1996

Analysis of the Electronic Kinetic Energy in Xenon Difluoride

Michael Fiore Amendola

College of William & Mary - Arts & Sciences

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Analysis of the Electronic Kinetic Energy
in Xenon Difluoride

A Thesis
Presented to
The Faculty of the Department of Chemistry
The College of William and Mary in Virginia

In Partial Fulfillment
of the Requirements for the Degree of
Master of Arts

by
Michael Fiore Amendola
1996
APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirements for the degree of

Master of Arts

Michael Fiore Amendola

Approved, August 1996

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Christopher J. Abelt, Ph. D.

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ACKNOWLEDGEMENTS

The writer wishes to express his sincere thanks to Professor Stephen K. Knudson for his guidance, instruction, and constructive criticism of the research contained within. The author is also indebted to Professors Christopher J. Abelt and Eric J. Dawnkaski for their careful reading and criticism of this manuscript.

The writer is most thankful to the faculty of the Department of Chemistry at the College of William and Mary for their continual commitment to the education of those in this discipline.

Finally, a special thanks to Heather Ewald for her encouragement, and as always to my family for their unending support of my pursuits.
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ABSTRACT

The objective of the present study was to characterize the bonding in the molecule xenon difluoride, XeF₂, by examination of the kinetic energy. An effective core potential approximated the large number of core electrons to a Gaussian type function. The valence electrons were calculated explicitly using a contracted Gaussian basis set. The molecular wavefunction of the system began at the SCF and TCSCF levels of calculation and compared favorably to all electron calculations of the same molecule over a series of bond lengths. Further MCSCF and CI energy curves were performed over a range of internuclear separations to obtain a lower molecular energy. The geometry optimization of the CI calculation yielded a 1.9866 Å value of the equilibrium bond length and a 1.82 eV dissociation energy, a 0.486% and 34% difference from experiment respectively. The molecular orbitals of the SCF wavefunction were examined for their energy and bonding types. These findings were confirmed with literature values. Additionally, the total and components of the kinetic energy of the SCF molecular orbitals were examined over a series of bond lengths. The study concluded the major bonding in the molecule occurs in the 2σ_u molecular orbital, a result support by the literature. Bonding of a smaller degree was discovered in other molecular orbitals but these were ruled out due to energy cancellations and nuclear repulsion effects. Thus, all orbitals except the 2σ_u molecular orbital were ruled out as major contributors to the stability of the XeF₂ molecule.
ANALYSIS OF THE ELECTRONIC KINETIC ENERGY
IN XENON DIFLUORIDE
I. INTRODUCTION

A. PURPOSE

The presented research was begun with the goal of increasing our understanding of chemical bonding by examining kinetic energy behavior. For our research we choose to examine a noble gas compound, xenon difluoride. The research was conducted on two fronts, one to establish various levels of calculations modelling the molecule, and the second to characterize the kinetic energy in the molecule.

The first phase established the wavefunction describing the molecular system. The total energy curves of various levels of calculation were found and compared to literature values to indicate the accuracy of the description.

The major aim of research was then to examine the kinetic energy of the molecule. Due to the potentially unique character of the bonding in noble gas compounds, we choose to explore the bonding in a different manner than common in the literature today.

Accepted chemical dogma emphasizes the decease of the potential energy as the important criteria for bond formation. Examination of the other component of the total energy, the
kinetic energy, is usually not invoked to explain chemical bonding processes.

In our present study we wish to explicitly examine the kinetic energy of the molecular orbitals of the xenon difluoride. We feel that such an analysis reveals unique characteristics about the bonding in the molecule, characteristics that might not have been as apparent from sole examination of the potential energy.

B. PHYSICAL PROPERTIES

The first stable noble gas compound, [Xe]⁺[PtF₆]⁻, was discovered in 1962 by Neil Bartlett.¹ That same year, scientist at Argonne National Laboratories discovered if elemental xenon and fluorine are heated at 400°C in a nickel canister the compound XeF₄ was formed.² During this synthesis evidence indicated a lower fluoride of xenon was present. This secondary compound was XeF₂. Since this accidental discovery, two research groups have independently described a practical room temperature synthesis.³,⁴

Raman and infrared studies have found XeF₂ to be a symmetrical and linear molecule belonging to the Dₘₘₘ point group.⁵ The molecule is a colorless crystalline solid at room temperature (mp 129°C) and is relatively unreactive with air.⁶ The first reported infrared gas phase experimental value for
Xe-F equilibrium bond length ($R_e$) value was $1.977 \pm 0.002 \text{ Å}$.\(^7\) A recent Raman spectrum of the molecule yielded a more accurate value of $1.9791 \pm 0.0001 \text{ Å}$.\(^8\) This value is close to more recent infrared region data of $1.97436 \pm 0.00001 \text{ Å}$.\(^9\) The solid state neutron diffraction value of the equilibrium bond length is slightly higher, $2.00 \pm 0.01 \text{ Å}$.\(^10\)

The dissociation of XeF$_2$ into its constituent elements

$$\text{XeF}_2 \rightarrow \text{Xe} + 2\text{F} \quad (1.1)$$

yields a dissociation energy of about 64 kcal/mole = 2.78 eV.\(^{11}\) In relation to other molecules, this dissociation energy is relatively low but by no means weak.\(^{12}\)

The simple model of bonding in XeF$_2$ has been put forth by Coulson\(^{13}\)

![Figure 1.1: Simple Lewis structures detailing the Coulson model of bonding in XeF$_2$.](image)

C. ELECTRONIC STUDIES

The task of successfully modelling the molecule by computational calculations is difficult due to its large number of electrons. Atomic xenon has the core electron configuration of krypton and valence electron configuration of $5s^2 \ 4d^{10} \ 5p^6$. Fluorine has the configuration of the helium core
and 2s\(^2\) 2p\(^5\) valence electrons. When these atoms are combined to form xenon difluoride, the total number of electrons is 72, two fluorines each providing 9 electrons and xenon contributing 54 electrons. The triatomic has 50 core electrons and 22 valence electrons.

The first study of the electronic structure of XeF\(_2\) appeared in 1971\(^\text{14}\). These researchers were confined to a less accurate description due to the limitation of computing resources available at the time to handle heavy atoms. Thus, only limited qualitative conclusions could be drawn from the work.

In their classic text on bonding, DeKock and Gray predicted the valence electron structure of XeF\(_2\) based on the analogous CO\(_2\) system\(^\text{15}\).

\[ [\sigma^b_g(F_{2s})]^2 \quad [\sigma^b_u(F_{2s})]^2 \quad [\sigma^b_g(s)]^2 \quad [\sigma^b_u(z)]^2 \quad [\pi^b_u(x,y)]^4 \quad [\pi^b_g(x,y)]^4 \quad [\pi^b_u(x,y)]^4 \quad [\sigma^*_g(s)]^2 \]

Simplifying this notation,

\[(1\sigma_g)^2 \quad (1\sigma_u)^2 \quad (2\sigma_g)^2 \quad (2\sigma_u)^2 \quad (1\pi_u)^4 \quad (1\pi_g)^4 \quad (2\pi_u)^4 \quad (3\sigma_g)^2\]

the authors proposed that there was only one net sigma bond and no net pi bonds. This conclusion is drawn on the premise that energy gains in a bonding orbital (denoted by a superscript \(b\)) are offset by electron losses from electron occupation in an antibonding orbital (superscript \(\ast\)), thus
making no "net bond" in the molecule. Nonbonded orbitals (nb) do not help nor hurt the bonding due to the non-interaction of the constituent atomic orbitals. Canceling these molecular orbitals out with this criteria, only the fourth molecular orbital (2σu) is believed to be responsible for the bonding in the molecule.

This orbital order is in conflict with the photo-electronic study on XeF₂.¹⁶ This experimental work indicated the outermost molecular orbital is not the 3σg but the 2πu. DeKock and Gray suggest that d orbital participation from the xenon might affect the orbital order. The participation of the outer orbitals of XeF₂ has been supported by phenomenological evidence and has been a source of debate in qualitative discussions of the molecular orbitals.¹⁷

To date the best level of analysis on XeF₂ has been the work of Bagus and co workers.¹⁸ This was a nonrelativistic study of the molecule that included several levels of electronic correlation calculations.

D. AB INITIO METHODS

One way to characterize molecular and atomic systems is to use an ab initio method. Ab initio means "from the beginning", thus it does not rely on empirical data formulation. These methods are used to detail characteristics
of selected systems.

To describe XeF₂ or any other molecule, one must use a wavefunction, ψ, which defines the state of the system. To obtain the energy of the system, the Schrödinger equation must be solved,

$$\hat{H}\psi = E\psi \quad (1.2)$$

where $H$ is the Hamiltonian that operates on the wavefunction and produces an eigenvalue $E$, the energy of the molecular system.

For almost all systems, solving the Schrödinger equation with the exact wavefunction is impossible. Instead a trial wavefunction ($\psi_{\text{TRIAL}}$) is utilized to approximate the true wavefunction. The Hamiltonian is modified to average the electron to electron interactions in the molecule. This simplifies the solving of the Schrödinger equation and makes it possible to deal with it in computational environments.

In describing molecular system, the trial wavefunction is a linear combination of known basis functions ($\chi_i$), or given by,

$$\psi_{\text{TRIAL}} = \psi_T = \sum_i c_i \chi_i \quad (1.3)$$

These functions, $\chi_i$, are usually atomic orbitals and are known as a linear combination of atomic orbitals (LCAO) or the basis set functions. The contribution of each atomic basis function
is controlled by a coefficient, $c_i$.

The overall description of the molecular system can be improved one of two ways. First, the basis set can have more and more "flexibility" built into it. This is achieved by increasing the number of functions that describe each atomic orbital. This flexibility in the basis allows the trial wavefunction to be modified closer and closer to the true wavefunction. The second way of achieving a better description is to account in a direct way for the electron to electron interactions that were originally averaged in the Hamiltonian. This is achieved by allowing a variety of electronic configurations to mix together to describe the molecular system. This does not change the Hamiltonian, but it overcomes the limitation that was imposed to solve the trial wavefunction. This mixing accounts for the instantaneous electron to electron interaction, or the electron correlation.

The method used to solve the Hamiltonian with the trial wavefunction is called the variational method. This method is based on the variational theorem,

Given a system whose Hamiltonian operator, $H$ is time independent and whose lowest energy eigenvalue is $E$, if $\Psi_T$ is any normalized, well-behaved function of the coordinates of the system's particles that satisfies the boundary conditions of the problem, then\(^{19}\)
\[ \int \psi^*_t \hat{H} \psi_t \, dt = E_t, \quad \psi_t \text{ normalized} \]

$E_t$ is the energy of the system which is obtained with the true wavefunction. Operating with the Hamiltonian on the linear combination of atomic orbitals of the trial wavefunction produces a series of equations with unknown coefficients. These coefficients are found such that the lowest energy of the system is obtained.

To formulate the electron structure of XeF$_7$, the General Atomic and Molecular Electron Structure System computer program (GAMESS) was utilized. This program evaluates the electron structure of atoms and molecules and offers a multitude of quantum mechanical approximations to detail atomic and molecular characteristics.

For the various levels of calculations in the present study an input file has been provided in APPENDIX A. GAMESS has a sequence of commands that are executed in reference to a series of key commands as listed in the input file. In an input file the first word on a line, denoted by a dollar sign, designates a command category which has a string of instructions that follow. Any lines preceded with an exclamation mark are comment cards and are ignored in the actual computational run. GAMESS takes this set of instructions and calculates the desired system properties.
placing their values into an output file.

E. EFFECTIVE CORE POTENTIAL

To reduce the computational demand of dealing with large atoms (atoms with large numbers of electrons), an effective core potential (ECP) can be utilized. This approximation sequesters away the core electrons on atomic centers, replacing their behavior by a function. This leaves the outer or valence electrons to be dealt with explicitly. Such a division is motivated by the accepted notions of chemical bonds being predominantly a function of these outer electrons.

An ECP approximation is a necessity in the present study due to the number of electrons in the XeF₂ system. The molecule has a total of 72 electrons, 50 of which are replaced by an effective core potential. The xenon contributes a total of 54 electrons to the molecule while the fluorine contributes nine. Therefore, the xenon has the majority of its core, 46 electrons removed by an ECP while each fluorine only has two electrons sequestered away. This leaves twenty-two electrons to occupy eleven valence orbitals on the molecule. This reduction in the number of electrons to be dealt with explicitly is realistic with regard to the current computational resources available to us for this study.
F. STRUCTURE OF THESIS

The first section, MOLECULAR WAVEFUNCTION, of this thesis details the background concerning the molecular wavefunction. This section explains various forms and differences in the approximate wavefunctions employed to model XeF₂. A general background will be introduced that explains the particulars of the basis sets used in the present work.

The second section, RESULTS - TOTAL ENERGIES AND WAVEFUNCTIONS, explains our results and methods obtained while working for a better wavefunction to describe the molecular system. The goal of these results was to minimizing the total energy curve of the system. A lower energy indicates an improving description of the system and a closer step to the actual form of the true wavefunction.

The next section, RESULTS - KINETIC ENERGIES, explains the modifications made to the GAMESS code for calculating the molecular orbital kinetic energy. Furthermore, the formal relations between the kinetic and potential energy are explained. This section also looks at the characteristics of the kinetic energy and ascertains the role it plays in describing the bonding in XeF₂.

In the last section, we summarize our results and draw our conclusions. Furthermore, recommendations for future
research directions on XeF₂ are made.
REFERENCES FOR INTRODUCTION


17. Bartlett, 223.


19. Levine, 189.

A. INTRODUCTION

This section discusses the different types of variational molecular wavefunctions used in our investigation of XeF₂. Hence forth, the variational wavefunction is simply referred to as a "wavefunction". This discussion is motivated by various quantum chemistry primers¹,² and is offered to establish a context for our results.

The first wavefunction and method discussed are termed Hartree-Fock-Slater (HFS) wavefunction. The HFS method is a widely used *ab initio* calculation. Due to its iterative nature, this method is usually referred to as a self consistent field calculation, or SCF for short. In this study, we employ this wavefunction to examine the bonding in the molecule. The expression of the SCF wavefunction in a series of basis functions is also examined.

The basis set section introduces the reader to the basic types of functions used in a basis set. After this discussion we introduce the formalism of the effective core potential approximation.

The next type of wave function explored is the two
configuration self consistent field calculation (TCSCF). This calculation provides more flexibility than the SCF calculation by allowing another electronic configuration to be used to find the lowest energy. These two configurations are governed by a variational coefficient that specifies the contribution each configuration has on the final molecular wave function.

The TCSCF calculation is a subset of a multi configuration self consistent field calculation (MCSCF). This calculation allows for two or more configurations to be used in the molecular wavefunction.

The last calculation is configuration interaction. This takes the wavefunction from the MCSCF calculation and allows for more mixing of configurations. This mixing better accounts for the electron to electron instantaneous interaction, or electron correlation. This calculation should lower the energy the most of all the methods thus far mentioned.

Readers who are familiar with the concept of the one electron approximation of molecular orbitals may prefer to skip to C. BASIS FUNCTIONS.

B. HARTREE-FOCK-SLATER METHOD

1. BASIS OF METHOD: The Hartree-Fock-Slater (HFS) method is a widely used calculation for ascertaining the properties of multielectron atoms and polyatomic molecules. Our discussion begins with general principles used in the calculation of atomic systems. Then an expanded discussion
follows with regard to a molecular system.

2. **ATOMIC CASE**: The Schrödinger equation is separable for atomic hydrogen, and thus relatively simple to solve. But when considered for a multielectron atom, or subsequently a molecule, the luxury of the separation of variables is not possible due to interelectronic repulsions. If these repulsions are ignored, the wavefunction becomes the product of $n$ hydrogenlike one-electron orbitals

$$\psi_{\text{atomic}} = f_1(x_1, \theta_1, \phi_1) f_2(x_2, \theta_2, \phi_2) \ldots f_n(x_n, \theta_n, \phi_n) \quad (2.1)$$

where each hydrogenlike orbital is expressed in terms of polar spherical coordinates (to be detailed in the basis set section). The general form of these orbitals are

$$f = R_{n}^{l}(r) Y_{l}^{m}(\theta, \phi) \quad (2.2)$$

where $R_{n}^{l}(r)$ is the radial part of the orbital and $Y_{l}^{m}(\theta, \phi)$ is the spherical harmonic function that describes the three dimensional character of the orbital.

To add more flexibility to the system, a general function, $g$, is used instead of hydrogenlike orbitals. This new function has a similar form to the hydrogenlike orbitals

$$g_i = h_i(x_i) Y_i^{l}(\theta_i, \phi_i) \quad (2.3)$$

To find a suitable wavefunction that yields an energy, one
must find a suitable \( \{ g_i \} \).

