1995

Theoretical Studies of Sodium Metal Clusters.

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THEORETICAL STUDIES OF SODIUM METAL CLUSTERS

A Dissertation

Submitted to the Graduate Faculty of
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Melissa R. Prince
B.S. Mathematics-Chemistry, Texas Lutheran College, 1989
August 1995
To my Parents Jimmie and Sylvia

To my Husband Philippe
ACKNOWLEDGMENTS

I would like to thank Professor Randall W. Hall for his help and guidance. He has always been there to provide ideas, encouragement, and enthusiasm.

I could not have attained this goal without the love and support of my husband Philippe and my parents. I would also like to thank my friends in Louisiana, especially Professor and Mrs. George Stanley, Dr. Melinda Oliver, and Carol Blanchard for their support and understanding.

I wish to express my gratitude to the faculty, staff, and graduate students in the Chemistry Department at LSU. In particular, I want to thank Professor George Stanley for his valuable assistance with my general exam and for his help making some of the figures for this document. I also want to thank the LSU Alumni Association for its financial support.
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ABSTRACT

Theoretical methods were used to study small sodium metal clusters. The goal was to find a simple way to model the electronic structure in these clusters that can be used to study large sodium clusters. Monte Carlo studies using Feynman's path integral formulation of quantum mechanics with Bose-Einstein statistics were used to study sodium metal clusters whose valence electrons with opposite spins were paired as bosons. Next, non-atom-based Gaussian s orbitals were used in a Hartree-Fock Monte Carlo procedure. Based on these results, standard quantum chemistry programs were used to test the utility of using non-atom-based basis sets made up of both s and p Gaussian functions to represent the valence electron density in sodium clusters. The Hartree-Fock Monte Carlo procedure was then modified to include Gaussian p functions in addition to the Gaussian s functions. Neutral and cationic clusters with three to six and eight atoms were studied to determine the geometries of the most stable isomers, the correlated energies, and the ionization potentials. Geometries were compared with published geometries and the ionization potentials were compared with experimental and theoretical ionization potentials. The small, non-atom-based basis set was found to be successful in modeling the electronic structure of small sodium metal clusters, and it is applicable to large sodium clusters and other metal systems.
CHAPTER I: BACKGROUND

I.1. INTRODUCTION.

Alkali metal clusters have been widely studied by theorists and experimentalists for a variety of fundamental reasons. Of primary importance is the intermediate role the physics underlying these clusters plays between atomic physics and condensed matter physics; clusters are a bridge between atoms and solids. By studying the evolution of various properties as a function of cluster size, one can gain insight into the physics of poorly understood phenomena such as the insulator-metal transition associated with the Mott transition. Examining how the electronic structure changes as the size of the cluster increases is especially interesting since the electronic states of these clusters are expected to evolve from being localized to being delocalized in nature.

I.2. EXPERIMENTAL STUDIES.

Experiments on sodium clusters have determined the existence of "magic" cluster sizes. Mass spectra were obtained on sodium clusters ranging in size from 1 to 600. Peaks for certain masses were noticeably large and therefore certain cluster sizes were particularly abundant. The large peaks correspond to clusters with \( N = 2, 8, 20, 40, 58, 92, 138, 260, 344, 440, \) and 558. These clusters are referred to as "magic" clusters because they appear to be particularly stable compared to neighboring cluster sizes. The abundance of certain clusters is thought to be due to thermodynamic stability rather than a product of some experimental condition because the same dominant cluster sizes appear in the spectra of different alkali metals as well as mixtures of alkali metals and under very different experimental conditions. There are two possible explanations for the added stability. The first is the geometric packing of the cluster which can be thought of as highly symmetric dense packing of hard spheres. The expected sizes from this approach \((13, 19, 25, 55, 71, 87, 147, \ldots)\), in which stability is gained by optimizing the geometric structure, do not agree with the experimental
"magic" cluster sizes for sodium. Geometric packing, which explains magic cluster sizes for some systems such as the rare gas xenon, would be important if the valence electrons were more or less localized on individual atoms or bonds.\textsuperscript{12}

I.3. \textsc{Jellium Model}.

