=(1.0/RT2S)*(-PF2-2.0/ROF2-3.0/RFF+SOF2S*(-PO1-1.5*RHOF2-1.5/R
     1OF2-1.5/ROF1-1.5/RFF))
```

```
 H117=0.0
 H97=(1.0/RT1P)*(-PF2-2.0/ROF1-3.0/RFF+SOF1P*(-PF2-RHO01-1.0/ROF1-1
1.5/ROF2-1.5/RFF))
 Z1111=PF2+AF2
 Z1122=((S12*S12)/4.0)*(PO1+AO1+PF2+AF2+(2.0/ROF2))
 Z1112=(S12/2.0)*(PF2+AF2+(1.0/ROF2))
 Z1212=0.5*((1.0/RFF)+(1.0/ROF2))
 Z1221=Z1122
 Z1222=(S12/4.0)*(PO1+AO1+(1.0/ROF1)+(1.0/ROF2)+(1.0/RFF))
 Z1211=Z1112
 Z2222=0.25*(PO1+AO1+PF2+AF2+(2.0/ROF1))
 Z2212=Z1222
 Z2211=Z1122
 Z1316=(1.0/RT2S)*(PF2+AF2+(SOF2S/2.0)*(PF2+AF2+(1.0/ROF2)))
 Z1326=(1.0/(RT1S*RT2S))*((SOF2P/2.0)*(PF2+AF2+(1.0/ROF2))+((SOF2P*
1SOF2S)/4.0)*(PF2+AF2+PO1+AO1+(2.0/ROF2)))
 Z1361=(1.0/RT2S)*(0.06040*(PF2+AF2))
 Z1362=0.0
 Z1416=0.0
 Z1415=(1.0/RT1P)*((1.0/RFF)+(SOF1P/2.0)*((1.0/RFF)+(1.0/ROF2)))
 Z1426=0.0
 Z1425=(1.0/(RT1S*RT1P))*((SOF2P/2.0)*((1.0/ROF1)+(1.0/RFF))+((SOF2
1P*SOF1P)/4.0)*(PO1+AO1+(1.0/ROF1)+(1.0/ROF2)+(1.0/RFF)))
 Z1461=0.0
 Z1451=0.0
 Z1462=0.0
 Z1452=0.0
 Z2326=(1.0/(RT1S*RT1S*RT2S))*(((1.0/ROF2)+(1.0/RFF))*(1.0+SOF1S)+(
1(SOF2S/2.0)*(PO1+AO1+(1.0/ROF1)+(1.0/ROF2)+(1.0/RFF))*(1.0+SOF1S))
2)
 Z2316=Z1326
 Z2362=0.0
 Z2361=0.0
 Z2426=0.0
 Z2425=(1.0/(RT1S*RT1S*RT1P))*(((PF2+AF2+(1.0/ROF1))*(1.0+SOF1S))+(
1(1.0+SOF1S)*(SOF1P/2.0)*(PO1+AO1+PF2+AF2+(2.0/ROF1))))
 Z2416=0.0
 Z2415=Z1425
 Z2462=0.0
 Z2452=(1.0/(RT1S*RT1S*RT1P))*(0.06040*(PF2+AF2))
 Z2461=0.0
 Z2451=0.0
 Z3366=(1.0/(RT2S*RT2S))*(PF2+AF2+(SOF2S*(PF2+AF2+(1.0/ROF2)))+((SO
1F2S*SOF2S)/4.0)*(PO1+AO1+PF2+AF2+(2.0/ROF2)))
 Z3456=0.0
 Z3465=(1.0/(RT2S*RT1P))*((1.0/RFF)+((SOF1P/2.0)*((1.0/ROF2)+(1.0/R
1FF)))+((SOF2S/2.0)*((1.0/ROF1)+(1.0/RFF)))+((SOF2S*SOF1P)/4.0)*(PO
21+AO1+(1.0/ROF1)+(1.0/ROF2)+(1.0/RFF)))
 Z3466=0.0
 Z4466=0.0
 Z4455=(1.0/(RT1P*RT1P))*(((SOF1P*SOF1P)/4.0)*(PO1+AO1+PF2+AF2+(2.0
1/ROF1))+(SOF1P*(PF2+AF2+(1.0/ROF1)))+PF2+AF2)
 Z4456=0.0
 Z4465=0.0
 EE1=(S36*S36*S45*S45)*(1.0-S12*S12)*(2.0*H11+2.0*H33)+(S12*S36*S36
1*S45*S45)*(-1.0+S12*S12)*(2.0*H13+2.0*H31)+S36*S45*S45*(1.0-S12*S1
22)*(1.0-S12*S12)*2.0*H511+S35*S36*S45*(1.0-S12*S12)*(1.0-S12*S12)*
3(-2.0*H711)+S36*S36*S45*(1.0-S12*S12)*(1.0-S12*S12)*(2.0*H79)
 EE2=S36*S36*S45*S45*(Z1111+2.0*Z1212+Z2222)+(S12*S36*S36*S45*S45)*
```