Douglas Hartree introduced the Hartree self-consistent field method to find such a set of unknown functions \( \{ g_i \} \) and solve for the energy. First an atomic wavefunction is written as

\[
\phi_{atomic} = g_1(x_1, \theta_1, \phi_1) g_2(x_2, \theta_2, \phi_2) \cdots g_n(x_n, \theta_n, \phi_n) \quad (2.4)
\]

where \( g_i \) is a normalized radial function multiplied by a spherical harmonic whose form is given in (2.3).

In expressing (2.4), the interelectronic interactions were excluded. These interactions are reintroduced explicitly by averaging the instantaneous interaction between some electron 1 and all other electrons in the system. Taking for example the potential energy of an interaction between electron 1 and 2.

\[
V_{12} = \frac{Q_1 Q_2}{4 \pi \varepsilon_o r_{12}} \quad (2.5)
\]

where \( Q_1 \) and \( Q_2 \) are the charges in coulombs on electrons 1 and 2 respectively \( (Q_1 = Q_2 = -e) \), \( r_{12} \) is the distance between electron 1 and 2, and \( \varepsilon_o \) is the permittivity of free space. To average the charge of \( Q_2 \), a smear of electronic density, \( \rho_2 \) must be integrated over a volume unit, \( dv_2 \). Rewriting (2.5)

\[
V_{12} = \frac{Q_1}{4 \pi \varepsilon_o} \int \frac{\rho_2}{r_{12}} dv_2 \quad (2.6)
\]

with \( \rho_2 = |g_2|^2 \)
Electron 1 has a similar charge of $-e$, thus

$$V_{12} = e^2 \int \frac{\left| g_2 \right|^2}{r_{12}} dv_2 \quad (2.7)$$

where $e^2$ is defined as $\frac{q^2}{4\pi\varepsilon_0}$, where $q$ is the charge on the electron. Summing the interactions of electron 1 with all other electrons

$$V_{12} + V_{13} + \ldots V_{1n} = \sum_{j=2}^{n} e^2 \int \frac{\left| g_j \right|^2}{r_{1j}} dv_j \quad (2.8)$$

To write the total potential for electron 1, the nuclear attraction term must be added in

$$V_1(r_1, \theta_1, \phi_1) = \sum_{j=2}^{n} e^2 \int \frac{\left| g_j \right|^2}{r_{1j}} dv_j - \frac{Ze^2}{r_1} \quad (2.9)$$

The potential is approximated over all angles and placed into the Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla_1^2 + V_1(r_1) \right\} g_1(1) = \epsilon_1 g_1(1) \quad (2.10)$$

where $-(\hbar^2/2m_e)\nabla_1^2$ is the kinetic energy operator, and $\epsilon_1$ is the energy of electron 1 in orbital one.

The HFS procedure begins by using some guess orbitals that are of the form of (2.4). Once these orbitals are
entered, a series of orbital energies can be generated, \( \{ \epsilon_i \} \). These functions correspond to an improved set of orbitals, or a new set of \( \{ \mathbf{c}_i \} \), that can be reentered to render an improved energy. At some point where the energy difference between two successive inputs differs slightly, the method is stopped and the energy is said to have converged at that value. The exact steps of this process are explained in the next section.

Taking this set of \( \epsilon_i \), the energy of the system could be calculated by summing \( \epsilon_i \) for all electrons. But in doing so each electron to electron repulsion is counted twice. For example, in solving the potential for electron 1, the interaction of electron 2 is included along with the interaction of electron 1 with all other \( n \) electrons. When the potential for electron 2 is solved, it takes into account its interaction with electron 1 as well as all other electrons. Therefore, by summing all \( \epsilon_i \), all electron to electron interactions are counted twice. To correct for this error the expectation value of the \( 1/r_{ij} \) interaction is subtracted from the sum of all \( \epsilon_i \).

\[
E = \frac{1}{n} \sum_{i=1}^{n} \epsilon_i - \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \int \int \frac{e^2 |g_i'(i)|^2 |g_j'(j)|^2}{r_{ij}} \, dv_i \, dv_j
\]

\[
= \frac{1}{n} \sum_{i=1}^{n} \epsilon_i - \sum_{i,j} J_{ij}
\]

(2.11)

where \( J_{ij} \) is defined as the Coulomb integral.

Slater and Fock independently pointed out in 1930 that
the Hartree wavefunction shown in (2.3) should be a spin orbital and not only a spatial orbital and should obey the Pauli Principle. Therefore, a Hartree calculation that uses such orbitals is called here a Hartree-Fock-Slater (HFS) calculation.

A general form of the Schrödinger equation in this method can written as

\[ \hat{F} \mu_i = \varepsilon_i \mu_i \quad i = 1, 2, 3, \ldots n \]  

(2.12)

where \( \mu_i \) is the spin-orbital, \( \hat{F} \) is the Fock operator which is a redefined Hamiltonian for the HFS (as seen in the brackets in (2.11)), and \( \varepsilon_i \) is the energy of the spin orbital \( i \).

Roothaan in 1951 proposed to represent the spatial part of the spin orbital as a linear combination of a complete set of known functions, called basis functions

\[ g_i = \sum c_i \chi_i \]  

(2.13)

In practice the expansion in terms of basis functions is truncated so they may be used realistically.

3. MOLECULAR CASE: In this section we discuss the use of the HFS method for the general closed shell molecular case. In the atomic section the HFS wavefunction was a product of a spin orbital and a spatial orbital, combined into a Slater determinant of spin-orbitals. Multiplying each side of (2.12) by \( \mu_i^* \) and integrating over all space
where $E_{\text{molecular}}$ is the molecular energy, or the HFS energy, $D$ is the Slater determinant, $H_d$ is the electronic Hamiltonian, and $V_{NN}$ is the nuclear repulsion potential. The molecular Hamiltonian can be separated in this way due to the Born-Oppenheimer Approximation. Equation (2.14) can be further reduced by bringing $V_{NN}$ outside of the brackets and the wavefunction is normalized.

$$E_{\text{molecular}} = \langle D|\hat{H}_{el}|D\rangle + V_{NN} \quad (2.15)$$

In HFS the electronic Hamiltonian is redefined in terms that simplify it making it advantageous for programming. Thus,

$$\hat{H}_{el}(1) = \hat{\Phi}(1) = H_{(1)}^{\text{CORE}} + \sum_{j=1}^{n/2} [2J_j(1) - K_j(1)] \quad (2.16)$$

$$H_{(1)}^{\text{CORE}} = -\frac{1}{2} v_1^2 - \sum \frac{Z_a}{r_{1a}} \quad (2.17)$$

$H_{(1)}^{\text{CORE}}$ is the one electronic core Hamiltonian which defines the properties of an electron except the interelectronic repulsions. $J_j$ is the coulomb operator and $K_j$ is the exchange operator each defined as

$$\hat{J}_j(1)f(1) = f(1)\int |\phi_j(2)|^2 \frac{1}{r_{12}} dv_2 \quad (2.18)$$
The Coulomb integral accounts for interactions of electron 1 with all other electrons. This term averages the potential generated by all other electrons and is termed "coulombic" because it takes into account electrostatic interactions. The exchange integral relates the exchange of electron 1 into the other orbitals of the molecule.

Now that the Fock operator has been defined, it can be applied to orbital 1. Beginning with a general form of the Schrödinger equation

\[ \epsilon_i \Phi_i = \hat{F} \Phi_i \quad (2.20) \]

multiplying by \( \Phi_i^* \) and integrating over all space

\[ \epsilon_i \int \Phi_i^* \Phi_i \, d\tau = \int \Phi_i^* \hat{F} \Phi_i \, d\tau \]
\[ \epsilon_i = \int \Phi_i^* \hat{F} \Phi_i \quad (2.21) \]

Substituting (2.16) into (2.21)

\[ \epsilon_i = \langle \Phi_i(1) | H^\text{CORE} | \Phi_i(1) \rangle + \sum_j [2 \langle \Phi_i(1) | J_{ij}(1) | \Phi_i(1) \rangle - \langle \Phi_i(1) | K_{ij}(1) | \Phi_i(1) \rangle] \]
\[ \epsilon_i = H^\text{CORE}_{ii} + \sum_{j=1}^{\frac{n}{2}} (2J_{ij} - K_{ij}) \quad (2.22) \]

summing (2.22) over all \( \frac{n}{2} \) occupied orbitals
It is generally known for a closed shell system

\[ E_{\text{HFS}} = 2 \sum_{i=1}^{n/2} H_{\text{CORE}} + n/2 \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{\text{NN}} \]  

(2.24)

Substituting (2.23) into (2.24) an expression for the total energy is found using the individual orbital energies

\[ E_{\text{HFS}} = 2 \sum_{i=1}^{n/2} \varepsilon_i - \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{\text{NN}} \]  

(2.25)

this expression of the HFS energy takes into account counting all interelectronic repulsions twice.

As in the atomic case, the molecular calculation utilizes an expansion of a linear combination of one electron basis functions \( \chi_s \)

\[ \phi_i = \sum_{j=1}^b c_{si} \chi_s \]  

(2.26)

For clarity all basis functions carry subscripts \( r, s, t, \ldots \) and all molecular orbitals have subscripts \( i, j, k, \ldots \) Placing the basis set into (2.20)

\[ \sum_{s} c_{si} \hat{\varepsilon} \chi_s = \varepsilon_i \sum_{s} c_{si} \chi_s \]  

(2.27)
multiplying by $\chi_r^*$ and integrating over all space

$$\sum_s \int \chi_r^* \Phi_s \, d\tau = \epsilon_i \sum_s \int \chi_i^* \chi_s \, d\tau$$  \hspace{1cm} (2.28)

rewriting

$$\sum_s C_{si} F_{Is} = \epsilon_i \sum_s C_{si} S_{Is}$$
$$\sum_s C_{si} (F_{Is} - \epsilon_i S_{Is}) = 0$$  \hspace{1cm} (2.29)
$$F_{Is} = \langle \chi_i | F | \chi_s \rangle \quad S_{Is} = \langle \chi_i | \chi_s \rangle$$

this forms a set of $b$ simultaneous linear homogeneous equations in $b$ unknowns $c_{si}$, $s = 1, 2, 3, \ldots b$. To obtain the nontrivial solution the determinant of (2.29) must be found

$$\det (F_{Is} - \epsilon_i S_{Is}) = 0$$  \hspace{1cm} (2.30)

The essence of the HFS calculation is an iterative process that produces orbitals and energies for a molecular system. The process begins by using a set of trial molecular orbitals as a linear combination of basis functions (2.26). These trial molecular orbitals in practice are formulated by a less rigorous calculation. With these trial orbitals the Fock operator is calculated using equations (2.16) to (2.19). Next the matrix elements must be calculated (2.29).

The secular determinant (2.30) can be solved for a set of $\epsilon_i$s. Using each of these $\epsilon_i$s to solve (2.29) generates a set of coefficients $\{c_{si}\}$ in the basis set. These coefficients yield
a different set of molecular orbitals from the entered trial orbitals.

Then the Fock operator is reevaluated using these improved orbitals and the process begins again. These steps are carried out until the energy difference of the entered orbitals is small in comparison to the energy of the output orbitals. This converged value of the energy is not guaranteed by the method and is called the Hartree-Fock-Slater energy, or the Self Consistent Field (SCF) energy.

4. ORBITAL OCCUPATION: In the HFS method the electronic configuration always places two electrons into the lowest energy molecular orbitals. This double occupation and selection of the ground state is a very "chemical" or standard way of examining the molecule. In actual systems, the electrons to some extent do populate the higher non occupied orbitals, or virtual orbitals. However, the HFS method chooses only to populate the lower energy orbitals. This approximation limits the HFS calculation in the accuracy of the energy value, but experience has shown that it does not affect to any considerable degree the calculation of other properties of the system.

5. MATRIX ELEMENTS FOR LCAO BASES: In the previous section, the determinant of equation (2.30) was solved to obtain an energy for the molecular system. The integrals $F_n$ and $S_n$ were given in terms of the basis set $\{\chi\}$
Calculation $S_n$ is usually easily performed. In contrast, $F_n$ needs to be expanded in terms of the basis functions $r$ and $s$. Substituting (2.31) into the Fock operator definition for electron 1

$$F_n = \langle \chi_r | \hat{\mathbf{F}} | \chi_s \rangle = \langle \chi_r | \hat{H}_{\text{CORE}} | \chi_s \rangle + \sum_{j=1}^{\Sigma} [2 \langle \chi_r | \hat{J}_j | \chi_s \rangle - \langle \chi_r | \hat{\mathbf{K}}_j | \chi_s \rangle]$$

Using the definition of the Coulomb operator $J_j$ (equation (2.18) using $f(l) = \chi_s(l)$)

$$J_j(1) \chi_s(1) = \chi_s(1) \int \frac{\phi_j^*(2) \phi_j(2)}{r_{12}}$$

$$= \chi_s(1) \sum_{i} \sum_{u} c_{uj}^* c_{uj} \int \frac{\chi_i^*(2) \chi_u(2)}{r_{12}} dv_2$$

Multiplying by $\chi_r(1)$ and integrating over all space it then follows,

$$\langle \chi_r(1) | \hat{J}_j(1) \chi_s(1) \rangle = \sum_{i=1}^{b} \sum_{u=1}^{b} c_{uj}^* c_{uj}$$

$$\int \int \frac{\chi_r^*(1) \chi_s(1) \chi_i^*(2) \chi_u(2)}{r_{12}} dv_1 dv_2$$

$$\langle \chi_r(1) | \hat{J}_j(1) \chi_s(1) \rangle = \sum_{i=1}^{b} \sum_{u=1}^{b} c_{uj}^* c_{uj} (rs | tu)$$

where the two electron repulsive integral is defined as
A similar reduction of the exchange operator \( K_j \) produces

\[
\langle \chi_r(1) | \hat{X}_j(1) \chi_r(1) \rangle = \sum_{i=1}^{\beta} \sum_{u=1}^{\beta} C_{ij}^* C_{u} \quad (ru|ts) \quad (2.36)
\]

Substituting (2.36) and (2.34) into the Fock operator definition, a new form of the Fock operator is found in terms of the basis set functions

\[
F_{rs} = H_{rs}^{\text{CORE}} + \sum_{i=1}^{\beta} \sum_{u=1}^{\beta} \sum_{j=1}^{n/2} C_{ij}^* C_{u} \quad [2(rs|tu)-(ru|ts)] \quad (2.37)
\]

Defining the electron-density matrix elements, \( P_{tu} \) as

\[
P_{tu} = 2 \sum_{j=1}^{n/2} C_{ij}^* C_{u} \quad t=1,2,3 \ldots \beta \quad u=1,2,3 \ldots \beta \quad (2.38)
\]

thus,

\[
F_{rs} = H_{rs}^{\text{CORE}} + \sum_{i=1}^{\beta} \sum_{u=1}^{\beta} \sum_{j=1}^{n/2} P_{tu} \quad [(rs|tu)-\frac{1}{2}(ru|ts)] \quad (2.39)
\]

Expressing the SCF energy in terms of the orbital energy, one electron core Hamiltonian, and the nuclear repulsion energy
The one electron core Hamiltonian can be found in terms of the basis set

\begin{equation}
H^\text{CORE}_{ii} = \langle \phi_i | \hat{H}^\text{CORE} | \phi_i \rangle = \sum_{r} \sum_{s} C^*_r C^s_s \langle \chi_r | \hat{H}^\text{CORE} | \chi_s \rangle = \sum_{r} \sum_{s} C^*_r C^s_s H^\text{CORE}_{rs}
\end{equation}

substituting this and the electron density matrix elements into equation (2.40)

\begin{equation}
E_{\text{HFS}} = \sum_{i=1}^{n/2} \varepsilon_i + \sum_{i=1}^{n/2} H^\text{CORE}_{ii} + V_{NN}
\end{equation}

The SCF energy of the system is now defined in terms of the basis functions, \{\chi_i\}. By changing the coefficients in front of each basis function, the orbital changes. As the orbital changes to better describe the system, the energy lowers. Thus, to solve for the Slater determinant and find the lowest energy solution, the contributions of the basis set functions must be altered. The coefficients are termed variational coefficients because they are the variables that must be changed to find the lowest energy solution to the Schrödinger equation.