The second explanation for the stabilities of sodium clusters is not due to geometric packing but rather to the electronic structure. The extra stability of certain clusters is due to electronic shell closing, which can be compared to the filling of electronic energy levels at the end of each row in the periodic table. Each of the rare gas elements has a filled electronic level or shell and, therefore, extra stability and low reactivity. This led to the development of a model called the shell or jellium model by Knight, Clemenger, deHeer, Saunders, Chou, and Cohen.\textsuperscript{9} Several groups later expanded on this model.\textsuperscript{12-14}

Knight's group based the jellium model on a series of mass spectra experiments.\textsuperscript{9} In these mass spectra, where the peaks represent cationic clusters, certain peaks are significantly larger than their neighbors. For a cluster with a filled shell, the ionization potential is much larger than the ionization potential for a cluster with a partially filled shell. The shell model is based on the assumption that the electrons are delocalized over the entire cluster. The behavior of these electrons is, as a result, similar to that of the electrons in a metal.

Knight's group also did calculations on alkali metal clusters using the jellium shell model to support and explain their experimental results.\textsuperscript{12} Shell structure is a concept that results from thinking about the cluster minus the valence electrons as a spherically symmetric positive charge distribution or jellium. If the valence electronic problem is solved in a manner similar to the solution of the hydrogen atom, cluster energy levels and molecular orbitals result. Several of the orbitals are degenerate. Each set of orbitals corresponding to a different energy level is called a shell. The ordering of the shells for sodium and other alkali metals is 1s, 1p, 1d, 2s, 1f, 2p, etc., where the notation is from
nuclear physics. Therefore, a shell is filled at clusters with 2, 8, 18, 20, 34, 40, etc. atoms, respectively. The idea that it is the shell structure which determines cluster stability indicates that the electronic structure is the driving force in determining the cluster geometry. This has led to intense study of the motion of the delocalized valence electrons in the mean field created by the ions. Before that, aside from some studies using classical methods, one either studied very small metal clusters, consisting of only a few atoms using quantum chemistry and molecular physics, or one studied large clusters, large enough to possess properties of the bulk metal, using solid-state and statistical physics which take advantage of the periodic nature of the bulk.

The jellium model consists of a Hamiltonian which treats the valence electrons in the usual manner but replaces the ionic cores with uniformly positively charged backgrounds. Thus, the valence electron density is given in terms of single-particle wave functions extending over the entire cluster. The electronic Hamiltonian can then be solved to determine the electronic states self-consistently using the local-spin density (LSD) version of density functional theory in the simple spherical jellium model or can be modified to treat non-spherical, deformed jellium cases.

In general, metal clusters provide us with a valuable tool for studying the properties of finite fermion systems ranging in size from atomic to mesoscopic. The jellium model has enjoyed tremendous success. Its simplicity allows it to be applied to very large systems (1000's of atoms) while maintaining the self-consistent microscopic description of the average field felt by the valence electrons. A major drawback with the jellium model is the nearly complete neglect of ionic structure. In order for the model to describe a system accurately, two conditions need to be met. The valence electrons must be strongly delocalized as is the case when the metal is a good conductor, and they must have s-wave character with respect to the ionic cores so there is no directionality to the binding, and therefore, the ionic cores can adjust their positions easily in response to perturbations of the single particle energies.
The clusters are assumed to gain stability as each electronic shell is filled, thus predicting the "magic" cluster sizes. This model presents a simple picture of the electrons in alkali metal clusters such as sodium. The success of the shell model in predicting stable cluster sizes suggests that it should be possible to develop a model that gives us a simple and accurate picture of the electronic structure of these clusters.

1.4. *Ab Initio* Quantum Chemistry Studies.

Besides the experimental and jellium work, much theoretical work has been done on sodium metal clusters. Extensive *ab initio* quantum chemistry calculations have been done on small sodium clusters (up to Na₉). These studies usually involve doing geometry optimizations at the Hartree-Fock (HF) level of theory. Correlated energies of the HF optimized structures are obtained using *ab initio* Hartree-Fock configuration interaction (HF-CI) procedures. These methods are restricted in their ability to find low energy isomers. Isomers of different symmetries are found, and then they are optimized at the HF level. The CI correlated energy is obtained on each HF optimized isomer. For clusters with more than a few atoms, this is a time consuming process because each calculation is long and there are many isomers to consider. The main advantage of these methods is that they are reliable for distinguishing between different isomers to determine the minimum energy geometry. These calculations are done at 0 K so there are no effects of temperature on the system.