```
     1((-2.0*Z1112)+(-2.0*Z1222)+(-2.0*Z1211)+(-2.0*Z2212))+(S12*S12*S36
     2*S36*S45*S45)*(Z1122+(2.0*Z1221)+Z2211)+(S36*S36*S45*S45*(1.0-S12*
     3S12))*(2.0*Z1212-(2.0*Z1221))+(S36*S45*S45*(1.0-S12*S12))*(4.0*Z13
     416-(2.0*Z1361)+(4.0*Z2326)-(2.0*Z2362))+(S12*S36*S45*S45*(1.0-S12*
     5S12)*(2.0*Z1362-(4.0*Z2316)+(2.0*Z2361)-(4.0*Z1326)))
      EE3=(S35*S36*S45*(-1.0+S12*S12))*((4.0*Z1416)-(2.0*Z1461)+(4.0*Z24
     126)-(2.0*Z2462))+(S36*S36*S45*(1.0-S12*S12))*((4.0*Z1415)-(2.0*Z14
     251)+(4.0*Z2425)-(2.0*Z2452))+(S12*S35*S36*S45*(1.0-S12*S12))*(4.0*
     3Z1426+(-2.0*Z1462)+(4.0*Z2416)+(-2.0*Z2461))+(S12*S36*S36*S45*(-1.
     40+S12*S12))*((4.0*Z1425)-(2.0*Z1452)+(4.0*Z2415)-(2.0*Z2451))
      EE4=(S45*S45*(1.0-S12*S12)*(1.0-S12*S12)*(Z3366))+(S36*S45*(-1.0+2
     1.0*S12*S12-S12**4)*(2.0*Z3456-4.0*Z3465))+ S35*S45*(-1.+2.0*S12*S1
     22-S12**4)*(Z3466*2.0)+((1.0-2.0*S12*S12+S12**4)*(S35*S35*Z4466+S36
     3*S36*Z4455-Z4456*S35*S36-Z4465*S35*S36))
      EE5=(S36*S36*S45*S45)*(1.0-S12*S12)*(2.0*H11+2.0*H33)+(S12*S36*S36
     1*S45*S45)*(-1.0+S12*S12)*(2.0*H13+2.0*H31)+S36*S45*S45*(1.0-S12*S1
     22)*(1.0-S12*S12)*2.0*H115+S35*S36*S45*(1.0-S12*S12)*(1.0-S12*S12)*
     3(-2.0*H117)+S36*S36*S45*(1.0-S12*S12)*(1.0-S12*S12)*(2.0*H97)
      EE=0.5*(EE1+EE5)+EE2+EE3+EE4
      ENUC=ZEFO1*ZEFF1*(1.0/ROF1)+ZEFO2*ZEFF2*(1.0/ROF2)+(9.0/RFF)
      HH12=EE+ENUC*SS12
   15 FORMAT(F10.5,5X,F10.5,F14.5,F13.5,F14.4,F14.4,8X,F14.8//)
      WRITE(6,15)ROF1,ROF2,SOF1S,SOF2S,SOF1P,SOF2P,EE
   81 FORMAT(6H SS12=,F12.8,6H HH12=,F12.8//)
      WRITE(6,81)SS12,HH12
   30 ROF1=ROF1+DR
      CONTINUE
      STOP
      END
```