C. BASIS FUNCTIONS

1. SLATER TYPE ORBITALS: As explained above, each orbital
can be expressed as a linear combination of known basis functions

\[ f = \sum_{i} b_i \chi_i \]  

(2.43)

\( \chi_i \) can be a well known orbital form. One such form is that of a hydrogenlike orbital. These orbitals, however, are difficult to use due to the oscillating nature of the functions and the presence of a number of nodes. Instead of implementing the hydrogenlike orbitals in electronic calculations, Slater Type Orbitals (STO) may be used

\[ \chi_{STO} = N r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi) \]  

(2.44)

where \( N \) is the normalization constant dependent on the orbital exponent \( \zeta \), \( n \) is the principle quantum number, and \( Y_l^m(\theta, \phi) \) is the spherical harmonic which describes the angular character of the orbital dependent on quantum numbers \( l \) and \( m \). This part of the orbital is expressed in terms of spherical coordinates. This coordinate system defines the cartesian system as

**FIGURE 2.1:** The physical definition of the three coordinates of the spherical harmonic system.
where $\phi$ ranges from 0 to $2\pi$ and is defined as the angle in the xy plane that is made by the line segment $OL$ with the x axis. $\theta$ ranges from 0 to $\pi$ and is the angle between the z axis and segment $OP$. The radius is the distance or the magnitude of the vector $OP$. A coordinate assignment in the cartesian system can be easily converted to a certain set of components in the spherical coordinate system using trigonometry.

$$
\begin{align*}
x &= rsin\theta \cos\phi \\
y &= rsin\theta \sin\phi \\
z &= r\cos\theta \\
r^2 &= x^2 + y^2 + z^2
\end{align*}
$$

The differential volume element in spherical coordinates is given by

$$
dv = r^2sin\theta dr d\theta d\phi = dr
$$

A Slater Type Orbital of the form in (2.44) is accurate for atomic systems. But when the atomic orbital becomes involved in the molecular environment, it must be able to change or adapt. One way to achieve this orbital "flexibility" is to approximate the orbital with the sum of two STOs, an inner function and an outer function (shown in FIGURE 2.2).

The contribution of the inner and outer portions can be controlled by the variational coefficients. During a variational calculation, each part of the STO pair can be adjusted to describe the change in the atomic orbital in the molecular environment. The orbital exponents are normally not adjusted but are fixed to a value that best describes the orbital in the atomic state.
FIGURE 2.2: Radial functions of the form \( r \exp(-\xi r) \) for two \( p \) type orbitals.

2. GAUSSIAN TYPE ORBITALS: A computational difficulty arises in using a set of STOs to describe a molecular system. When the two electron integrals are evaluated (2.35), the product of two STOs makes the integrand complicated and not easy to handle. A more computationally convenient set of functions are the Gaussian type orbitals (GTO)

\[
\chi_{\text{GAUSSIAN-CARTESIAN}} = N x^l y^m z^n e^{-\xi r^2} \quad (2.47)
\]

where \( N \) is a normalization constant dependent on \( l, m, n \), and \( \xi \). For an \( s \) type orbital \( l+m+n = 0 \), a \( p \) orbital has the relation \( l+m+n = 1 \), for a \( d \) type orbital \( l+m+n = 2 \), etc. The explicit
s type orbital has the general form $N \exp(-\frac{1}{2}r^2)$, a $p_x$ orbital has the form $N \exp(-\frac{1}{2}r^2)$, a $d_y$ orbital has the form $N \exp(-\frac{1}{2}r^2)$, and so on. This cartesian form of a GTO can be converted to spherical form

$$x_{\text{gaussian-spherical}} = N r^{n-1} e^{-\frac{r^2}{2}} \frac{1}{\sqrt{2}} (Y_l^m^* \pm Y_l^m) \quad (2.48)$$

where $N$ is the normalization factor, $r^{n-1} \exp(-\frac{1}{2}r^2)$ the radial portion of the orbital, and $(Y_l^m^* \pm Y_l^m)$ is the spherical harmonic portion.

The Gaussian orbital is used because of the ease of integrating a product of two Gaussian type orbitals. When two GTOs are multiplied together the resulting function is a new Gaussian centered at some point between the two original functions. This simplifies the integrand and substantially reduces the computational resources needed for the evaluation.

The Gaussian orbitals have their limitations in comparison to the more accurate STOs. At vanishingly small values of $r$, the GTO satisfies the boundary condition of a zero amplitude in the $p$ and $d$ functions and some constant value of amplitude for the $s$ orbital. What is incorrect about this description is the slope of these changes. This proves to be a poor description of the short range behavior of the orbital, a limitation not observed in the STO. Furthermore, GTOs diminish at larger distances at a faster rate due to their $r^2$ exponential dependence verses the STO exponential dependence of $r$. Aside from the extreme values of $r$, the
Gaussian function does have a reliable orbital description. This poor description is troubling because these regions are very important in chemical bonding. To address these concerns, one may use a contracted Gaussian type orbital, or the cGTO.

3. CONTRACTED GTO: To overcome the limitations of GTOs while minimizing computational demands, a linear combination of Gaussians can be constructed. This new form is called a modified or contracted Gaussian (cGTO)

\[ \chi_{\text{cGTO}} = \sum_i c_i N_i Y_{\ell_i}^{m_i}(\theta, \phi) r_{\ell_i}^{-1} e^{-\frac{\xi_i r^2}{2}} \]  

(2.49)

A CGTO captures through multiple functions, or primitives, the character of a STO and still remains uncomplicated to integrate. This reduces the size of the matrices involved in solving for the energy of the molecule.

When basis sets are developed the \( \{ \xi_i \} \) are fixed at some value to fix certain characteristics of the orbitals. What is changed in the variational calculation is \( \{ c_i \} \) that controls the linear combination of contracted Gaussians. In altering these coefficients the molecular wavefunction of the system is transformed and therefore the energy is changed.

D. EFFECTIVE CORE POTENTIAL

1. INTRODUCTION: To reduce the computational demand of dealing with heavy atoms, an effective core potential can be used. This approximation redefines the core electrons on
atomic centers using potential functions. This leaves the outer or valence electrons to be dealt with explicitly. Such a division is motivated by the accepted notions of chemical bonds being predominantly governed by these outer electrons.

2. DEVELOPMENT: This treatment of the effective core potential is based on a review article by Krauss and Stevens. Derivation of the effective core potential begins by taking the molecular wavefunction and expressing it explicitly in terms of valence and core electrons

$$\Psi(1,2,\ldots,n) = A\Phi_{\text{CORE}}(1,2\ldots n_c)$$
$$\Phi_{\text{VAL}}(n_c+1,n_c+2,n_c+3\ldots n)$$

where $A$ is the antisymmetrizer, $\Phi_{\text{CORE}}$ is the core wavefunction, and $\Phi_{\text{VAL}}$ is the valence wavefunction. The true molecular wavefunction cannot be expressed in terms of this product. Approximate wavefunctions, such as the Hartree-Fock-Slater wavefunction, can be expressed in this manner because they are already in the form of an orbital product.

The valence portion can be substituted into the Schrödinger equation

$$H_{\text{VAL}}\Phi_{\text{VAL}} = E_{\text{VAL}}\Phi_{\text{VAL}}$$

where $E_{\text{VAL}} = E_{\text{TOTAL}} - E_{\text{CORE}}$ and

$$H_{\text{VAL}} = \sum_{i=1}^{n_v} \left( h_i + \sum_{j \neq i}^{n_v} \frac{1}{\xi_{ij}} \right) + V_{\text{CORE}}$$

where $V_{\text{CORE}}$ is the potential that accounts for valence-core
interactions. It is a nonlocal integral operator because of the presence of exchange terms.

In solving equation (2.51), the valence orbitals must be maintained orthogonal to the core orbitals. In using a HFS core, this restraint is satisfied by requiring the valence orbital to be orthogonal to the core orbital.

This explicit requirement of orthogonality can be resource intensive and could be as much of an investment of computational resource as a full electron calculation. This process is simplified by replacing the valence orthogonal constraint and nonlocal core-valence interaction term by a single operator that prevents the valence wavefunction collapse into the core region implicitly. This new potential maintains orthogonality without explicitly imposing it. These potentials were initially called effective potentials, denoted $V_{\text{eff}}$. Presently they are called effective core potentials (ECP). Forms of ECPs that include relativistic effects of the inner core orbitals are called, relativistic effective core potentials (RECP). Henceforth, RECP is referred to as ECP.

ECPs are derived from atomic all electron calculations, defining the valence Hamiltonian

$$H_v \phi_v = (h + V_{\text{CORE}}) \phi_v = E_v \phi_v \quad (2.53)$$

where $\phi_v$ is orthogonal to the core orbital. The same Hamiltonian can be applied to the core orbitals to produce the
energy of each core orbital. Each valence orbital can be written as

\[ \phi_v = \chi_v - \sum_c <\chi_v|\phi_c>\phi_c \]  

(2.54)

for any \( \chi_v \), \( \phi_v \) is orthogonal to the core orbital. Substituting (2.54) into (2.53)

\[ (h+V_{\text{CORE}}+V^{PK})\chi_v = E_v \chi_v \]  

(2.55)

where

\[ V^{PK} = \sum_c [E_v - E_c] |\phi_c> <\phi_c| \]  

(2.56)

is called the pseudopotential and \( \chi_v \) is the pseudo-orbital. The form of the pseudo-orbital that satisfies (2.56) is

\[ \chi_v = a_v \phi_v + \sum c_a_c \phi_c \]  

(2.57)

where the coefficients \( a_v \) and \( a_c \) are such that they make the pseudo-potential as smooth as possible to reduce computational modelling.

HFS orbitals can be chosen as a set of pseudo-orbitals. Using the Hamiltonian from HFS method in terms of angular momentum \( L \)

\[ \left( -\frac{1}{2}\frac{\nabla^2}{r^2} - \frac{Z}{r} + \frac{L(L+1)}{2r^2} + V_{\text{VAL}} + V_{\text{CORE}} \right) \phi_i = \varepsilon_i \phi_i \]  

(2.58)

where \( V_{\text{CORE}} \) and \( V_{\text{VAL}} \) represent the Columbic and exchange operators over the core and valence orbitals respectively.
Solving (2.58) by an atomic HFS calculation, it is possible to use $\epsilon_i$ and $\phi_i$ to construct a valence-electron-only HFS equation which employs an effective core potential, $V^{\text{eff}}$, to make $\phi_i$ the lowest energy of (2.58)

$$
\left(-\frac{1}{2}\nabla_r^2 - \frac{Z_{\text{eff}}}{r} + \frac{L(L+1)}{2r^2} + V_{\text{val}} + V_{\text{eff}}^L\right)\chi_v = \epsilon_i\chi_v
$$

(2.59)

this equation can be inverted to solve for the effective core potential

$$
V_{\text{eff}}^L = \epsilon_i + \frac{Z_{\text{eff}}}{r} - \frac{L(L+1)}{2r^2} + \frac{(1/2\nabla_r^2 - V_{\text{val}})\chi_v}{\chi_v}
$$

(2.60)

This potential can be fitted with a set of Gaussian functions to produce a new approximate ECP

$$
r^{2\psi_{\text{eff}}} = \sum_k A_k r^{n_k} e^{-B_k r^2}
$$

(2.61)

where $n_k$ is 0, 1, or 2 depending on the pseudo-orbital type and $A_k$ and $B_k$ are varied to minimize the energy.

3. IMPLEMENTATION: Implementation of the effective core potential in GAMESS for fluorine is discussed in reference to an article by Stevens, Krauss and Basch (SBK). The implementation of the ECP for xenon is based on the work of the above authors with Jasien (SBKJ).

SBK found that an expansion of the ECP with four Gaussian Type Orbitals (4GTO) produced results within 5 mhartrees of a
6GTO expansion. The 6GTO result was not utilized because the computational cost was not worth the small gain in accuracy. From this expansion, SBK found the appropriate pseudo-orbitals and potentials by minimizing the energy of the ground state multiplet for numerous atomic centers.

To describe the remaining valence electrons, SBK undertook two "contraction schemes" of the basis. The first contraction was a double-zeta contraction where the three largest-exponent Gaussian primitives were contracted into one basis function and the fourth primitive was the second basis function (31G). In the triple-zeta contraction the largest and smallest primitives were taken as basis functions while the remaining two where contracted into a second basis function (121G).

To verify the accuracy of the effective core potential, SBK performed a series of SCF calculations with and without an ECP on a series of small hydrocarbons and selected diatomics. In their hydrocarbon runs they found a double-zeta contraction of the basis set gave bond lengths and bond angle differences within 0.02 Å and 0.4° respectively to the all electron calculations. The margin of difference for a triple-zeta contraction scheme did decrease, but the authors felt the double-zeta contraction yielded satisfactory results. Diatomic calculations extended the *ab initio* treatment to compare a variety of molecular properties. These calculations yielded bond lengths, bond angles, and dipole moments all in close
proximity to the all electron results on the same molecules. SBKJ used a similar contraction scheme as SBK but instead calculated the energy with a relativistic Hamiltonian operator for xenon.

E. TCSCF

1. GENERAL FORM: The two configuration self consistent field calculation (TCSCF) is based on the contribution of two different electronic configurations to the molecular wavefunction. Each of these contributions is governed by a variational variable or coefficient

\[ \Psi_{\text{molecular}} = c_1 \psi_1 + c_2 \psi_2 \]  \hspace{1cm} (2.62)

where \( \psi_1 \) and \( \psi_2 \) are the configurations with their respective coefficients. This makes the wavefunction no longer an antisymmetric product of atomic orbitals. The molecule can no longer be thought of in the strict chemical way as was done with the HFS method.

2. METHOD: In deciding the forms of \( \psi_1 \) and \( \psi_2 \), one must make a choice of which configurations are allowed to mix. For example, an arbitrary system can be broken down into two configurations. The first has its electronic configuration like that of the HFS calculation, that is, all electrons are placed into the lowest energy orbitals possible (i.e. the ground state). In this state the HOMO has an electron pair in
it. The second state is an excited state, where the electron pair is taken from the HOMO and now populates the LUMO. For example, the core orbitals are frozen and two configurations can be written as

\[ \Psi_1 = \Psi_{\text{GROUND}} = \left[ \text{CORE} \right] \sigma_g^2 \]

\[ \Psi_2 = \Psi_{\text{EXCITED}} = \left[ \text{CORE} \right] \sigma_u^2 \]

In this example we are forcing a normal occupation in \( \psi_1 \), or occupation into the HOMO (\( \sigma_g^2 \)). In \( \psi_2 \) we are creating an excited system by forcing occupation into an excited or non occupied orbital, in this case the LUMO (\( \sigma_u^2 \)). This orbital mixing between the HOMO and LUMO provides a better description of the molecule, in particular its dissociation character.

The TCSCF calculation is dependent on an initial set of input orbitals to determine the ground state and excited state occupancies of the system. These orbitals are usually SCF orbitals that have already been calculated with the same coordinates.

The dissociation description in the SCF calculation may not be correct because the wavefunction maintains the ground state configuration of the molecule, even though the molecule is falling apart into its constituent atoms. The SCF calculation attempts to keep the electrons of the constituent atoms in the bond configuration found in the ground state. This constraint does not describe the system as the molecule
becomes distinct well separated atoms. The result is that the fundamental constraint of the HFS method, mainly each orbital is occupied by two electrons and the wavefunction is the antisymmetrized product, is lost.

F. MCSCF

1. GENERAL FORM: The TCSCF calculation is a subset of the multiconfiguration self consistent field calculation (MCSCF). The MCSCF calculation uses more than two configurations in its formulation of the molecular wavefunction.

\[ \Psi_{\text{molecular}} = N \sum_i c_i \psi_i \]  

(2.65)

where \( N \) is the normalization constant and \( c_i \) is the coefficient contribution of the \( i \) configuration (\( \psi_i \)).

2. METHOD: The MCSCF method minimizes the energy of the system in two ways. First, the configuration contributions are altered to control the contribution each configuration has. Secondly, the functional form of the basis that represents each configuration is varied as was done in the SCF calculation.

The MCSCF energy curve should be lower than its TCSCF and SCF predecessors. The MCSCF is however, still linked to these initial calculations due to its necessity of having a set of input orbitals that are derived from these calculations.
G. CI

1. GENERAL FORM: To improve still further on the molecular wavefunction, the configuration interaction (CI) calculation is utilized. CI takes a larger sample of configurations of the molecule and mixes them together to form the wavefunction. This makes a similar wavefunction to the one shown in (2.65). However, the CI calculation does not vary the functional form of the individual configurations. This constraint is placed on the calculation due to the vast amount of computing resources needed to deal with the large numbers of configurations that form the molecular wavefunction.

If the MCSCF and CI calculations use the same initial set of orbitals, the MCSCF yields a lower energy because it varies the configuration contributions as well as the functional forms of each configuration. The CI is best utilized when it uses input orbitals from the MCSCF calculation at the same coordinates. This extends the configuration mixing begun at the MCSCF level of calculation. Therefore, the CI calculation can be thought of as an extension of the MCSCF calculation.

2. ELECTRONIC CORRELATION: In all the methods thus far discussed, the electron to electron interaction has been an average effect included in the Hamiltonian. The TCSCF and MCSCF calculations attempt to correct for this approximation by including two and multiple configurations of the system.