For sodium clusters, the number of electrons \(N_e\) is 11 per atom making all-electron calculations difficult so "valence-only" effective-core potentials (ECP) are used to study clusters with several atoms. The optimized structures obtained for neutral clusters using these methods, the all-electron and the ECP, include: a \(C_{2v}\) triangle for Na₃, a \(D_{2h}\) rhombus for Na₄, a \(C_{2v}\) planar structure for Na₅, a \(D_{3h}\) planar triangular structure for Na₆, a \(D_{5h}\) pentagonal bipyramidal structure for Na₇, a tetrahedral (\(T_d\)) structure for Na₈, and a \(C_5\) bicapped pentagonal bipyramidal structure for Na₉. For the cationic clusters, the minimum energy isomers are: a \(D_{3h}\) triangle for Na₃⁺, a \(C_{2v}\) yield
sign like structure for Na$_4^+$, a D$_{2h}$ planar bow-tie structure for Na$_5^+$, a C$_5$ tent-like structure for Na$_6^+$, a D$_{5h}$ pentagonal bipyramidal structure for Na$_7^+$, a C$_{2v}$ tetrahedral-like structure for Na$_8^+$, and a C$_{2v}$ 3-D structure for Na$_9^+$. These studies have determined that, in general, ionization potentials decrease as a function of cluster size, but there is a strong oscillation between even and odd clusters, higher IP's for even clusters and lower for odd. Also, these studies show a large drop in ionization potential between a magic number cluster and the next larger cluster (e.g., Na$_8$ to Na$_9$). This is due presumably to the extra stability gained by the shell closing. Also, they have concluded that the planarity of the small clusters is due to quasi-Jahn-Teller effects. That is, the clusters have a tendency to avoid electronic structures with only partially filled one-electron levels. Ab initio calculations of the electronic structure of sodium clusters using a Gaussian basis set and a core-valence interaction were done by Spiegelmann et al. They used effective core potentials and polarized atomic orbitals instead of the typical self-consistent-field (SCF) HF molecular orbitals. The geometries of the lowest energy isomers are qualitatively similar to those obtained by Bonacic-Koutecký's group (i.e. they have the same symmetry and shape but slightly different bond lengths).

I.5. DENSITY FUNCTIONAL THEORY AND MOLECULAR DYNAMICS STUDIES.

The local spin density (LSD) version of density functional theory (DFT) can also be used to study the electronic structure of sodium metal clusters. Many groups have calculated electronic properties of sodium clusters using methods based on density functional theory. In density functional theory, the energy is a functional of the electron density as opposed to being obtained from a set of molecular orbitals as it is in ab initio quantum chemistry methods. Most of these studies treat a wide range of cluster sizes (from a few to several hundred atoms). Geometries that are reported agree qualitatively for most cluster sizes with those reported above for the ab initio HF studies.
An extensive \textit{ab initio} molecular dynamics study of neutral clusters of sodium ranging in size from 4-20 atoms was done by Röthlisberger et al. in 1991. This group used the Car-Parrinello method which is a unified density-functional theory and molecular dynamics (MD) approach. They search for the low energy minima on the potential energy surface using a dynamical simulated annealing approach, which is done at finite temperatures (> 0 K) and then study the electronic and structural properties. These studies use only short time dynamics. They usually only calculate a few trajectories of less than 5 picoseconds in length each. Very recently Jellinek performed an \textit{ab initio} Hartree-Fock self-consistent-field molecular dynamics study of the structure and dynamics of the lithium octamer. These studies involve longer times to allow for a more complete dynamical analysis. They have shown that it is possible to provide more detail and completeness than the other MD studies. These studies are at the HF level of theory. They are interested in extending these studies to include correlation effects and in lengthening the simulations so that more quantities can be obtained. This method (\textit{ab initio} HF SCF MD) is not applicable to sodium clusters at this time because of the increased number of electrons per atom, 11 instead of 3.