```
C THIS PROGRAM COMPUTES THE MATRIX ELEMENTS,H23 AND S23, IN PLANE AO BASIS SET.
 1234 FORMAT(8F10.4)
   12 FORMAT(I3)
   13 FORMAT(F10.4)
   14 FORMAT(6F10.4)
   16 FORMAT(1H1,5X,4HROF1,10X,4HROF2,10X,5HSOF1S,9X,5HSOF2S,9X,5HSOF1P,
     19X,5HSOF2P,14X,2HEE///)
      DR=0.01
      WRITE(6,16)
      READ(5,14)PF2,PO1,AF2,AO1,RHOF2,RHOO1
      READ(5,13)ROF1
      READ(5,12)N
      DO 30 J=1,N
      READ(5,1234)SOF1S,SOF2S,SOF1P,SOF2P,ZEFO1,ZEFF1,ZEFO2,ZEFF2
      ROF2=4.000-ROF1
      RFF=SQRT(ROF1*ROF1+ROF2*ROF2)
      RT1S=SQRT(2.0+2.0*SOF1S)
      RT2S=SQRT(2.0+2.0*SOF2S)
      RT1P=SQRT(2.0+2.0*SOF1P)
      RT2P=SQRT(2.0+2.0*SOF2P)
      S17=(1.0/RT2P)*(1.0+SOF2P)
      S27=(1.0/(RT1S*RT2P))*(1.0+SOF2P+SOF1S)
      S28=(1.0/RT1S)*(1.0+SOF1S)
      S53=(1.0/(RT1P*RT2S))*(1.0+SOF2S+SOF1P)
      S63=(1.0/RT2S)*(1.0+SOF2S)
```