The CI calculation with its numerous configurations mixed into the final form of the wavefunction, can best correct for
this energy loss. The best energy that is obtained with a SCF wavefunction is called the Hartree-Fock energy limit. The wavefunction is the best form it can possible be in and the only limitation on the calculation is the average effect of the electron to electron interaction. The energy difference between the Hartree-Fock limit and the true energy of the system is called the correlated energy. This energy is due to the instantaneous effects all electrons have on one another. This effect is most efficiently captured in the CI calculation that uses an initial set of MCSCF input orbitals.
NOTES FOR MOLECULAR WAVEFUNCTION


III. RESULTS - TOTAL ENERGIES AND WAVEFUNCTIONS

A. INTRODUCTION

In all explored levels of calculation, the internuclear separation was altered and the molecular energy found. The bond angle was only varied in obtaining a preliminary SCF energy surface of the molecule. When the level of calculation was extended beyond SCF, the linear case was calculated exclusively. Any change in bond length is symmetrical in nature, thus the term internuclear separation refers to the distance between the central xenon to each fluorine.

B. SCF ENERGY CURVE

1. COORDINATE SYSTEM: The XeF₂ molecule was set up into an input format for GAMESS. The experimentally determined point group is D₁₉, the GAMESS code however, does not support this point group. We used the suggested D₄ᵥ point group instead and in preliminary runs we found great computational limitations. Thus, we choose the C₂ᵥ point group which eliminated some of the computational demands of the higher
level calculations. This point group selection placed each fluorine on the z axis of a cartesian system.

\begin{figure}
\centering
\includegraphics[width=0.3\textwidth]{figure3.1}
\caption{A bent molecule of XeF$_2$ displaying the coordinate convention used. Xe to F internuclear axis lies in the ZY plane.}
\end{figure}

To adjust for various bond lengths we altered the z coordinate assignment for one fluorine which the program mirrored by using symmetry for the other fluorine. The y coordinate can be altered to accommodate changes in the bond angle $\theta$.

2. **ATOMIC CALCULATIONS:** To begin our SCF calculations on the molecule we first examined the atomic energies for fluorine and xenon using only the SBK basis. Fluorine produced an energy of $-23.79484$ a.u. This value is comparable to the literature value of $-23.79311$ a.u.\(^1\) The same calculation was preformed on xenon which yielded an energy of $-15.3012$ a.u.\(^2\) which is the reported value of the atom with this basis.\(^2\) Summing these energies together a value of $-62.8908$ a.u. is obtained. The dissociation limit of our calculations should match closely to this sum.
3. **BARE BASIS:** The molecular case was set up in a linear fashion to vary the bond length and determine the molecular energy. An expected parabolic energy curve with a geometry optimized minimum total energy of $-62.7666$ a.u. at a radius of 2.04 Å was obtained.

The energy curve is a very crude accounting of the molecular energy of the system because its dip in energy around $R_{eq}$ is very shallow. We attribute this poor result to the basis that we used in describing the molecule. To augment the functional description of the system, additional atomic basis set functions were added to the SBK basis. These functions have a Gaussian form with an exponent that can be varied by the user.

4. **BASIS EXPANSION AND OPTIMIZATION:** A summary of the expanded and optimized basis set exponents is given here. A full description of the obtained exponential values are given elsewhere.  

We began our selection of orbital exponents by setting up a SCF calculation at a bond length close to $R_{eq}$. The basis was expanded with initial exponential values of a xenon $s$ ($Xe-s \approx 0.3$) and $d$ orbitals ($Xe-d \approx 0.88$), and a fluorine $s$ ($F-s \approx 1.21$). These and other initial exponent values were motivated by listed literature values for xenon and fluorine. Using these values, the molecule energy was minimized by optimizing
each of them independently. Only the xenon d and fluorine s changed considerably when optimized, \( \approx 0.29 \) and \( \approx 0.55 \) respectively.

Then the initial values of Xe-d and F-s were simultaneously optimized to values of \( \approx 0.29 \) and \( \approx 0.62 \) respectively. Since the xenon s and d orbital came to about the same value of 0.30 and the fluorine came to the value of \( \approx 0.6 \), we used a new initial value of 0.3 for all s, p, and d orbitals on xenon and a value of 0.6 for s, p, and d orbitals on fluorine. Then these values were again optimized simultaneously with an additional f orbital placed on the xenon (value \( \approx 0.2 \)). The optimized orbital exponent results were found to be:

<table>
<thead>
<tr>
<th>ORBITAL</th>
<th>Xe-s</th>
<th>Xe-p</th>
<th>Xe-d</th>
<th>Xe-f</th>
<th>F-s</th>
<th>F-p</th>
<th>F-d</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXPONENT</td>
<td>0.10</td>
<td>0.42</td>
<td>0.32</td>
<td>0.56</td>
<td>0.67</td>
<td>0.43</td>
<td>0.67</td>
</tr>
</tbody>
</table>

**TABLE 3.1:** Expanded basis set function exponential values (EBS).

Using these values at a smaller bond length (\( \approx 1.67 \) Å), the energy was again minimized by varying the orbital exponents. This process yield similar values to those given in **TABLE 3.1**. We conclude for our ECP description of the XeF\(_2\), the stated exponents are the best functions to be used with the SBK basis to aid in the description of the molecule.
5. **BOND LENGTH RANGE**: We reran our original SCF calculations on the molecule through a range of bond lengths and bond angles with our newly expanded basis set, known henceforth as SBK-EBS. This produced an energy surface of the molecule which confirmed the linear case as the minimum energy geometry arrangement of the molecule. We restrict this calculation and the remainder of the calculations in this study to the linear case of XeF₂, hence **FIGURE 3.2**

![Figure 3.2: The total SCF energy of linear XeF₂ employing the SBK-EBS basis set.](image)

This deeper parabolic curve yielded a more accurate value of $R_{eq} \approx 1.94 \text{ Å}$. Using this value for the geometry optimization, we found the molecule to be linear with its lowest energy value of -62.85675 a.u. and an equilibrium bond length of
1.93 Å. This value is two percent different from the experimental gas phase bond length.

We found at larger values of internuclear separation (≈ 3.60 Å), the SCF calculation for the molecule did not converge. We hypothesize this could be where our model begins to fall apart into three separate atoms. As such the model begins to become confused as the atomic orbital states begin to take over the description of the system. This could produce a series of states that would be close in energy making it difficult for the SCF method to converge on some final energy.

To overcome this limitation in the calculation, we used a different set of input orbitals for the SCF calculation. Up to this point the initial set of input orbitals were generated from an extended Hückel calculation at each bond length. We instead chose to input the orbitals of the nearest converged SCF calculation. This technique of using the input orbitals of the nearest converged calculation is called "bridging". Bridging the SCF results extended the electronic configuration of the molecule that converged at lower bond lengths into this region of nonconvergence.

In comparing the geometry optimized SCF energy to the sum of the atomic energies using this extended basis, the molecule is found not to be bound in the sense that the molecular energy is not as low as the sum of the atomic energies. We are not concerned about this finding because previous experience
has shown that this level of calculation is a good starting point for higher level calculations on the molecule. Furthermore, we use this calculation for specification and characterization of the occupied and unoccupied molecular orbitals formed in the molecule. These molecular orbitals are given in the next section.

C. SCF MOLECULAR ORBITALS

1. INTRODUCTION: The SCF calculation yields the closest "chemical picture" of the molecule of the levels of calculations executed. This picture includes taking the twenty-two valence electrons and placing them in pairs from the lowest to highest energy molecular orbitals.

We chose to examine the molecular orbital types, energies, and order to characterize the molecular bonding. Analysis of the orbital type and energy also gives us a guide of how these orbitals influence the electronic configuration.

2. ORBITAL TYPES AND ENERGY: TABLE 3.2 shows a pictorial view of the XeF₂ molecular orbitals as they are found near Rₐ⁻. These types were determined by examining the individual atomic orbital contributions to each molecular orbital.

The representations show only orbital phase and orientation, not the actual quantity of each orbital contribution. The z axis is the internuclear axis, while the
TABLE 3.2: The order and type of the molecular orbitals of XeF₂ at the equilibrium bond length.

<table>
<thead>
<tr>
<th>1</th>
<th>2σ_g</th>
<th>5</th>
<th>1π_u</th>
<th>9</th>
<th>3σ_g</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1σ_u</td>
<td>6</td>
<td>1π_u</td>
<td>10</td>
<td>2π_u</td>
</tr>
<tr>
<td>3</td>
<td>2σ_g</td>
<td>7</td>
<td>1π_g</td>
<td>11</td>
<td>2π_u</td>
</tr>
<tr>
<td>4</td>
<td>2σ_u</td>
<td>8</td>
<td>1π_g</td>
<td>12</td>
<td>3σ_u</td>
</tr>
</tbody>
</table>

The order and type of the molecular orbitals of XeF₂ at the equilibrium bond length.
x and y axis are not designated. Both orbitals of degenerate pairs are shown with no specified axis designated. The individual initial contributions for each molecular orbital are given in the correlation diagram presented in FIGURE 3.3. For notation reasons the molecular orbitals are referred to by their equilibrium bond length order or their symmetry type and occurrence.

FIGURE 3.3: The correlation diagram of XeF₂ using the SCF orbitals of the constituent atoms and of the molecule at equilibrium internuclear separation.

SIGMA ORBITALS: Of the twelve orbitals examined, five are sigma type orbitals, the four lowest energy states and MO#9. The first three molecular orbitals MO#1, MO#2, and MO#3 are 1σₓ, 1σₓ, 2σₓ respectively. 1σᵧ and 1σᵧ are formed respectively from the gerade and ungerade 2s orbitals on each fluorine. The 2σₓ is formed from a positive 5s phase on xenon and a negative 2s phase on fluorine. Additionally there is a slightly less pₓ
contribution from each fluorine.

In the range from $R_{eq}$ to dissociation, these orbitals have energies that are much less than the other occupied molecular orbitals. This energy difference encourages us to select these orbitals as frozen in subsequent MCSCF and CI calculations. In doing so, the orbitals are excluded from orbital mixing restricting them to be doubly occupied in all configurations used to define the molecular wavefunction. FIGURE 3.4 represents the orbital energy verses the bond length for all sigma type orbitals (where graph notation has s for $\sigma$).

The graphical representation of the orbital energies indicates a possible repulsion between $1\sigma_z$ and $2\sigma_z$ beginning around 2.30 Å. This repulsion seems to be alleviated at each end of the bond length range. We attribute this $\sigma_z$ repulsion behavior to the noncrossing rule.

MO#4 and MO#12, $2\sigma_u$ and $3\sigma_u$, are each formed from the $p_z$ orbitals of all the constituent atoms. In $2\sigma_u$, the phases match while in $3\sigma_u$ they do not. These orbitals display the same noncrossing behavior as their gerade counterparts.

The $2\sigma_u$ molecular orbital is close in energy to $3\sigma_z$, a similar effect to that found in MO#1/MO#2. But $2\sigma_u$ does not lie directly on top of $3\sigma_z$. This is because these orbitals are farther away from the nucleus, and thus allowed to have a larger range of possible energy values.
FIGURE 3.4: The total energy of the sigma molecular orbitals as a function of internuclear separation.
**PI ORBITALS:** There are three sets of pi orbitals occupied in the molecule. The first set, MO#5/#6 are $1\pi_u(x,y)$, and are formed from the $p_{x,y}$ on each fluorine and xenon. The next set, $1\pi_g(x,y)$ or MO#7/#8, are formed from nonbonding pairs of $p_{x,y}$ on each fluorine. The last set of pi orbitals are developed from out of phase xenon and fluorine $p_{x,y}$ orbitals.

The noncrossing rule is also observed in the pi molecular orbitals. A repulsion is occurring between the $\pi_u$ degenerate pair of orbitals, MO#5/#6 and MO#10/#11. This $\pi_u$ repulsive interaction comes the closest in energy of the three repulsions mentioned thus far (0.1 a.u. difference compared to 0.25 a.u. in each of the $\sigma_z$ and $\sigma_u$ repulsions). **FIGURE 3.5** shows the pi type orbital energy over the same range of bond lengths (where graph notation has p for $\pi$).

**UNOCCUPIED ORBITALS:** Noncrossing is not a concern in the unoccupied orbitals. MO#12, $3\sigma_u$, rises above MO#13, $4\sigma_z$, around 1.75 Å which is a concern for the TCSCF calculation. The energies of the unoccupied pi orbitals remain fairly constant do not cross energy of any of the lower energy orbitals. The upper unoccupied molecular orbitals are shown in **FIGURE 3.6**.

3. **MOLECULAR ELECTRONIC CONFIGURATION:** The energy of each orbital determines the order the orbitals are given in. For example, the orbital order shifts at various points. These shifts are determined when the energy curves from **FIGURES 3.4**
FIGURE 3.5: The total energy of the pi molecular orbitals as a function of internuclear separation.
FIGURE 3.6: The total energy of the first three unoccupied molecular orbitals as a function of internuclear separation.
cross one another. Order shifts might affect later levels of calculations that depend on the SCF calculation to generate a set of input orbitals. Individual orbital shifts are explained as needed, otherwise for a complete explanation please refer to APPENDIX B.

The orbital order found at \( R_\alpha \) can be compared to that given by DeKock and Gray.\(^7\) Their proposed order was based on the analogous case of \( \text{CO}_2 \) and the photoelectronic spectrum of \( \text{XeF}_2 \).

\[
(1\sigma_g)^2 \quad (1\sigma_u)^2 \quad (2\sigma_g)^2 \quad (2\sigma_u)^2 \\
(1\pi_u)^4 \quad (1\pi_g)^4 \quad (2\pi_u)^4 \quad (3\pi_g)^2
\]

**FIGURE 3.7:** The orbital order in \( \text{XeF}_2 \) as proposed by DeKock and Gray.

Our molecular orbital order from the SCF calculation on the molecule is

\[
(1\sigma_g)^2 \quad (1\sigma_u)^2 \quad (2\sigma_g)^2 \quad (2\sigma_u)^2 \\
(1\pi_u)^4 \quad (1\pi_g)^4 \quad (3\pi_g)^2 \quad (2\pi_u)^4
\]

**FIGURE 3.8:** \( \text{XeF}_2 \) orbital order result using the SCF calculation with the SBK-EBS.

The only difference between our order is the position of \( 3\sigma_g \) orbital. The photoelectronic spectrum of \( \text{XeF}_2 \) indicates the \( 2\pi_u(x,y) \) set is the highest energy molecular orbital because they are the first ionized orbitals.\(^8\) In looking at **FIGURE 3.7**, our findings are in accord with this experimental result.
When we removed the d orbital basis function from our expanded basis set, we obtain the same order as Dekock and Gray. These authors discuss the possibility of the d orbital, in particular the $d_{z^2}$ orbital, playing a part in bonding. We found that this d orbital played a small, less than 10% quantitative role in the characterization of the antibonding $4\sigma_v$ molecular orbital. This indicates the d orbital participation has a small quantitative role but a large qualitative consequence. We share this conclusion with others who have observed the same d orbital participation effect.9 These researchers observed that the d function played a part in the polarization of the basis but a small role in the bonding.

DeKock and Gray proposed that there was only one net sigma bond and no net pi bonds in $\text{XeF}_2$. This net sigma orbital has ungerade symmetry formed from the $p_z$ orbitals of fluorine and xenon and is termed the bonding orbital of $\text{XeF}_2$.

Our SCF calculation designated this molecular orbital to MO#4, or the $4\sigma_v$ orbital. In looking at the contours of this molecular orbital, the xenon $p_z$ lobe may not seem to be present but this is an artifact of the graphics and is fact present. When the xenon contribution to the molecular orbital is removed, however, the fluorine $p_z$ lobes are present but with smaller contours. This indicates that $p_z$ overlap is
occurring between the xenon and each of the fluorines. This is confirmed when the individual atomic contributions are examined in numerical format.

The $2\sigma_u$ molecular orbital is formed from the antibonding fluorine molecular orbital number eight. This orbital is composed of a fluorine $p_z$ atomic orbitals.

\begin{center}
\includegraphics[width=0.5\textwidth]{fig3_9.png}
\end{center}

**FIGURE 3.9:** The F$_2$ $2\sigma_u$ antibonding orbital.

By adding xenon to the F-F molecular orbital, the xenon $p_z$ orbital interacts so that its phases match the phases of the fluorines.

\begin{center}
\includegraphics[width=0.5\textwidth]{fig3_10.png}
\end{center}

**FIGURE 3.10:** The F$_2$ $2\sigma_u$ antibonding orbital with an addition of a xenon $p_z$ of matched phase.

In doing so, the original antibonding orbital on F$_2$ becomes a bonding orbital of XeF$_2$. The energy of $2\sigma_u$ drops substantially,
by 0.4 a.u., from its energy in the F₂ molecule. We would expect such a large drop as a molecular orbitals goes from being an antibonding orbital to a bonding orbital. All molecular orbitals found for F₂ at this level of calculation are listed in APPENDIX C.