1.6. HÜCKEL GROWTH METHOD STUDIES.

Recently Poteau et al. have studied Na\textsubscript{n} clusters (n=4-21, 34) using a Hückel model and a Monte Carlo growth method to generate various cluster isomers. This method obtains the same geometrical shapes for Na\textsubscript{3}-Na\textsubscript{9} as the other methods discussed. This method is capable of optimizing large geometries (up to 100 atoms). Geometries obtained can serve as a starting point for the SCF CI calculations. Many clusters can be generated quickly but there is no guarantee that the minimum energy isomer will be found.

1.7. PATH INTEGRAL STUDIES.

Path integral Monte Carlo techniques have been used to study the electronic structure and properties of sodium clusters ranging from 3-6 and 8 atoms. In these
studies, core electrons are treated using an effective pseudopotential. The important advantages of this method are that these calculations are done at finite temperatures, allowing for cluster vibrations and that they include electron correlation, so the geometries obtained are due to the correlated electron density. The geometries obtained in these path integral studies also agree qualitatively with \textit{ab initio} HF and DFT studies. However, due to the correlated electrons, some localization of the electron density is seen. Electrons pair up in the centers of triangles formed by three atoms in the planar clusters (up to Na\textsubscript{6}) and in the centers of tetrahedra formed by four atoms in Na\textsubscript{8}.

I.8. **Summary.**

It is difficult to study large alkali metal clusters with a high level of theory. Cluster sizes that are interesting from a theoretical standpoint have too many electrons to study using sophisticated quantum chemistry methods. Classical methods have been used and the jellium model has been applied extensively to clusters ranging in size up to 1000's of atoms. Density functional theory and \textit{ab initio} quantum chemistry methods have been used to study small sodium clusters. The knowledge acquired is then used to try to understand larger systems. There is a need for a method that gives precise results like the quantum chemistry but is simple enough computationally so that it can be extended to larger systems than traditional \textit{ab initio} quantum chemistry programs.

I.9. **Overview of Research Project.**

Various theoretical methods were used to investigate the electronic structure of small sodium metal clusters. From previous path integral studies, it is known that valence electrons in sodium clusters pair up in the centers of triangles formed by sets of three sodium atoms in small clusters ranging from 3 to 6 atoms.\textsuperscript{31-32} We wanted to find a way to model these electron pairs to correctly give the electronic structure of small sodium clusters. The goal was to be able to extend our work to larger clusters. Feynman's path integral formulation of quantum mechanics was used and pairs of electrons with opposite spins were treated as bosons so that Bose-Einstein statistics
could be used instead of Fermi-Dirac statistics. The results obtained with the boson model differed slightly from those obtained with the path integral calculations using Fermi-Dirac statistics. The electron pairs were not staying far enough apart. Various attempts were made to make up for this difference between path integral methods by including different forms of an additional repulsive potential to keep the electron pairs farther apart. Eventually, we considered the idea of placing the paired electrons into Gaussian-like orbitals. The positions of these orbitals could be optimized as well as the positions of the sodium centers (nucleus + core electrons). Since the simplest Gaussian function is an s orbital, our first attempt using Gaussian functions involved only s functions. This method gave the desired results for most small clusters with the exception of Na$_7$. For this cluster, we incorrectly obtained a planar geometry. We believed that the Gaussian orbitals consisting only of s functions were too simple to completely and correctly mimic the electronic structure of sodium clusters. We decided to include p functions in the Gaussian-like orbitals to allow for some directionality of bonding. In order to test the validity of this idea, we used standard quantum chemistry programs to develop and test a basis set made up of s and p Gaussian functions.$^{33}$ The basis set was evaluated by comparing calculated values such as ionization potentials and absorption spectra to other published theoretical and experimental values. Good agreement was obtained with a much smaller basis set than typically used in more accurate quantum chemistry studies. This small basis set would allow the study of larger clusters than was previously possible using Monte Carlo path integral simulations. The Hartree-Fock Monte Carlo program using non-atom-centered orbitals with both s and p Gaussian functions has given promising results for small neutral and cationic sodium clusters (Na$_4$-Na$_8$). For Na$_5^+$ and Na$_6^+$, new isomers were found and they were shown to be lower in energy than the lowest energy isomers reported in the literature. For Na$_7$, Na$_7^+$, and Na$_8^+$, more work needs to be done and is currently in progress.
REFERENCES.