```
 S54=(1.0/RT1P)*(1.0+SOF1P)
 SS23=S17*S17*S28*S28*S54*S54*S63*S63
 H17=(1.0/RT2P)*(-PF2-2.0/ROF2-3.0/RFF+SOF2P*(-PO1-1.5/RFF-1.5/ROF1
1-1.5*RHOF2-1.5/ROF2))
 H18=0.0
 H28=(1.0/RT1S)*(-PF2-2.0/ROF1-3.0/RFF+SOF1S*(-PF2-RHOO1-1.0/ROF1-1
1.5/ROF2-1.5/RFF))
 H54=(1.0/RT1P)*(-PF2-2.0/ROF1-3.0/RFF+SOF1P*(-PF2-RHOO1-1.0/ROF1-1
1.5/ROF2-1.5/RFF))
 H63=(1.0/RT2S)*(-PF2-2.0/ROF2-3.0/RFF+SOF2S*(-PO1-1.5/RFF-1.5/ROF1
1-1.5*RHOF2-1.5/ROF2))
 H64=0.0
 H71=(1.0/RT2P)*(-PF2-2.0/ROF2-3.0/RFF+SOF2P*(-PF2-RHOO1-1.0/ROF2-1
1.5/ROF1-1.5/RFF))
 H81=0.0
 H82=(1.0/RT1S)*(-PF2-2.0/ROF1-3.0/RFF+SOF1S*(-PO1-1.5*RHOF2-1.5/RO
1F1-1.5/ROF2-1.5/RFF))
 H45=(1.0/RT1P)*(-PF2-2.0/ROF1-3.0/RFF+SOF1P*(-PO1-1.5*RHOF2-1.5/RO
1F1-1.5/ROF2-1.5/RFF))
 H36=(1.0/RT2S)*(-PF2-2.0/ROF2-3.0/RFF+SOF2S*(-PF2-RHOO1-1.0/ROF2-1
1.5/ROF1-1.5/RFF))
 H46=0.0
 Z1177=(1.0/(RT2P*RT2P))*(PF2+AF2+SOF2P*(PF2+AF2+1.0/ROF2)+(SOF2P/4
1.0)*(PF2+AF2+PO1+AO1+2.0/ROF2)*(SOF2P))
 Z1178=0.0
 Z1188=0.0
 Z1278=(1.0/(RT2P*RT1S))*((SOF1S*SOF2P/4.0)*(PO1+AO1+1.0/ROF1+1.0/R
1OF2+1.0/RFF)+0.5*SOF2P*(1.0/ROF1+1.0/RFF)+0.5*SOF1S*(1.0/ROF2+1.0/
2RFF)+1.0/RFF)
 Z1287=0.0
 Z1574=(1.0/(RT2P*RT1P))*(0.25*SOF2P*SOF1P*(PO1+AO1+1.0/ROF1+1.0/RO
1F2+1.0/RFF)+0.5*SOF2P*(1.0/ROF1+1.0/RFF)+0.5*SOF1P*(1.0/ROF2+1.0/R
2FF)+1.0/RFF)
 Z1547=0.0
 Z1584=0.0
 Z1548=0.0
 Z1673=(1.0/(RT2P*RT2S))*(0.25*SOF2P*SOF2S*(PF2+AF2+PO1+AO1+2.0/ROF
12)+0.5*SOF2P*(PF2+AF2+1.0/ROF2)+0.5*SOF2S*(PF2+AF2+1.0/ROF2)+PF2+A
2F2)
 Z1637=(1.0/(RT2S*RT2P))*(0.06040*(PF2+AF2))
 Z1683=0.0
 Z1638=0.0
 Z1674=0.0
 Z1647=0.0
 Z1684=0.0
 Z1648=0.0
 Z1288=0.0
 Z2288=(1.0/(2.0+2.0*SOF1S))*(0.25*SOF1S*SOF1S*(PO1+AO1+PF2+AF2+2.0
1/ROF1)+SOF1S*(PF2+AF2+1.0/ROF1)+PF2+AF2)
 Z2584=(1.0/(RT1P*RT1S))*(0.25*SOF1S*SOF1P*(PO1+AO1+PF2+AF2+2.0/ROF
11)+(.5*SOF1S+0.5*SOF1P)*(PF2+AF2+1.0/ROF1)+PF2+AF2)
 Z2548=(1.0/(RT1S*RT1P))*(0.06040*(PF2+AF2))
 Z2684=0.0
 Z2648=0.0
 Z2683=(1.0/(RT1S*RT2S))*(0.25*SOF1S*SOF2S*(PO1+AO1+1.0/ROF1+1.0/RO
1F2+1.0/RFF)+0.5*SOF1S*(1.0/ROF2+1.0/RFF)+0.5*SOF2S*(1.0/ROF1+1.0/R
2FF)+1.0/RFF)
 Z2638=0.0
 Z5544=(1.0/(RT1P*RT1P))*(0.25*SOF1P**2 *(PO1+AO1+PF2+AF2+2.0/ROF1)
```