Our SCF molecular orbitals were less than 5% different than an all electron result performed by Malli and coworkers.¹⁰ This comparison indicates the ability of the ECP to effectively model the inner core electrons of the molecule. A slightly higher percent difference, less than 6%, was found in comparison to another all electron calculation of the molecule by Huzinaga et. al.¹¹

4. ELECTRON CORRELATION: The SCF calculations performed thus far have only taken into account the average electron to electron interactions. The instantaneous interaction between electrons make up the difference between the best SCF energy curve and the true energy curve. This energy is called the correlation energy and can only be recovered or accounted for by allowing the molecular wavefunction to become more flexible. The subsequent calculations begin to include more electronic configurations of the system and thus allow for more wavefunction flexibility. All remaining calculations employ the expanded ECP basis (EBS-SBK).
D. TCSCF ENERGY CURVE

1. SETUP: The next level of calculation on the molecule uses the two configuration self consistent field method. TCSCF was defined by setting ten core orbitals as frozen and allowing for the eleventh orbital to promote to the LUMO.

These ten core orbitals were decided upon by examining the SCF orbitals at large bond lengths and identifying the highest occupied molecular orbital and the lowest unoccupied orbital. The HOMO was identified at large internuclear separations to be MO#9, or the 3σ orbital. The LUMO, MO#12, or 3σ_u, had maintained its position since R=... This allowed the TCSCF to be defined as follows

\[ \Psi_{TCSCF} = C_1 \Psi_1 + C_2 \Psi_2 \]
\[ \Psi_1 = \Psi_{GROUND} = [CORE] (3\sigma_g)^2 \]
\[ \Psi_2 = \Psi_{EXCITED} = [CORE] (3\sigma_u)^2 \]

with the core being defined as

\[ [CORE] = (1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 \\
(1\pi_u)^4 (1\pi_g)^4 (2\pi_u)^4 \]

This HOMO/LUMO mixing was maintained throughout the bond length range by reordering the SCF input orbitals when necessary. This reordering maintained the asymptotic forms of MO#9 and MO#12.

2. ENERGY CURVE CALCULATION: Using the SBK-EBS basis the
TCSCF energy curve was calculated. The extended Hückel calculation does not produce a good enough initial guess for orbitals to be used in the TCSCF calculation, thus SCF input orbitals are used instead.

**FIGURE 3.11:** The molecular SCF(0) and TCSCF (*) energy of XeF$_2$ in a.u. over a range of internuclear separations.

As the bond length increases, the TCSCF method describes complete molecular dissociation. In doing so, the molecular energy should approach that of the sum of the constituent atomic energies. This TCSCF energy limit was found to be 62.88952 a.u., a 0.01% difference from the sum of the atomic energies with the same basis. For our purposes we choose to use this TCSCF energy value as the sum of the atomic energies of the system. We base this on the fact that TCSCF is the best
level of calculation that explicitly depends on the long range behavior. Furthermore, the calculation yields a description that does not depend on an open shell case (unlike that of the SCF atomic fluorine energy calculation).

In addition to this energy characteristic, the coefficients of each of the two configurations can be examined. As the bond length increases, each coefficient should approach a value of $1/\sqrt{2}$ ($\approx 0.707$). This indicates that the overlap integral for the molecule is approaching zero and each configuration is contributing equally to the molecular description as shown in FIGURE 3.12.

![FIGURE 3.12: The configuration coefficient over a range of bond lengths. The dashed line indicates a value of approximately equal $1/\sqrt{2}$.](image)

This behavior of the energy and configuration coefficient demonstrates that the molecule has been successfully defined using the TCSCF method with the SBK-EBS basis. In comparing our TCSCF calculation to the work of Bagus et. al.\textsuperscript{12}, we find our energy curve closely matches the all electron TCSCF
result.

![Graph showing energy vs. internuclear separation]

FIGURE 3.13: Comparison of TCSCF (*) energy curve with the work of Bagus and coworkers' (x) full electron calculation.

The individual internuclear separation energies differed on average by 10%. Our TCSCF molecular orbital energies and those found by the all electron calculation compared well at \( R_{eq} \).

The geometry optimized energy of the system was \(-62.87868\) a.u. This still indicates that the molecule is not bound, however, the TCSCF calculation is primarily a calculation of long range behavior. We feel, by reasons stated above, that this behavior does give us an accurate value of the sum of the atomic energies. Thus, for the remainder of the energy curves examined we add this energy to all energies found. This makes
all negative energies indicative of a bound system.

**E. MCSCF ENERGY CURVE**

1. **SETUP:** At this point, we have correctly described the molecule at large bond lengths. We now focus on lowering the energy curve near the equilibrium bond length. To do so we employ the multiple configuration description of the system, or a MCSCF calculation.

   Of all calculations performed, the MCSCF is the most time consuming because it optimizes the individual electronic configurations as well as the basis function contribution to each molecular orbital. Any orbitals that we can exclude from this configuration mixing without sacrificing a large amount of energy is beneficial. From examination of the SCF orbitals we found there to be a large energy difference between this set of the three lowest molecule orbitals and the remainder of the molecular orbitals. Thus, we choose to freeze these orbitals out of the configuration mixing used to formulation the MCSCF wavefunction.

   The remaining eight of the eleven occupied orbitals are designated doubly occupied orbitals and are allowed to mix with the unoccupied orbitals to form the configurations that define the MCSCF wavefunction.

   The unoccupied valence orbitals, or virtual orbitals, are generated from the SCF input orbitals. The number of these orbitals allowed to mix are specified by a NVAL assignment in
2. ENERGY CURVE CALCULATION: We begin our search for the best MCSCF wavefunction by setting the number of valence orbitals to one (NVAL=1). This valence orbital assignment of the MO\#12, or $3\sigma_u$, defines the system close to the one set for TCSCF. What differs in this calculation is that promotion is allowed from not only the HOMO but from the other seven occupied molecular orbitals not frozen in the core. The other difference is that the promotion of the electrons in MCSCF method can occur one at a time and is not restricted to promotion in pairs.

The NVAL=1 calculation yields a curve that is slightly lower in energy than the TCSCF energy curve (see FIGURE 3.12). We expect the energy to be lower due to the promotion from all eight doubly occupied reference state orbitals. This energy decrease is limited due to only one valence orbital being allowed to mix with the doubly occupied orbitals. This energy, however, still does not indicate a bound state of XeF$_2$. This calculation demonstrates how accurate a TCSCF description of the system is compared to the more computationally robust MCSCF calculation.

To lower the energy curve, we changed NVAL to two. This resulted in a 0.03 a.u. drop in energy near the equilibrium bond length. This is not a drastic improvement in the energy and only yields a fraction of the dissociation energy.

For more gains in energy, we choose an NVAL assignment of
We make this selection due to the fact that the next two unoccupied orbitals are a set of degenerate pi orbitals. This gave us the best MCSCF energy curve with a dissociation energy of about 1.30 eV.

![Figure 3.14: MCSCF energy curves of various NVAL assignments.](image)

Convergence problems occurred at internuclear separations greater than 3.00 Å that could not be resolved by the bridging method. We chose to stop with further formulation of the MCSCF wavefunction due to this convergence problem. Furthermore, we feel any other virtual orbital inclusions in the NVAL assignment could increase the computational demand unrealistically for our current resources. The present level of calculation is on average taking up only 9 MB of disc space but requires an extended period of time, about 150 minutes per point.
F. CI ENERGY CURVE

1. SETUP: Now that the MCSCF calculation has been formulated for a series valence orbitals, we focus on configuration interaction. This calculation sets up a reference state as the MCSCF ground state. For example, if the MCSCF had three frozen core orbitals, eight doubly occupied orbitals, and one valence orbital, then the reference state is double occupancy into the first eleven MCSCF orbitals. To this reference state the CI calculation allows additional unoccupied MCSCF orbitals, or virtual orbitals, to be mixed in. Thus, one could include one external orbital to these twelve orbitals to formulate the configurations that sum to form the molecular wavefunction. The number of orbitals to be mixed with the reference state are controlled in GAMESS by a NEXT assignment.

As stated in the MOLECULAR WAVEFUNCTION section, the CI calculation varies the individual configurations or configuration state functions (CSF) to find the best molecular wavefunction. Unlike the MCSCF, the CI calculation does not alter the functional form of each CSF. This allows for more configurations to be mixed into the final form of the wavefunction.

2. ENERGY CURVE CALCULATION: We initially used our best MCSCF calculation, NVAL=4, and read it into the CI. We obtained an insignificant gain in energy in relation to the starting MCSCF energy. Furthermore, due to our limited
computation resources, we were only able to add one virtual orbital for mixing with this NVAL=4 reference state.

We then read in our NVAL=2 MCSCF states into the CI calculation. This allowed us to extend the number of virtual orbitals mixed to ten, but only a 0.08 a.u. decrease in energy was obtained at \( R_{eq} \).

In a last effort the NVAL=1 MCSCF orbitals were placed into the CI calculation. We began with a small NEXT assignment and increased until we reached a resource limit of 25 orbitals. At this point we obtained a 0.28 a.u. drop in the energy in comparison to the starting MCSCF energy at equilibrium bond length. Furthermore, this CI energy was 0.11 a.u. lower than the best MCSCF energy curve (NVAL =4 in FIGURE 3.14).

The limitation of the 25 external orbitals was checked by seeing if any included virtual orbitals were not populated thus eliminating them from making a contribution to the wavefunction. This was done by reading the orbitals into the CI calculation in small sets of four or five orbitals each. We then looked at the largest configuration contributors to the wavefunction to see if any orbitals were not populated. If an orbital was found not to be populated, we could reorder all the orbitals and switch this non-contributor with another virtual orbital outside the 25 NEXT limit that might contribute to the wavefunction.

We found that all 25 external orbitals had electron
population placed in them, thus making them all necessary to formulate the molecular wavefunction. Taking this same CI set, other internuclear separations were calculated with the resulting energy curve shown below in FIGURE 3.15. All the energy curves are scaled to our prior TCSCF asymptotic energy.

FIGURE 3.15: The MCSCF NVAL=1, CI NEXT=25, and literature CI energy curves. There has been a great drop in energy from the MCSCF input curve to the CI curve. The literature CI curve is from Bagus and coworkers.\textsuperscript{13}

It was discovered at larger internuclear separations that GAMESS had trouble obtaining the lowest energy solution for the system. This was overcome by setting the program to find multiple energy roots. We suspect that GAMESS is calculating a series of close energy states in this internuclear
separation range. As such the possibility of getting trapped in a local minimum and missing the global minimum is a strong possibility. This accounts for some deviation of our CI calculation from the zero line in FIGURE 3.15.

The TCSCF and MCSCF calculations shown above each had a hump in their energy curves, a characteristic that seems to have greatly lessened in the CI curve. This effect could be an artifact of the calculation or actually present in the molecule. As seen in the figure, the CI curve by Bagus and et. al. does not have a hump. Furthermore, when we calculated the more rigorous NVAL=4 MCSCF energy curve, the hump appeared to have subsided from the NVAL=1 and NVAL=2 curves. Therefore, we feel our calculation on the molecule is producing this energy curve character. If we were able to include more external orbitals in the CI calculation we predict this hump would disappear altogether.

The geometry optimized CI calculation obtained an equilibrium bond length of 1.9866 Å and a dissociation energy of 1.82 eV.
NOTES FOR

RESULTS - TOTAL ENERGIES AND WAVEFUNCTIONS


5. Amendola, M. F., 14-16.


IV. RESULTS - KINETIC ENERGY

A. KINETIC ENERGY

1. ROLE OF KINETIC ENERGY: Current chemical literature emphasizes the drop in the potential energy as the driving force of bonding. But examination of the kinetic energy might be useful in shedding light on atypical bonding situations. We begin our examination of the molecular orbital kinetic energy by examining the formal relationship between the potential and kinetic energy as given by the virial theorem.

2. VIRIAL THEOREM: The virial theorem connects together the average potential, kinetic, and total energies. The total energy of a system is the sum of the average potential and kinetic energies

\[ E = \langle T \rangle + \langle V \rangle \]  \hspace{1cm} (4.1)

The formulation of the virial theorem begins by writing the Schrödinger Equation

\[ \hat{H} \psi = E \psi \]  \hspace{1cm} (4.2)

\( \psi \) is the wavefunction of the system for which \( \hat{H} \) is the
Hamiltonian. For a linear time independent operator $A$ commutator relation with $H$ becomes

$$\langle [\hat{H}, \hat{A}] \rangle = \int \psi^* [\hat{H}, \hat{A}] \psi \, dt = \langle \psi | \hat{H} \hat{A} - \hat{A} \hat{H} | \psi \rangle$$

(4.3)

Reducing the bracket expression in (4.3) using (4.2)

$$\langle \psi | \hat{H} \hat{A} - \hat{A} \hat{H} | \psi \rangle = \langle \psi | \hat{H} | \hat{A} \psi \rangle - E \langle \psi | \hat{A} | \psi \rangle$$

(4.4)

Since $\hat{H}$ is taken as Hermitian, the first expression in (4.4) can be converted

$$\langle \psi | \hat{H} | \hat{A} \psi \rangle = \langle \hat{A} \psi | \hat{H} | \psi \rangle^* = E \langle \hat{A} \psi | \psi \rangle^*$$

$$= E \langle \psi | \hat{A} \psi \rangle = E \langle \psi | \hat{A} | \psi \rangle$$

(4.5)

where it cancels with the second expression in (4.4), thus

$$\int \psi^* [\hat{H}, \hat{A}] \psi \, dt = 0$$

(4.6)

This is known as the hypervirial theorem. This theorem holds only if $H$ is Hermitian and if the wavefunction is a bound state, in other words, $\psi$ vanishing at $\pm \infty$. Furthermore, the wavefunction must be stationary or time independent because $H$ is time independent.

Choosing $A$ such that
\[ \hat{H} = \sum q_i \ p_i = -i\hbar \sum q_i \frac{\partial}{\partial q_i} \]  

(4.7)

The range of the sum is the \(3n\) cartesian coordinates (designated with \(q_i\)) of \(n\) particles. The linear momentum for particle \(i\) is designated by \(p_i\) and is defined as \(-i\hbar \partial/\partial q_i\).

Using this definition for \(A\) into the center of (4.6)

\[ [\hat{A}, \sum q_i \ p_i] = \sum q_i [\hat{A}, q_i \ p_i] = \sum q_i [\hat{A}, p_i] + \sum q_i [\hat{A}, q_i] p_i \]

(4.8)

using the following relations

\[ [q_i, H] = \hbar^2 \frac{\partial}{m \partial q_i} = \frac{i\hbar}{m} p_i \quad [p_i, H] = -i\hbar \frac{\partial V}{\partial q_i} \quad \hat{T} = \frac{p_i^2}{2m} \]

(4.9)

\([H, A]\) of (4.6) can be reduced to

\[ i\hbar \sum q_i \frac{\partial V}{\partial q_i} - i\hbar \sum \frac{p_i^2}{m} = i\hbar \sum q_i \frac{\partial V}{\partial q_i} - 2i\hbar \hat{T} \]

(4.10)

where \(T\) and \(V\) are defined as the kinetic and potential energy operators. Invoking the definition of an average value and canceling \(-i\hbar\) yields the virial theorem.
The bound stationary state condition still applies to the virial theorem as it did to the hypervirial theorem.

The virial theorem can take on various forms depending on the type of potential, \( V \). In all cases the potential must be homogenous. The form of the virial theorem given for polyatomic molecules is

\[
2\langle \hat{T}_{el} \rangle = -\langle \hat{V} \rangle - \sum_{\alpha \beta} R_{\alpha \beta} \left( \frac{\partial U}{\partial R_{\alpha \beta}} \right)
\]

(4.12)

where \( T_d \) in the electronic kinetic energy, \( V \) is the potential energy, \( R_{\alpha \beta} \) is the internuclear separation, \( U \) is the total energy curve of the system, and the sum runs over either all internuclear distances or the bond length only.

Both at the equilibrium bond length and at large internuclear separations, the last term in (4.12) becomes zero due to the form of the total energy curve. A virial ratio \( R_v \) can be found between the potential and the kinetic energy of the system for these two internuclear separation ranges

\[
R_v = \frac{\langle \hat{T}_{el} \rangle}{\langle \hat{V} \rangle}
\]

(4.13)

The GAMESS code allows for explicitly imposing of the
virial theorem by providing an exponential variable which gives satisfactory flexibility to the wavefunction. This allows for a shift of electronic density such that the requirements of the theorem are satisfied. When we imposed this restriction either the run failed or the energy was poor. We attribute these results to the fact that the effective core potential is not a homogenous function. The using of the ECP approximation for our system means the virial theorem does not apply.