II.1. FEYNMAN'S PATH INTEGRAL FORMULATION OF QUANTUM MECHANICS.

Our path integral method is based on Feynman's path integral formulation of quantum mechanics. The path integral treatment offers several advantages. It uses a complete basis set, it is done at finite temperatures, and it includes an exact treatment of correlation.

The density operator for the canonical ensemble is $e^{-\beta H}$. $H$ is the Hamiltonian and for a system with $N$ electrons is written:

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + V(r_i^N),$$

where $\nabla^2$ is the Laplacian and $V(r^N)$ is the potential energy, and $\beta=1/kT$ where $k$ is Boltzmann's constant and $T$ is the temperature in Kelvin. The elements of the density matrix, $\rho$, are defined as:

$$\rho(t_1^N, r_2^N; \beta) = \langle r_1^N | e^{-\beta H} | r_2^N \rangle,$$

and the partition function $Q$ is defined as the trace of the density matrix. That is,

$$Q = \text{Tr}(e^{-\beta H}) = \sum_i \langle \psi_i | e^{-\beta H} | \psi_i \rangle = \sum_i e^{-\beta E_i}.$$  

This last equality is true if $|\psi_i\rangle$ are eigenfunctions of $e^{-\beta H}$.

We do not usually have eigenfunctions of the Hamiltonian, but instead we have another basis set $|j\rangle$. Therefore,

$$Q = \sum_j \langle j | e^{-\beta H} | j \rangle.$$  

Q can also be written as:

$$Q = \sum_j \rho_{jj}, \text{ where } \rho_{jj} = \langle i | e^{-\beta H} | j \rangle.$$  

Therefore, we can write

$$Q = \text{Tr}(\rho).$$  

12
Since the trace is invariant to the basis set, we can express $Q$ using the position basis set $|r_1^N\rangle$ which is complete and continuous. Therefore, the path integral treatment is exact and

$$Q = \int dr_1^N \langle r_1^N | e^{-\beta H} | r_1^N \rangle,$$  \hspace{1cm} (7)

where $N$ is the number of particles or electrons being treated by the path integral and each $r_1$ is a vector representing the coordinates of a particle. In this continuous representation, the partition function is expressed as an integral rather than a sum. Therefore,

$$Q = \int dr_1^N \langle r_1^N | e^{-\beta H} | r_1^N \rangle \equiv \int dr_1^N \rho(r_1^N, r_1^N; \beta).$$  \hspace{1cm} (8)

For large temperatures ($T$) or small $\beta$ ($\beta = 1/kT$), we can make a semiclassical approximation. By dividing and multiplying the exponent in $Q$ by a factor of $P$, we can make $\beta$ as small as we want. Thus,

$$Q = \int dr_1^N \langle r_1^N | e^{-\beta H/P} | r_1^N \rangle.$$

Expanding the exponential into a product of $P$ exponentials gives the Trotter product formula:

$$Q = \int dr_1^N \langle r_1^N | e^{-\epsilon H} e^{-\epsilon H} \ldots e^{-\epsilon H} | r_1^N \rangle,$$  \hspace{1cm} (10)

where $\epsilon = \beta/P = 1/kTP$. We can now insert a complete set of states

$$\hat{1} = \int dr_2^N \langle r_2^N | r_2^N \rangle$$  \hspace{1cm} (11)

between each of the terms in the Trotter product obtaining

$$Q = \int dr_1^N dr_2^N \ldots dr_p^N \langle r_1^N | e^{-\epsilon H} | r_2^N \rangle \langle r_2^N | e^{-\epsilon H} | r_3^N \rangle \ldots \langle r_p^N | e^{-\epsilon H} | r_1^N \rangle.$$

This is a $3PN$-dimensional integral. We need to know what $\langle r_1^N | e^{-\epsilon H} | r_2^N \rangle$ is for each of the terms when $\epsilon$ is small. Using a Taylor series expansion, we can write

$$e^{-\epsilon H} = 1 - \epsilon H + \frac{\epsilon^2}{2!} H^2 - \frac{\epsilon^3}{3!} H^3 + \ldots.$$
Substituting this approximation of $e^{-el}$ into the equation for each $p$ gives

$$\rho(r_1^N, r_2^N; \varepsilon) = \langle r_1^N | e^{-eV/2} e^{-eV/2} | r_2^N \rangle + \theta(\varepsilon^2).$$