```
    1+SOF1P*(PF2+AF2+1.0/ROF1)+PF2+AF2)
     Z5643=(1.0/(RT1P*RT2S))*(0.25*SOF1P*SOF2S*(PO1+AO1+1.0/ROF1+1.0/RO
    1F2+1.0/RFF)+0.5*SOF1P*(1.0/ROF2+1.0/RFF)+0.5*SOF2S*(1.0/ROF1+1.0/R
    2FF)+1.0/RFF)
     Z5634=0.0
     Z5644=0.0
     Z6633=(1.0/(RT2S*RT2S))*(0.25*SOF2S*SOF2S*(PO1+AO1+PF2+AF2+2.0/ROF
    12)+SOF2S*(PF2+AF2+1.0/ROF2)+PF2+AF2)
     Z6643=0.0
     Z6644=0.0
     EE1=S17*S28*S54*S54*S63*S63*(2.0*H17*S28-2.0*H18*S27+2.*H28*S17)+S
    154*S63*S17*S17*S28*S28*(2.0*H54*S63+2.0*H63*S54-2.0*H64*S53)
     EE2=S54*S54*S63*S63*(Z1177*S28*S28+( -2.0*Z1178)*(S27*S28)+Z1188*S
    127*S27+S17*S28*(4.0*Z1278-2.0*Z1287))+S17*S28*S54*S63*(S28*S63*(4.
    20*Z1574-2.0*Z1547)-S27*S63*(4.0*Z1584-2.0*Z1548)+S28*S54*(4.0*Z167
    33-2.0*Z1637)+S27*S54*(-4.0*Z1683+2.0*Z1638)+S28*S53*(-4.0*Z1674+2.
    40*Z1647)+S27*S53*(4.0*Z1684-2.0*Z1648))
     EE3=S54*S54*S63*S63*(-2.0*Z1288*S17*S27+Z2288*S17*S17)+S17*S17*S28
    1*S54*S63*(S63*(4.0*Z2584-2.0*Z2548)+S53*(-4.0*Z2684+2.0*Z2648)+S54
    2*(4.0*Z2683-2.0*Z2638))
     EE4=S17*S17*S28*S28*S63*(S63*Z5544+S54*(4.0*Z5643-2.0*Z5634)+S53*(
    1-2.0*Z5644))+S17*S17*S28*S28*(S54*S54*Z6633+S53*S54*(-2.0*Z6643)+S
    253*S53*Z6644)
     EE5=S17*S28*S54*S54*S63*S63*(2.0*H71*S28-2.0*H81*S27+2.*H82*S17)+S
    154*S63*S17*S17*S28*S28*(2.0*H45*S63+2.0*H36*S54-2.0*H46*S53)
     EE=0.5*(EE1+EE5)+EE2+EE3+EE4
     ENUC=ZEFO1*ZEFF1*(1.0/ROF1)+ZEFO2*ZEFF2*(1.0/ROF2)+(9.0/RFF)
     HH23=EE+ENUC*SS23
  15 FORMAT(F10.5,5X,F10.5,F14.5,F13.5,F14.5,F14.5,8X,F14.8//)
     WRITE(6,15)ROF1,ROF2,SOF1S,SOF2S,SOF1P,SOF2P,EE
  91 FORMAT(6H SS23=,F12.8,6H HH23=,F12.8)
     WRITE(6,91)SS23,HH23
  30 ROF1=ROF1+DR
     CONTINUE
     STOP
     END
```

```
C THIS PROGRAM COMPUTES THE MATRIX ELEMENTS,H11 AND S11,OUT OF PLANE AO BASIS
C SET.
1234 FORMAT(8F10.4)
  21 FORMAT(2F10.4)
  22 FORMAT(I3)
  23 FORMAT(F10.4)
  24 FORMAT(6F10.4)
  25 FORMAT(1H1,5X,5H ROF1,5X,5H ROF2,4X,6H SOF1S,4X,6H SOF2S,10X,3H EE
    1)
     DR=0.10
     WRITE(6,25)
     READ(5,24)PF2,PO1,AF2,AO1,RHOF2,RHOO1
     READ(5,23)ROF1
     READ(5,22)N
     DO 30 J=1,N
     READ(5,1234)SOF1S,SOF2S,SOF1P,SOF2P,ZEFO1,ZEFF1,ZEFO2,ZEFF2
     ROF2=4.000-ROF1
     RFF=SQRT(ROF1*ROF1+ROF2*ROF2)
```