Thus, our analysis on the kinetic energy doesn't explicitly impose the virial theorem. We assert, however, that our wavefunction does describe the molecule due to its lower energy. Granted, the SCF wavefunction indicates a non-bonded molecule, but in subsequent calculations it provides an adequate description of the molecule.

At equilibrium bond length we obtain a virial ratio of 2.49, while (4.13) predicts a ratio of 2.0. This demonstrates that our system is close to satisfying the virial theorem, but fails to do so absolutely. At large internuclear separations the virial ratio of our SCF calculation becomes 2.51.

3. FORMULATION: The use of the effective core potential also means that we are unable to quantify accurately the kinetic energy of the molecular orbitals in XeF₂ in the sense that the contribution from the core is omitted. However,
general trends in the kinetic energy can still be used to qualitatively describe the effects on bonding. This assertion is supported by similar trends we observed between a test case which imposed the virial theorem and a case that did not (i.e. used an ECP). We present our quantitative results to detail qualitative aspects of the bonding process. The preliminary comparisons with the test case are given in APPENDIX D.

The GAMESS code was used to calculate the total molecular orbital kinetic energy. Additional code was written to formulate explicitly the cartesian components of the kinetic energy. Each has the form of the kinetic energy operator:

\[ \langle T_q \rangle = -\frac{\hbar}{2m} \langle \frac{d^2}{dq^2} \rangle \quad (4.14) \]

where \( q \) is the appropriate coordinate of the kinetic energy one wishes to examine, \( \hbar \) is Planck's constant, and \( m \) is the mass of the electron. \( \langle T_q \rangle \) is actually the expectation value of the kinetic energy in the \( q \) coordinate. For sake of brevity, we have and continue to refer to this expectation value simply as the kinetic energy. The \( x, y, \) and \( z \) components generated from (4.14) when summed together form the total kinetic energy of each molecular orbital.

In this analysis we examine the kinetic energy curves as well as the coefficients of the atomic contributions to each molecular orbital. All contributions are given in tabular form
for a variety of internuclear separations in Appendix E.

B. TOTAL KINETIC ENERGY

1. BONDING ORBITAL: Figure 4.1 displays the kinetic energy of the occupied sigma and pi orbitals in the system as well as of the lowest unoccupied molecular orbital. The notation used for the total energy curves, s for σ and p for π, applies to Figure 4.1 and to the remainder of the orbital total and kinetic energies found in the text and appendix.

Of all the molecular orbitals plotted, the greatest change occurs in the kinetic energy of the 2σ_u orbital. As mentioned in prior section, this orbital is the bonding orbital in XeF₂ on the basis of bond order. The observed sharp rise in the kinetic energy with decreasing internuclear separation lends credence to this statement. The increase in the kinetic energy can be explained in terms of the Particle In the Box Model (PIB). As the walls of the imaginary box are moved closer to one another, the kinetic energy of the confined particle increases°. In the current molecule, the electrons in the sigma bonding orbital become more confined,

°The energy of PIB is \( E=n^2\hbar^2/(8mL^2) \), where \( n \) is the principle quantum number, \( \hbar \) is Planck's constant, \( m \) is the mass of the particle, and \( L \) is the length of the box. PIB is defined as having no potential energy, therefore, the total energy is composed solely of kinetic energy (KE). Therefore, the relation \( KE_{\text{PIB}} \propto n^2/L^2 \) can be made for any \( n \).
FIGURE 4.1: The kinetic energy of the molecular orbitals as a function of internuclear separation.
thus their kinetic energy should increase.

Other researchers in looking at the $\text{H}_2^+$ molecule have called this property the kinetic energy pressure. This tendency captures the desire of the wavefunction to expand as much as possible to allow the kinetic energy to decrease. When a bond is initially formed the wavefunction expands over a larger area between the nuclear centers allowing for a slight decrease in kinetic energy. As the nuclear centers come into closer contact, the electron becomes more confined than in its pre-bonded environment, the PIB walls move in, and the kinetic energy pressure is raised due to the localization of the electron. This confinement makes the kinetic energy increase. The converse is true as you move the walls of the PIB system out; the kinetic energy should be less because the kinetic energy pressure is being alleviated and the wavefunction is allowed to expand.

2. **SIGMA MOLECULAR ORBITALS:** FIGURE 4.2 details the kinetic energy of the sigma type orbitals in the molecule. The large increase in the $2\sigma_u$ kinetic energy can be plainly seen in this figure. The kinetic energy rises steadily throughout most of the internuclear separation range.

A similar effect is occurring in $2\sigma_g$ as the internuclear separation decreases toward $R_a$. This rise is again seen the $1\sigma_u$ orbital but not as pronounced. All remaining orbitals have
a decrease in the kinetic energy (3σ_g and 3σ_u) or seem to be rising to some plateau value (1σ_g) as internuclear separation is decreased.

We begin our discussion of the sigma molecular orbitals by examining the 2σ_u bonding orbital. The 2σ_u total molecular orbital energy found in the last section dropped below that of 1σ_g, 1σ_u and 2σ_g. This sharp drop of the total energy along with the substantial rise in the kinetic energy in FIGURE 4.2 leads us to conclude that the potential energy of 2σ_u is decreasing. Furthermore, this sharp decrease dominates the rise in the kinetic energy to lower the total energy of the molecular orbital. The drop in the potential energy can be attributed to the localization of the electron between the nuclear centers. In becoming localized, the electron feels the columbic attraction of both nuclei, thus its potential energy decreases. Therefore, we strongly believe this to be the bonding orbital of the molecule due to its large drop in total energy and its sharp rise in kinetic energy.

Additionally we can examine the atomic contributions to 2σ_u orbital to explain its sharp rise in kinetic energy. In the prior section we found this orbital to be mainly constructed of xenon p_z and fluorine p_z orbitals such that positive overlap along the internuclear axis is possible. The orbital begins solely with an atomic contribution coefficient
FIGURE 4.2: The kinetic energy of the sigma molecular orbitals as a function of internuclear separation.
value of 0.794 for the Xe $p_z$ orbital; this value drops rapidly to about 0.382 at the equilibrium bond length. The coefficient of F $p_z$ on the other hand increases its contribution from a trivial amount to about 0.457 at $R_{eq}$. At smaller separations these values remain about the same. These shifts in orbital contributions lead to the conclusion that electron density is being built up between the xenon and fluorine atomic centers. This build up confines the electron and increases the kinetic energy.

The $3\sigma_g$ orbital consists of a Xe $s$ and a F $p_z$ in an antibonding fashion at $R_{eq}$. The molecular orbital begins with an atomic contribution coefficient of 0.530 for the F $p_z$ orbitals. As the internuclear separation decreases toward $R_{eq}$, a xenon $s$ orbital coefficients of 0.300 begins and remains about constant. At separation values lower than $R_{eq}$, the xenon contribution increases and the fluorine contributions decrease a small amount. Only when the xenon $s$ component gets large does the kinetic energy greatly decrease. We attribute this to a shift in the molecular orbital character which is going from a $p$ type orbital to an $s$ type orbital. The $s$ type orbital has a smaller angular momentum, thus its kinetic energy is lower. Therefore, since its character is increasing in the description of the $3\sigma_g$ molecular orbital, the kinetic energy should decrease. This effect can also be explained using the
PIB model. The p orbital has a node thus its principle quantum number, \( n \) is larger than an s orbital which does not have a node. From the stated PIB energy relation, the kinetic energy is proportional to the square of the principle quantum number.

The slight increase in the kinetic energy of \( 1\sigma_u \) can be explained by the increase in the antibonding character of the orbital, which increases as the F s orbitals of different phases are moved closer together. This slight rise in the kinetic energy is due to the unfavorable interaction that must occur over a region of space containing the xenon nuclear center.

The \( 1\sigma_g \) is the one orbital that seems to have a rather constant kinetic energy which can be attributed to its coefficients maintaining relatively the same values throughout the bond length range. The unoccupied molecular orbital, \( 3\sigma_u \), has a large drop off in the kinetic energy. We associate this with the shifting of the electron density away from fluorine \( p_z \) to the xenon s orbital.

3. PI MOLECULAR ORBITALS: The three sets of pi molecular orbital kinetic energies are presented in FIGURE 4.3. There seems to be two types of kinetic energy curves present in the figure. The first is a somewhat constant decrease in kinetic energy as internuclear separation decreases, this describes the \( 1\pi_z(x,y) \) molecular orbital. The other type of curve is
FIGURE 4.3: The kinetic energy of the pi molecular orbitals as a function of internuclear separation.
sigmoidal in nature and begins with a constant value and progresses either upward or downward as the separation is increased, this describes the \( 1\pi_u(x,y) \) and \( 2\pi_u(x,y) \) molecular orbitals.

The atomic contributions for \( 1\pi_x(x,y) \) indicates that the orbital is mainly composed of \( F \) \( p_{x,y} \) orbitals. These contributions remain roughly the same throughout the internuclear separation range and are confirmed by a relatively constant total kinetic energy for the molecular orbital. The rise in kinetic energy below \( R_{eq} \) is a similar antibonding effect as seen in the \( 1\sigma_u \) molecular orbital.

\( 1\pi_u(x,y) \) has a constant kinetic energy value at large internuclear separations and decreases to a lower value as \( R_{eq} \) is approached. This is indicative of the wavefunction being able to expand over the whole molecule, thus the kinetic energy pressure is reduced and the kinetic energy decreases. In looking at the coefficients we see that the molecular orbitals begin as \( F \) \( p_{x,y} \) and a \( Xe \) \( p_{x,y} \) orbitals. This formation of the \( p \) orbital on the xenon allows for the wavefunction to expand, an effect we are observing in the kinetic energy between 3.00 Å and 2.30 Å. Once this decrease occurs, the \( p \) lobes interact favorably causing modest bond formation and a slight increase in the kinetic energy beginning around 2.25 Å.

The \( 2\pi_u(x,y) \) has an opposite trend in its kinetic energy
curve. It starts at a constant value and increases its kinetic energy as internuclear separation decreases. The molecular orbitals begins with a 0.800 Xe p_{x,y} contribution. As the bond length decreases F p_{x,y} orbitals begin to form. This would again indicate that the wavefunction has more orbitals to spread over, thus the kinetic energy should decrease. However, in this case, the kinetic energy increases. This is due to the electronic density transfer in the molecular orbital such that the antibonding character increases.

The average of 1\pi_u(x,y) and 2\pi_u(x,y) is shown in FIGURE 4.3. This average kinetic energy closely parallels the 1\pi_u(x,y) kinetic energy curve. This indicates that the net contribution from all pi orbitals is approximately constant from 1.70 \AA{} to 6.00 \AA{}.

4. SUMMARY: In examining the kinetic energy of the XeF_2 we are beginning to gain an understanding of the nature of the molecular orbitals. We feel the 2\sigma_u is the major bonding orbital in the molecule due to its steep increase in kinetic energy as the internuclear separation is decreased. Additionally, we have concluded that there is no net bonding occurring the pi molecular orbitals. At this point we feel we can confirm some of these conclusions by examining the components of the total kinetic energy for each molecular orbital. By assigning a direction to the kinetic energy, we
are able to break down the above trends in kinetic energy to obtain a greater insight into the bonding characteristics of the molecular orbitals.

C. KINETIC ENERGY COMPONENTS

1. INTRODUCTION: The components of the kinetic energy for each molecular orbital were calculated. The x, y, and z components of each sigma orbital are given in FIGURE 4.4a-c and the pi orbital components in FIGURE 4.5a-c. The markers representing the total kinetic energy of each molecular orbital are the same among these six figures. Additionally, the kinetic energy component curves include the asymptotic atomic kinetic energy limits. These limits are represented by solid black lines at the far right of each figure.

2. SIGMA MOLECULAR ORBITALS: The x and y components of the kinetic energy for each sigma orbital is the same, with $T_x$ shown in FIGURE 4.4a. This occurs because each sigma orbital is symmetric in the x and y directions, thus the kinetic energy should be degenerate and is in these directions.

The $1\sigma_z$ and $1\sigma_u$ have roughly the same kinetic energy in all directions until 2.50 Å. Then a decrease in kinetic energy occurs in the $1\sigma_z$ orbital and the $1\sigma_u$ orbital increases in kinetic energy. This change can be explained by the presence of a node in the $1\sigma_u$ orbital and the lack of a node in the $1\sigma_z$. 

The $\times$ component of the kinetic energy of the sigma molecular orbitals as a function of internuclear separation.
FIGURE 4.4b: The y component of the kinetic energy of the sigma molecular orbitals as a function of internuclear separation.
FIGURE 4.4c: The z component of the kinetic energy of the sigma molecular orbitals as a function of internuclear separation.
orbital. The nodal presence raises a question, how can these two orbitals have the same kinetic energy in all directions up to 2.50 Å when one is clearly higher in energy due to a node present? The answer lies in the treatment of the molecular orbital.

At large internuclear separations the molecular orbital is really two noninteracting orbitals, i.e. two well separated s type fluorine orbitals. This is supported by the fact that each of these molecular orbitals has a kinetic energy close to that of an atomic fluorine s orbital at large internuclear separations. There is a slight difference in the atomic value and the dissociating molecular orbital value, but this is attributed to these orbitals being closest to the ECP approximation. As the internuclear separation decreases, the atomic orbitals begin to acquire significant molecular orbital character. Thus, at small internuclear separations the nodal character of each orbital plays an important role in determining the kinetic energy value it has. This accounts for the large increase in the $1\sigma_g$ orbital kinetic energy.

A slight dip in the z component of the kinetic energy around 1.75 Å in $1\sigma_g$ orbital indicates a slight expansion of the wavefunction as the isolated fluorine s orbitals of like phase come into contact with one another. After this dip there is a slight increases in the kinetic energy which indicates
the possibility of bond formation. We rule out this conclusion
for our system based on two reasons. First, the increase is
not as pronounced as in the $2\sigma_g$ bonding orbital. Secondly, the
rise takes place at a separation far below the equilibrium
bond length and the dominate interaction in this range is the
internuclear repulsion. This force cancels any bonding that
occurs because of this orbital.

The $2\sigma_g$ orbital at large internuclear separations is a
xenon s orbital which is close to the atomic xenon s orbital
kinetic energy. This molecular orbital overall maintains this
xenon s character with a slight decrease as the internuclear
separation decreases. There is a slight decrease in this
contribution to the fluorine s and p$_z$ orbitals. By
transferring electronic density to the fluorine p$_z$ orbital, a
favorable s and p orbital interaction occurs, thus bonding
results. These bonding effects are canceled out by the
antibonding orbital $3\sigma_g$. The average kinetic energy of these
two orbitals is relatively constant throughout the
internuclear separation range, thus there is no net effect on
the total energy from either orbital.

The rise in the kinetic energy is also augmented by the
transfer of xenon s electron density to opposite signed
fluorine s orbitals. This transfer at first would seem to
indicate an expansion of the wavefunction and thus a decrease
in the kinetic energy, however, this trend is not observed. It is true that the wavefunction is expanding, but this expansion is occurring into region that increases the antibonding character of the molecular orbital and therefore increases the kinetic energy.

In the $2\sigma_u$ molecular orbital, electron density transfer from the xenon $p_z$ to the fluorine $p_z$ occurs as internuclear separation decreases. This transfer involves the shifting of electron density to an atomic orbital that allows for more orbital overlap, or greater bonding. As such, the wavefunction can expand in this direction. However, by allowing for this overlap the bond becomes the predominant effect because the electron is more confined between nuclear centers. This accounts for the sharp rise in the kinetic energy in all directions. But this rise is greatest in the $z$ direction. This is due to the confinement of the electron along the internuclear axis, or the $z$ axis. In all directions the asymptotic kinetic energy limit of this molecular orbital matches closely to the fluorine $p_z$ orbital value.

The $3\sigma_g$ orbital has an initial electron transfer from the fluorine $p_z$ to the xenon $s$ orbital as the internuclear separation decreases. This slight shift of density accounts for the slight dip in the kinetic energy beginning at 4.00 Å and ending at 2.80 Å. Then the electron density is shifted
back to the fluorine $p_z$ orbital which can be observed in a slight rise of the kinetic energy. Finally, the electron density is transferred in large part to the xenon $s$ orbital around 1.80 Å. This accounts for the large drop in the kinetic energy of the molecular orbital. Even though this molecular orbital begins as an antibonding fluorine $p_z$ orbital, it kinetic energy did not match the atomic fluorine $p_z$ value. We thus conclude this orbital begins as an excited state fluorine $p_z$ orbital at large internuclear separations.

The LUMO has a large decrease in the kinetic energy as internuclear separation decreases. This is linked to a shift of electron density from the F $p_z$ orbital to the Xe $p_z$ orbital which allows for expansion of the wavefunction. As with the $3\sigma_g$ orbital, this molecular orbital is suspected to begin as an excited fluorine $p_z$ orbital.