```
      H11=-PF2-2.0/ROF2-3.0/RFF
      H33=0.5*(1.0/(1.+SOF1S))*(-PO1-PF2-5.0/ROF1-3.0/ROF2-3.0/RFF+SOF1S
     1*(-PF2-PO1-RHOO1-1.5*RHOF2-2.5/ROF1-3.0/ROF2-3.0/RFF))
      H55=0.5*(1.0/(1.0+SOF2S))*(-PO1-PF2-3.0/ROF1-5.0/ROF2-3.0/RFF+SOF2
     1S*(-PF2-PO1-RHOO1-1.5*RHOF2-3.0/ROF1-2.5/ROF2-3.0/RFF))
      H77=-PF2-2.0/ROF1-3.0/RFF
      Z12=PF2+AF2
      Z34=0.25*(PO1+AO1+PF2+AF2+2.0/ROF1)
      Z56=0.25*(PO1+AO1+PF2+AF2+2.0/ROF2)
      Z13=0.5*(1.0/ROF2+1.0/RFF)
      Z15=0.5*(PF2+AF2+1.0/ROF2)
      Z35=0.25*(PO1+AO1+1.0/ROF1+1.0/ROF2+1.0/RFF)
      Z17=1.0/RFF
      Z37=0.5*(PF2+AF2+1.0/ROF1)
      Z57=0.5*(1.0/ROF1+1.0/RFF)
      Z78=PF2+AF2
      ZK13=0.0
      ZK15=0.5*(1.0/(1.0+SOF2S))*(0.0604*(PF2+AF2))
      ZK17=0.0
      ZK35=0.25*(1.0/(1.0+SOF1S)*(1.0+SOF2S))*(0.0604*(PO1+AO1))
      ZK15=0.0
      ZK57=0.0
      ZK37=0.5*(1.0/(1.0+SOF2S))*(0.0604*(PF2+AF2))
      EE=2.0*H11+2.0*H33+2.0*H55+2.0*H77+Z12+4.0*Z13+4.0*Z15+4.0*Z35+Z34
     1+Z56+4.0*Z17+4.0*Z37+4.0*Z57+Z78-2.0*ZK13-2.0*ZK15-2.0*ZK35-2.0*ZK
     215-2.0*ZK17-2.0*ZK37-2.0*ZK57
      ENUC=ZEFO1*ZEFF1*(1.0/ROF1)+ZEFO2*ZEFF2*(1.0/ROF2)+(9.0/RFF)
      HH11=EE+ENUC
   20 FORMAT(4F10.4,F15.8/)
      WRITE(6,20)ROF1,ROF2,SOF1S,SOF2S,EE
   27 FORMAT(9H SS11=1.0,6H HH11=,F12.8//)
      WRITE(6,27)HH11
   30 ROF1=ROF1+DR
      CONTINUF
      STOP
      END
```

```
C THIS PROGRAM COMPUTES THE MATRIX ELEMENTS,H22 AND S22,OUT OF PLANE AO BASIS
C SET.
 1234 FORMAT(8F10.4)
   11 FORMAT(4F10.4)
   12 FORMAT(I3)
   13 FORMAT(F10.4)
   14 FORMAT(6F10.4)
   16 FORMAT(1H1,5X,4HROF1,10X,4HROF2,10X,5HSOF1S,9X,5HSOF2S,9X,5HSOF1P,
     19X,5HSOF2P,14X,2EE///)
      DR=0.01
      WRITE(6,16)
      READ(5,14)PF2,PO1,AF2,AO1,RHOF2,RHOO1
      READ(5,13)ROF1
      READ(5,12)N
      DO 30 J=1,N
      READ(5,1234)SOF1S,SOF2S,SOF1P,SOF2P,ZEFO1,ZEFF1,ZEFO2,ZEFF2
      ROF2=4.000-ROF1
      RFF=SQRT(ROF1*ROF1+ROF2*ROF2)
```

```
      RT1S=SQRT(2.0+2.0*SOF1S)
      RT1P=SQRT(2.0+2.0*SOF1P)
      S56=(1.0/RT1P)*SOF2S
      SS22=1.0-S56*S56+S56**4
      H11=-PF2-2.0/ROF2-3.0/RFF
      H33=(0.5*(1.0/(1.0+SOF1S)))*(-PO1-PF2-5.0/ROF1-3.0/ROF2-3.0/RFF+SO
     1F1S*(-PF2-PO1-RHOO1-1.5*RHOF2-2.5/ROF1-3.0/ROF2-3.0/RFF))
      H99= 0.5*(1.0/(1.0+SOF1P))*(-PO1-PF2-5.0/ROF1-3.0/ROF2-3.0/RFF+SOF
     11P*(-PF2-PO1-RHOO1-1.5*RHOF2-2.5/ROF1-3.0/ROF2-3.0/RFF))
      H1111=-PF2-2.0/ROF2-3.0/RFF
      H911=(SOF2S/RT1P)*(-PF2-RHOO1-1.5/ROF1-1.0/ROF2-1.5/RFF)
      H119=(SOF2S/RT1P)*(-PO1-1.5*RHOF2-1.5/ROF1-1.5/ROF2-1.5/RFF)
      Z1111=PF2+AF2
      Z1212=0.5*(1.0/ROF2+1.0/RFF)
      Z1515=0.5*(1.0/ROF2+1.0/RFF)
      Z1616=PF2+AF2
      Z2222=0.25*(PO1+AO1+PF2+AF2+2.0/ROF1)
      Z2525=0.25*(PO1+AO1+PF2+AF2+2.0/ROF1)
      Z2626=0.5*(1.0/ROF2+1.0/RFF)
      Z5555=0.25*(PO1+AO1+PF2+AF2+2.0/ROF1)
      Z5656=0.5*(1.0/ROF2+1.0/RFF)
      Z6666=PF2+AF2
      Z1661=0.0604*(PF2+AF2)
      Z2552=0.25*(1.0/(1.0+SOF1S)*(1.0+SOF1P))*(0.0604*(PO1+AO1+PF2+AF2)
     1)
      Z5665=((SOF2S*SOF2S)/(8.0*(1.0+SOF1P)))*(PO1+AO1+PF2+AF2+2.0/ROF2)
      Z1516=(1.0/RT1P)*(SOF2S/2.0)*(PF2+AF2+1.0/ROF2)
      Z2526=(SOF2S/4.0)*(1.0/RT1P)*(PO1+AO1+1.0/ROF1+1.0/ROF2+1.0/RFF)
      Z5556=(SOF2S/4.0)*(1.0/RT1P)*(PO1+AO1+1.0/ROF1+1.0/ROF2+1.0/RFF)
      Z5566=((SOF2S*SOF2S)/8.0)*(1.0/(1.0+SOF1P))*(PO1+AO1+PF2+AF2+2.0/R
     1OF2)
      Z5566=Z5665
      Z5666=(SOF2S/2.0)*(1.0/RT1P)*(PF2+AF2+1.0/ROF2)
      EE=(2.0*H11+2.0*H33+Z1111+4.0*Z1212+Z2222)*(1.0-(2.0*S56*S56)+(S56
     1**4))+(2.0*H99+2.0*H1111+4.0*Z1515+4.0*Z1616+4.0*Z2525+4.0*Z2626+2
     2.0*Z5656-2.0*Z5665-2.0*Z1661-2.0*Z2552)*(1.0-S56*S56)+(2.0*H911+2.
     30*H119+8.0*Z1516+8.0*Z2526)*(-S56+S56**3)+Z5555+2.0*Z5656+Z6666+(4
     4.0*Z5556+4.0*Z5666)*(-S56)+(2.0*Z5566+2.0*Z5665)*(S56*S56)
      ENUC=ZEFO1*ZEFF1*(1.0/ROF1)+ZEFO2*ZEFF2*(1.0/ROF2)+(9.0/RFF)
      HH22=EE+SS22*ENUC
   15 FORMAT(F10.5,5X,F10.5,F14.5,F13.5,F14.4,F14.4,8X,F14.8//)
      WRITE(6,15)ROF1,ROF2,SOF1S,SOF2S,SOF1P,SOF2P,EE
   27 FORMAT(6H SS22=,F12.8,6H HH22=,F12.8//)
      WRITE(6,27)SS22,HH22
   30 ROF1=ROF1+DR
      CONTINUE
      STOP
      END
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VITA

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Candidate for the Degree of

Doctor of Philosophy

Thesis: THEORETICAL INVESTIGATION OF THE BOND-BOND INTERACTION FORCE CONSTANT IN XF_2 MOLECULES

Major Field: Chemistry

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