3. PI MOLECULAR ORBITALS: The pi molecular kinetic energy components show a difference in the $x$ and $y$ directions. This should be observed as the pi orbitals are given in degenerate pairs with a $p$ orbital oriented either along the $x$ or $y$ direction. So for a $p_x$ orbital, $T_x$ differs from $T_y$, but $T_x$ for the $p_x$ orbital has the same value as $T_y$ for the $p_y$ orbital. This is as well true for $T_y$ of a $p_x$ orbital having the same value as $T_x$ for a $p_y$ orbital. For our purposes we choose to comment only on the $p_x$ orbital of each degenerate pair, the
FIGURE 4.5a: The x component of the kinetic energy of the pi molecular orbitals as a function of internuclear separation.
FIGURE 4.5b: The y component of the kinetic energy of the pi molecular orbitals as a function of internuclear separation.
**FIGURE 4.5c:** The z component of the kinetic energy of the pi molecular orbitals as a function of internuclear separation.
same analysis applies with appropriate exchange of nomenclature to the $p_y$ orbitals.

The first set of pi orbitals is labeled $1\pi_u(x,y)$. At large internuclear separations this molecular orbital is composed of fluorine $p_{x,y}$ orbitals. This is confirmed by the agreement between the molecular orbital kinetic energy values and the atomic fluorine $p_{x,y}$ kinetic energy. As the bond length decreases there is an electron density transfer from the fluorine $p_{x,y}$ to the xenon $p_{x,y}$ orbital. This allows for an expansion of the wavefunction and thus a large drop in the $x,y,$ and $z$ components of the kinetic energy beginning around 3.00 Å. As the $p$ orbitals come closer together they favorably interact with one another. In doing so the kinetic energy should rise and does so in each component slightly around 2.25 Å. This bonding becomes even more of a factor and raises the kinetic energy drastically in the $x$ and $z$ directions around 1.50 Å. The $y$ components do not see as much of a rise since the molecular orbital is not oriented in this direction.

The next set of pi orbitals are the nonbonded pair of $p$ orbitals on each fluorine that form the $1\pi_e(x,y)$ degenerate set. DeKock and Gray concluded that these orbitals are nonbonding. However, when examining the kinetic energy in the $x$ direction a characteristic decrease occurs. This indicates that there is an interaction occurring in this molecular
The molecular orbital begins at large internuclear distances as a set of atomic fluorine $p_{x,y}$ orbitals. As the internuclear separation decreases these lone $p_z$ and $p_y$ orbitals on each fluorine begin to shift their electronic density in small amount into the $d_{xz}$ and $d_{yz}$ orbitals respectively. The shift of density brings the $d$ orbitals from an insignificant contribution to about $1/8$ the total $p$ orbital contribution to the molecular orbital. This might seem insignificant, however, these $d$ orbitals are of like phase and interact in a favorable or bonding way. Only when the internuclear separation decreases to around $1.65 \, \text{Å}$ is this effect most exemplified. Near this bond length the kinetic energy decreases from its asymptotic limit by $0.2 \, \text{a.u.}$. The total energy decreases by about $0.1 \, \text{a.u.}$ from its maximum. Therefore, the potential energy in this region is decreasing by a value of about $0.3 \, \text{a.u.}$ In light of these trends, the wavefunction is thought to be expanding as these slightly bonding $d$ orbitals that are approaching each other. This allows for orbital overlap above and below the internuclear axis. This begins the localization of the electron and a decrease in the potential. This bonding, however, is very slight at the equilibrium bond distance. But these results indicate that the small contribution of the $d$ orbital in the bonding of the molecule has a large impact in
the interaction of these nonbonded "inert" pairs. This effect though is canceled in large part by the internuclear repulsions and the distance the d orbitals must transverse for the interactions to occur.

The final set of pi orbitals are the antibonding pairs of p orbitals on each fluorine and xenon that form the 2π_u(x,y) degenerate set. This molecular orbital is initially a xenon p_x,y orbital. As the internuclear separation decreases, there is an initial shift of electron density from the xenon p_x,y orbital to the fluorine p_x,y orbitals around 3.00 Å. This accounts for the increase in the kinetic energy in the x and z direction due to the increase of antibonding character in the molecular orbital. Again, there is little molecular orbital density in the y direction, thus the kinetic energy remains relatively constant. The electron density then shifts back to the xenon and this is captured by the decrease of the x component of the kinetic energy.

4. SUMMARY: Analysis of the kinetic energy components has allowed us to check our initial conclusions made in the total kinetic energy analysis of each molecular orbital. We feel that the 2σ_u molecular orbital is the major bonding orbital of the molecule. The 1σ_g molecular orbital was found to have slight bonding but this interaction was considered to be negligible due to the internuclear repulsions. The 1π_u(x,y)
degenerate set of pi orbitals was additionally found to be slightly bonding. This effect, however, is very small due to the weak nature of delta bonds.

It was hoped to find a dip in the z direction of the kinetic energy at large internuclear separations in one of the eleven occupied molecular orbitals. This slight dip has been attributed to the expansion of the wavefunction at the onset of bonding. Such a dip has been deemed an important precursor to bonding in H$_2^+$.\textsuperscript{2} We found no such dip in the orbitals we examined.

There are three possible reasons for the absence of this characteristic. First, there is a dip, but the level of calculation is not adequate enough to characterize it. Second, such a dip is not present in XeF$_2$. Third, the dip in kinetic energy could not be observed because the initial bonding of the molecule might occur in a bent form of XeF$_2$. In the analogous XeCl$_2$, researchers found the bent form of the molecule to be the Van der Waals complex which initiated bonding\textsuperscript{3}.

Thus, to capture this dip in the kinetic energy we would have to obtain a kinetic energy surface of the molecule to encompass the angular dependency of the initial bonding. We have limited our study of the molecule to the linear case and thus such analysis is beyond the scope of the present
research. However, in future work the XeF or XeF\(^+\) fragment could be studied and its kinetic energy examined for such a characteristic.
NOTES FOR RESULTS - KINETIC ENERGY


V. CONCLUSIONS

We began this study in hopes of increasing our understanding of the bonding in xenon difluoride. We principally used trends in the kinetic energy to gain insight into the character of the molecular orbitals as the molecule forms.

To obtain the molecular orbitals we used a series of calculations that continually improved the description of the molecular environment. From our CI energy curve calculation we only found approximately 66% of the expected dissociation energy for the molecule. We feel this value is quite good when considering the large numbers of electrons not explicitly accounted for due to the effective core potential approximation. It is our contention that we have established a wavefunction that is an adequate description of the molecule.

We observed the total and component kinetic energy trends of the molecular orbitals produced by the Hartree-Fock-Slater method. These orbitals were employed because they yield the closest "chemical" picture of the bonding and seemed a
reasonable starting point for this type of analysis.

Examination of the kinetic energy and its components confirmed that the $2\sigma_g$ is the principal bonding molecular orbital in XeF$_2$. Bonding in this molecular orbital is unique due to its three-center sigma character. The significant rise in the kinetic energy coupled with a large drop in the potential energy indicates significant localization of the electron between the nuclear centers. The $2\sigma_g$ molecular orbital was also found to be bonding in the molecule, nonetheless, this bonding was for the most part canceled by occupation in the antibonding $3\sigma_g$ molecular orbital. The same effect was found for $1\pi_u(x,y)$ and $2\pi_u(x,y)$ molecular orbitals. The $1\sigma_g$ orbital was also slightly bonding but this effect occurs at such small internuclear separations that the nuclear to nuclear repulsions dominate any energy decrease found in this molecular orbital.

The one conclusion that was not expected was the interaction in the $1\pi_u(x,y)$ molecular orbital. As the internuclear separation decreases, p orbitals on each fluorine lose some of its electronic density to form d type orbitals of like phase. This slight shift in electronic density allows for a long range interaction of these d orbitals on each fluorine to begin a delta bond in the molecule.

We have increased our understanding of the bonding in the
xenon difluoride molecule. The kinetic energy analysis did reveal some interesting characteristics of the molecular orbitals. Possible future research could center on the role of the kinetic energy in the higher levels of calculations established in this study. Examining these kinetic energy trends might allow for greater understanding of the molecular orbitals that bind together the molecule.
APPENDIX A:
GENERAL ATOMIC AND
MOLECULAR ELECTRONIC STRUCTURE SYSTEM

A. INTRODUCTION

This appendix will provide the reader with an introduction to the General Atomic Molecular Electron Structure System (GAMESS). These input descriptions are drawn from our experience with the program and implementing it on XeF₂ and related systems. For a full description of input types and examples please see refer to the GAMESS manual.

B. GENERAL INPUT PHILOSOPHY

GAMESS interacts with the user with two types of files, input files and log files. The input file gives the program a set of instructions to follow and conditions to perform the desired calculations. The input file is designated with a ".inp" suffix.

The second file type is a log file, designated with a ".log" suffix. The log file gives the results of the calculation that one asks the program to perform. GAMESS is
run by entering the command \texttt{rgms} with an input file name after it (when executing the input file "test.inp", one would type \texttt{rgms test} leaving off the suffix). GAMESS then executes the input file and creates a log file with the same name but with a .log suffix. Additionally, GAMESS will create other file types to handle a variety of output data.

\section*{C. INPUT GROUPS}

Within an input file there are a set of instructions that control the calculation GAMESS is performing. These instructions fall into one of several input groups. Each group has a name that indicates the set of programming instructions, or flags, that are contained within it. The name has a $ in front of it. After each input group name comes the control strings which oversee the aspects of the calculation for that particular control group. Each group then terminates with an $END$.

All default values listed here are designated with by a *. All integer values are designated with an x. Any values we chose in our calculations are indicated in parenthesis.

\section*{D. INPUT GROUP LISTINGS}

The various general input groups for most all GAMESS runs have been listed below. The first control group is \texttt{$CONTROL$}. This group gives general instructions to GAMESS. A summary of
the assignment for this group are given in FIGURE A.1.

<table>
<thead>
<tr>
<th>SCFTYP</th>
<th>RHF</th>
<th>SCF method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GVB</td>
<td>TCSCF method</td>
</tr>
<tr>
<td></td>
<td>MCSCF</td>
<td>MCSCF</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>CI</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RUNTYPE</th>
<th>ENERGY*</th>
<th>single point energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OPTIMIZED</td>
<td>optimize the geometry of the molecule</td>
</tr>
<tr>
<td></td>
<td>TRUDGE</td>
<td>optimize the orbital coefficients</td>
</tr>
</tbody>
</table>

| ECP | SBK | Stevens, Basch, Krauss, Jasien, Cundari effective core potential. |

| NZVAR | 0* | cartesian coordinates for other coordinate choices. Compute using 3N-6 (linear uses 3N-5 but we used 3N-6 and came up with the same answer). |

<table>
<thead>
<tr>
<th>EXETYP</th>
<th>CHECK</th>
<th>checks input file but does not calculate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RUN*</td>
<td>calculates</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PLTORB</th>
<th>.FALSE.*</th>
<th>does not produce molecular orbital plot data.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.TRUE.</td>
<td>writes molecular orbital plot data to name.dat in the designated scr folder.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COORD</th>
<th>(nothing)</th>
<th>used assigned values in $DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HINT use Hilderbrandt article assignment- SEE GEOMETRY OPTIMIZATION SECTION.</td>
<td></td>
</tr>
</tbody>
</table>

**FIGURE A.1** General assignments for the $CONTROL$ group.

The next control group is $SYSTEM$ which supervises the computer environment in which GAMESS is run. **FIGURE A.2** gives a summary.
TIMLIM x limits the computing time (wall clock time)
MEMORY . x. limit of the memory used for the calculation.

FIGURE A.2 The assignments for the $SYSTEM control group.

The $GUESS control group gives GAMESS instructions about the orbitals to be read into a calculation. FIGURE A.3 displays some of the assignments made in this group.

HUCKEL extended Hückel approximation
MOREAD uses the $VEC assigned to the input file for initial guess. $VEC is derived from .dat file that is written to folder scr upon each execution of GAMESS.
NORB the number of orbitals to be read into the run.

FIGURE A.3 The assignments for the $GUESS control group.

The $ZMAT and $LIBE control the z matrix and linear bends of the molecule respectively. These groups are summarized in FIGURE A.4

$ZMAT z matrix information (internal coordinates)
IZMAT(1) 1 followed by two atom numbers (I-J bond length)
5 followed by three numbers (I-J-K linear bend) see $LIBE

$LIBE details linear bends
APTS(1) defines the coordinates of the degenerate linear bend. We used 1.0, 0.0, 0.0

FIGURE A.4: The assignments used in $ZMAT and $LIBE.
$ZMAT$ can easily be explained by examining the actual values we used in our calculations. We examined the linear case of F-Xe-F (or using atom numbers 2-1-3). In letters this is J-I-J. Thus we defined $IZMAT(1)= 1,1,2$ (defines the 1-2 bond) 1,2,3 (which defines the symmetry degenerate 2-3 bond) 5,2,1,3 (which defines the molecule as a whole 2-1-3).

The $BASIS$ group defines the basis set being used in the calculation. For our calculations we used the SBK basis. This was indicated to GAMESS by setting GBASIS equal to SBK (Stevens, Basch, Krauss, Jasien, Cundari effective core potential basis).

The last general control group that we used was $DATA$. This group gives GAMESS the run title, symmetry, atom names, coordinates, and extended basis set controls. FIGURE A.5 displays an example of a line by line $DATA$ assignments

```
LINE1: $DATA
LINE1:TITLE
LINE2:SYMMETRY (linear - Dnh 4 or bent - Cnv 2
LINE3:SKIP!!! (must be entered or GAMESS WILL NOT RUN!)
LINE4:ATOM(1) NAME ATM # x y z
LINE5:ATOM(1) NAME ATM # x y z
LINE6:SKIP!!! (must be entered or GAMESS WILL NOT RUN!)
LINE7:EXTENDED BASIS SET
LINE8: $END
```

FIGURE A.5: The line input description of the $DATA$ group.

Please examine this input style in one of the examples provided in the GAMESS manual. GAMESS is very particular with
E. SCF CALCULATION

The SCF calculation is given in GAMESS manual as EXAMPLE 8. The calculation chooses a guess set of orbitals, in our case an extended Hückel calculation on the system suffices, and iterates to find the lowest energy wavefunctions by modifying the orbitals.

We set NZVAR=3 using the formula 3N-6, were the program states to use the formula 3N-5. We found it not to matter. Most of these calculations and calculations to follow used cartesian coordinates.

F. SCF EXTENDED BASIS CALCULATION

An extended basis set calculation takes the given basis set, in our case SBK, and adds additional functions to it. The input file is similar to a SCF calculation with the exception of the $DATA section. It should resemble FIGURE A.6.

It should be noted that this input description is very particular because GAMESS will not run a file unless the proper spacing and arrangement is provided.

The program assumes Gaussian primitives. The (a) is the exponential value and the (b) is the coefficient of the exponential value. The selection of (b) does not matter and can be chosen to be one as in our case.
G. SCF TRUDGE CALCULATION

A trudge is usually an optimization in which orbital exponents are found that minimize the energy. One must provide in the $DATA a set of orbital exponents for GAMESS to optimize (see GAMESS EXAMPLE 20).

The first change is that RUNTYP=TRUDGE. In doing so a new group called $TRUDGE must be included. This tells GAMESS what type of trudge one desires. The main flag to be set OPTMIZ = BASIS which tells GAMESS to optimize the basis set. The other value for OPTMIZ is GEOMETRY which will be explained later.

The program must then know the number of parameters one
wishes to trudged, NPAR=x. The parameters to be optimize are done with IEX(1). This equals the serial number of the Gaussian primitives to be optimized. This is found by running an expanded basis set SCF and looking at the "ATOMIC BASIS SET SECTION" of the log file. The serial number is the primitive number of the listed shells. If the expanded basis set is used, the same $DATA assignments must be kept.

For this type of calculation an extended run time must be entered. Generally the more orbitals that are optimized, the longer the run. In our case six orbitals took up to 300 minutes, thus TIMLIN=300. Once an optimization is run, one must feed those values back into the program in a different input file so the energy value of each of the individual molecular orbital of the system can be obtained.

H. TCSCF CALCULATION

This calculation defines the system as a combination of two configurations, each is denoted by "coeff1" and "coeff2" in the .log file. For this calculation one must set SCFTYP=GVB (generalized valence of which TCSCF is a subcase). A new $SCF group must be inputed. The assignments in this group are given in FIGURE A.7. All of our calculations used the values in the parenthesis.

The user must set GUESS=MOREAD. This informs GAMESS to read the orbitals that are provided at the end of the input
file in the $VEC group. To get $VEC, an SCF must first be run at the same conditions that one wishes to run the TCSCF. Then the .dat group from that correspondingly named SCF run has to have its $VEC description placed into the tail end of the TCSCF input file. This type of calculation can be found in GAMESS manual, EXAMPLE 4)

I. MCSCF CALCULATION

The multiconfiguration self consistent field calculation (MCSCF) is a rigorous calculation of which TCSCF is a subcase. For this calculation the SCFTYP is set to MCSCF. The user must create a new $MCSCF group which has two control strings contained in it. First, MAXIT tells GAMESS the maximum number of iterations to perform before quitting. Second, NORBS signifies the number of guess orbitals to be read into the MCSCF run. These orbitals are read in as a $VEC as just described for the TCSCF calculation.

The MCSCF calculation must be defined by the user in the $DRT group. The NMCC assignment tells GAMESS how many frozen core orbitals are to be placed into the calculation. The number of orbitals that allow electron promotion are
controlled by the NDOC assignment. Lastly, the number of virtual orbitals to be included in the calculation is controlled by the NVAL assignment. An example of the MCSCF input file is given in GAMESS EXAMPLE 9.

J. CI CALCULATION

The configuration interaction (CI) calculation is NOT A SELF CONSISTENT result! Therefore, it takes the orbitals feed into it and does not modify them. GUESS=MOREAD must again be entered, but this time the TCSCF or MCSCF $VEC orbitals must be used instead of a SCF. This calculation takes a considerable amount of time due to the configurations it uses to formulate the molecular wavefunction.

First the SCFTYP is set to CI and a $DRT group must be made similar to that given in the MCSCF calculation.

<table>
<thead>
<tr>
<th>SOCI=</th>
<th>second order CI (.TRUE.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GROUP=</td>
<td>geometry assignment (C2V, note this form is different than the form found in $DATA)</td>
</tr>
<tr>
<td>NFZC=</td>
<td># of frozen core orbitals (8)</td>
</tr>
<tr>
<td>NDOO=</td>
<td># of orbitals to interact (3)</td>
</tr>
<tr>
<td>NALP=</td>
<td># of orbitals with alpha spin 1/2 (0)</td>
</tr>
<tr>
<td>NVAL=</td>
<td># of orbitals that are empty (1)</td>
</tr>
<tr>
<td>NEXT=</td>
<td># of external orbitals (-1 means all others)</td>
</tr>
</tbody>
</table>

FIGURE A.8: The $DRT assignments for the CI calculation. The values used in our calculations are given in parenthesis.
The orbitals read in for the CI calculation is indicated by the $GUESS which informs GAMESS of the number of guess orbitals being entering (NORB=x). An example of a CI calculation input file is given in GAMESS manual as EXAMPLE 5.

K. GEOMETRY OPTIMIZED CALCULATION

All the above calculations can have a geometry optimization carried out on them. This is done by setting the SCFTYP to the type of calculation one desires and making the following assignments.

First the RUNTYPE is set to TRUDGE. This will set up the optimization. Then a new group, $TRUDGE must be created. The assignments for this group are given in FIGURE A.9.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPTIMIZ= GEOMETRY</td>
<td>telling it to optimize the geometry.</td>
</tr>
<tr>
<td>CIDRT= CIDRT</td>
<td>tells it where (what group farther down in the input file will have the $DRT group assignments for the optimization).</td>
</tr>
<tr>
<td>NPAR= x</td>
<td>number of parameters to be optimized</td>
</tr>
<tr>
<td>IEX(1)=</td>
<td>21 radius 22 angle</td>
</tr>
<tr>
<td>P(1)=</td>
<td>value of either the radius or angle to start the optimization with (GAMESS will fill in a value if the user does not).</td>
</tr>
</tbody>
</table>

FIGURE A.9: The $TRUDGE assignments for a geometry optimization.
The $TRUST group controls the optimization parameters. These assignments are given in FIGURE A.10. We used the parenthesis values which were recommended from the GAMESS manual.

| KSTART= indicates the conjugate gradient direction in which the optimization will run (0). |
|-------|--------------------------------------------------------------------------------------------------|
| TOLF= accuracy of the function (0.0001) | |
| TOLR= accuracy require of the conjugate directions (0.001) | |
| FNOISE= accuracy of function values (0.00001) | |

FIGURE A.10: The $TRUST assignments which control the optimization criteria.

Some optimizations were found to require a coordinate system other than cartesian assignments for the atoms. The coordinate system we found to work well was COORD = HINT. FIGURE A.11 gives the assignments for this group.
| NAME= | 10 character atomic name |
| ZNUC= | nuclear charge |
| CONX= | connection |
| LC | linear connection |
| PCC | planer central atom |
| NPCC | non-planer central atom |
| PTC | planer -terminal connection |
| CCPA | central connect. w/ planar atm |
| TCT | term. connect. w/ torsion |
| R= | connection distance |
| ALPHA= | first connection angle |
| BETA= | second connection angle |
| SIGN= | connection sign, either - or + |
| POINT1, POINT2, POINT3= | connection points, a serial number of a previously input atom, one to four standard O, I, J, K. |

**FIGURE A.11**: The assignments for defining the molecule with HINT coordinates.
APPENDIX B:
ORBITAL ORDER IN XeF₂

A. INTRODUCTION

This appendix provides the reader with the orbital order shifts we obtained from the SCF calculation on the molecule. The order of the orbitals is dependent on the individual orbital energies. Thus, when these energies rise above or below one another, orbital order shifts occur.

B. NOMENCLATURE

To better understand these shifts, the individual orbital energies were graphed. Then the position of the orbitals were catalogued and assigned to sections. Each section is defined as a range of bond lengths that maintain the same orbital order. The orbital type are assigned to each orbital as they appear at the equilibrium bond length. The pictorial representation of the molecular orbitals were given in TABLE 3.2.
C. ORBITAL ORDER

The orbital order was found by examining the atomic contribution to each molecular orbital at the equilibrium bond length. Then the molecular orbitals were followed at regular intervals throughout the internuclear separation range. Energies of the molecular orbitals were tracked as well. The results of the orders are summarized in TABLE B.1.
<table>
<thead>
<tr>
<th>REGION</th>
<th>APPROX. RANGE</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.00 - 1.05+</td>
<td>1s-u</td>
<td>1s-g</td>
<td>1p-u</td>
<td>1p-u</td>
<td>1p-g</td>
<td>2s-g</td>
<td>2s-u</td>
<td>3s-g</td>
<td>2p-u</td>
<td>2p-u</td>
<td>3s-u</td>
<td>4s-g</td>
<td>2p-g</td>
<td>2p-g</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>1.05+ - 1.15+</td>
<td>1s-u</td>
<td>1s-g</td>
<td>1p-u</td>
<td>1p-u</td>
<td>2s-g</td>
<td>1p-g</td>
<td>2s-u</td>
<td>3s-g</td>
<td>2p-u</td>
<td>2p-u</td>
<td>4s-g</td>
<td>3s-u</td>
<td>2p-g</td>
<td>2p-g</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>1.15+ - 1.18+</td>
<td>1s-u</td>
<td>1s-g</td>
<td>1p-u</td>
<td>1p-u</td>
<td>2s-g</td>
<td>2s-u</td>
<td>1p-g</td>
<td>3s-g</td>
<td>2p-u</td>
<td>2p-u</td>
<td>4s-g</td>
<td>3s-u</td>
<td>2p-g</td>
<td>2p-g</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>1.18+ - 1.33+</td>
<td>1s-u</td>
<td>1s-g</td>
<td>2s-g</td>
<td>1p-u</td>
<td>1p-u</td>
<td>2s-u</td>
<td>1p-g</td>
<td>3s-g</td>
<td>2p-u</td>
<td>2p-u</td>
<td>4s-g</td>
<td>3s-u</td>
<td>2p-g</td>
<td>2p-g</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>1.33+ - 1.75+</td>
<td>1s-g</td>
<td>1s-u</td>
<td>2s-g</td>
<td>2s-u</td>
<td>1p-u</td>
<td>1p-u</td>
<td>1p-g</td>
<td>3s-g</td>
<td>2p-u</td>
<td>2p-u</td>
<td>4s-g</td>
<td>3s-u</td>
<td>2p-g</td>
<td>2p-g</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>1.75+ - 2.10+ (Req)</td>
<td>1s-g</td>
<td>1s-u</td>
<td>2s-g</td>
<td>2s-u</td>
<td>1p-u</td>
<td>1p-u</td>
<td>1p-g</td>
<td>3s-g</td>
<td>2p-u</td>
<td>2p-u</td>
<td>4s-g</td>
<td>3s-u</td>
<td>4s-g</td>
<td>2p-g</td>
<td>2p-g</td>
</tr>
<tr>
<td>VII</td>
<td>2.10+ - 2.45</td>
<td>1s-g</td>
<td>1s-u</td>
<td>2s-g</td>
<td>2s-u</td>
<td>1p-u</td>
<td>1p-u</td>
<td>1p-g</td>
<td>2p-u</td>
<td>3s-g</td>
<td>3s-u</td>
<td>4s-g</td>
<td>2p-g</td>
<td>2p-g</td>
<td>2p-g</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>2.45 - 2.85</td>
<td>1s-g</td>
<td>1s-u</td>
<td>2s-g</td>
<td>1p-u</td>
<td>1p-u</td>
<td>2s-u</td>
<td>1p-g</td>
<td>2p-u</td>
<td>3s-g</td>
<td>3s-u</td>
<td>4s-g</td>
<td>2p-g</td>
<td>2p-g</td>
<td>2p-g</td>
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</tbody>
</table>

**TABLE B.1:** The molecular orbital order regions of XeF₂.
APPENDIX C: MOLECULAR ORBITALS OF $F_2$

A. INTRODUCTION

This appendix provides the reader with a full listing of the molecular orbitals of $F_2$ obtained from our SCF calculation on the molecule. TABLE C.1 shows schematically the molecular orbital types and symmetries of the seven lowest occupied molecular orbitals as well as the lowest unoccupied molecular orbital. The energies of all eight molecular orbitals are given in FIGURE C.1. FIGURE C.2 displays the occupied sigma molecular orbital energies while FIGURE C.3 displays the pi occupied molecular orbital energies.

B. SIGMA ORBITALS

The sigma orbitals alternate $\sigma_z$ to $\sigma_u$. There are no close interactions with the same symmetry type in these orbitals. The interesting point is the separation of the first two molecular orbitals and their closeness in energy starting around 2.75 Å. These molecular orbitals in $F_2$ are responsible
for the first two molecular orbitals in XeF₂.

C. PI ORBITALS

The pi molecular orbitals seem to come together as well, but in this case the initial separation is over 0.2 a.u. and comes to almost on top of each other.

D. LITERATURE COMPARISON

In F₂ the literature value¹ for the orbital order is

\[(1σ_g)^2 (1σ_u)^2 (1π_u)^4 (1σ_g)^2 (1π_g)^4 (2σ_u)^2\]

Our SCF study of F₂ arrives at the same order for the molecular orbitals at the equilibrium bond length (≈ 1.40 Å). This match in order is an indication that we are properly modelling the F₂ molecule with our ECP basis.
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<td>2σ_g</td>
<td>1π_g</td>
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</table>

**TABLE C.1:** The order and type of the molecular orbitals of F₂ at the equilibrium bond length.
FIGURE C.1: The total energy of the sigma and pi molecular orbitals of F, as a function of internuclear separation.
Figure C.2: The total energy of the sigma molecular orbitals of F₂ as a function of internuclear separation.
FIGURE C.3: The total energy of the pi molecular orbitals of $F_2$ as a function of internuclear separation.
NOTES FOR APPENDIX C

APPENDIX D:
F₂ KINETIC ENERGY ANALYSIS

A. INTRODUCTION

We set forth a study of the kinetic energy of the F₂ system for three reasons. First, the F₂ system can have a full and ECP basis set applied to it. Second, the total and component kinetic energies can also be compared between an ECP calculation and a full electron calculation. Lastly, we know the F₂ system well making it is easier to analyze.

B. SETUP

The F₂ molecule was set up with the Double Zeta Valance basis set (DZV) and our EBS-SBK basis. The DZV basis set will include all eighteen electrons while the EBS-SBK will only explicitly calculate ten electrons.

To check if the written code is correctly calculating the kinetic energy, a full electron run was setup at the equilibrium bond length. This kinetic energy was compared to a run with the same geometry but with the virial flag imposed explicitly. The total energies and molecular orbital energies
of these two runs were the same. The kinetic energies of the molecular orbitals differed at most by 0.01 a.u. We conclude from this difference that our written code seems to be correctly calculating the kinetic energy in the $F_2$ system.

C. RESULTS

The kinetic energy of the sigma and pi orbitals of DZV and ECP are shown in FIGURES D.1a, D.1b, D.2a, and D.2b. The components are shown in FIGURES D.3a-c and D.4a-c. In each figure the all electron calculation (denoted AE) has solid lines and filled markers while the ECP calculations have a dotted line connecting the same marker types but empty. The bold numbers refer to the numerical order of the bond types at the equilibrium bond length.

All kinetic energy curves were scaled by adding the difference between the DZV and ECP basis calculations to each ECP kinetic energy. This scaling is seen graphically by comparing the a and b plots of the total kinetic energy in FIGURE D.1 and FIGURE D.2. For briefness, we chose not to show the pre-scaled set of graphs for the component kinetic energy figures.

In all graphs there is a difference between the two basis set treatments (DZV verses ECP). This is expected due to the fact that the DZV basis describes the molecule more fully
while the ECP eliminates the core electrons, therefore affecting the potential.

Aside from this qualitative difference, all graphs indicate good trend agreement between the ECP and DZV basis calculations. The only notable exception is the low lying $1\sigma_g$ and $1\sigma_u$ molecular orbitals. These orbitals are mainly composed of $s$ character. The deviation is attributed to the fact that these molecular orbitals because of their $s$ character, are the closest to the ECP approximation and are affected the greatest out of all the molecular orbitals.

D. CONCLUSIONS

We have successfully implemented the new kinetic energy code for $F_2$ and found some deviations of the orbitals close in proximity to the ECP core. The trends in these low lying orbitals are of little importance because we chose them to be frozen in all our upper level calculations.

Differences between the ECP and DZV can be rectified with an additive constant that scales the kinetic energy curves. What is important in our analysis are the trends in the kinetic energies which affect the bonding. Our inability to quantify the differences only limits us in detailing quantitative contributions from each orbital. What remains is a qualitative analysis which leads to insights about the
chemical bonding of the subject under investigation, XeF₂.
FIGURE D.1a: A sigma orbital kinetic energy comparison of an ECP vs. DZV basis on F$_2$.
FIGURE D.1b: A scaled sigma orbital kinetic energy comparison of an ECP vs. DZV basis on $F_2$. 

KINETIC ENERGY (a.u.)

INTERNUCLEAR SEPARATION (Angs.)

- 1s-g
- 1s-g(AE)
- 1s-u
- 1s-u(AE)
- 2s-g
- 2s-g(AE)
FIGURE D.2b: A scaled pi orbital kinetic energy comparison of an ECP vs. DZV basis on $F_2$. 

KINETIC ENERGY (a.u.) vs. INTERNUCLEAR SEPARATION (Angs.) 

- 1p-u 
- 1p-u(AE) 
- 1p-g 
- 1p-g(AE) 

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FIGURE D.3a: A scaled sigma orbital x component kinetic energy comparison of an ECP vs. DZV basis on $F_2$. 
FIGURE D.3b: A scaled sigma orbital y component kinetic energy comparison of an ECP vs. DZV basis on $F_2$.
FIGURE D.3c: A scaled sigma orbital z component kinetic energy comparison of an ECP vs. DZV basis on F₂
FIGURE D.4a: A scaled pi orbital x component kinetic energy comparison of an ECP vs. DZV basis on F₂
FIGURE D.4b: A scaled pi orbital y component kinetic energy comparison of an ECP vs. DZV basis on $F_2$. 
FIGURE D.4c: A scaled pi orbital z component kinetic energy comparison of an ECP vs. DZV basis on F₂
APPENDIX E:  
ATOMIC ORBITAL CONTRIBUTIONS IN XeF$_2$

A. ORGANIZATION

This appendix provides the reader with the atomic orbital contribution coefficients for the eleven occupied and first unoccupied molecular in XeF$_2$. This data is summarized in TABLE E.1.

The molecular orbital type and equilibrium bond length order number are across the top of the chart. Down the left side of the chart are various internuclear separation values where each atomic orbital contribution was examined.
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</tr>
</tbody>
</table>

**TABLE E.1:** Atomic orbital contributions to each molecular orbital over a series of internuclear separations.
VITA

Michael Fiore Amendola

Born in Richmond, Virginia, July 29, 1972. Graduated from Douglas S. Freeman High School in that city, June 1991. Earned a Bachelor of Science with a concentration in chemistry from the College of William and Mary, May 1995. Master of Arts candidate, the College of William and Mary, August 1995-August 1996. The course requirements and thesis have been completed.