(14)

Operating with the potential terms on the basis functions $\{|r^N\rangle\}$ gives

$$\rho(r_1^N, r_2^N; \varepsilon) = \langle e^{-eV/2} r_1^N | e^{-eV/2} r_2^N \rangle = e^{-e^2/N} e^{-e^2/N}\langle r_1^N | e^{-eV} | r_2^N \rangle.$$  

(15)

Thus, we need to know $\langle r_1^N | e^{-eV} | r_2^N \rangle$. By inserting a complete set of momentum states

$$\hat{\rho} = \int \frac{dk^N}{(2\pi)^N} \langle k^N \rangle \langle k^N \rangle,$$

(16)

our equation becomes

$$\langle r_1^N | e^{-eV} | r_2^N \rangle = \int \frac{dk^N}{(2\pi)^N} \langle r_1^N | e^{-eV} | k^N \rangle \langle k^N | r_2^N \rangle.$$  

(17)

Operating on $\langle k^N \rangle$ with $e^{-eV}$ gives

$$\langle r_1^N | e^{-eV} | r_2^N \rangle = \int \frac{dk^N}{(2\pi)^N} e^{-\frac{e^2}{2m} k^N} \langle r_1^N | k^N \rangle \langle k^N | r_2^N \rangle = e^{-\frac{e^2}{2m} \sum k^N} \langle r_1^N | e^{-eV} | r_2^N \rangle.$$  

(18)

After integrating, we obtain

$$\langle r_1^N | e^{-eV} | r_2^N \rangle = \frac{1}{(2\pi)^N} \left( \frac{2\pi m}{\hbar^2} \right)^{-\frac{N}{2}} \sum_{k} e^{\frac{-k^2}{2m^{\frac{1}{2}}}}.$$  

(19)

Finally we set $\hbar = 1$ and $m = 1$ to obtain

$$\langle r_1^N | e^{-eV} | r_2^N \rangle = \frac{1}{(2\pi)^N} \left( \frac{2\pi}{\hbar^2} \right)^{-\frac{N}{2}} \sum_{k} e^{\frac{-k^2}{2m^{\frac{1}{2}}}}.$$  

(20)

Substituting into equation (15), we obtain

$$\rho(r_1^N, r_2^N; \varepsilon) = \frac{1}{(2\pi)^N} \left( \frac{2\pi}{\hbar^2} \right)^{-\frac{N}{2}} e^{-e/2N} e^{-e/2N} \sum_{k} e^{\frac{-k^2}{2m^{\frac{1}{2}}}}.$$  

(21)
And finally, the partition function is given by:

\[ Q = \int dr_1^N dr_2^N \cdots dr_p^N \frac{1}{(2\pi\epsilon)^{3N/2}} e^{-\frac{1}{\epsilon} \sum_{m=1}^{p} V(r_m^N)} e^{-\frac{1}{2\epsilon} \sum_{m=1}^{p} \sum_{a=1}^{N} (r_m^a - r_{m1}^a)^2} \text{, with } r_{p+1}^a = r_1^a. \] (22)

In general if the particles being treated are indistinguishable, all possible permutations of the particles have to be considered. That is we have to allow for exchange of the particles. So the Fermi density matrix is written

\[ \tilde{\rho}(r_1^N, r_2^N; \epsilon) = \frac{1}{N!} \sum_{\rho} (-1)^{\rho} \rho(r_1^N, \rho(r_2^N); \epsilon). \] (23)

where \( \rho \) is from Eq. 21, the sum is over all possible permutations and \( \rho(r_2^N) \) is a permutation of \( r_2^N \). Therefore, the partition function with exchange is:

\[ Q = \int dr_1^N dr_2^N \cdots dr_p^N \tilde{\rho}(r_1^N, r_2^N; \epsilon) \tilde{\rho}(r_2^N, r_3^N; \epsilon) \cdots \tilde{\rho}(r_p^N, r_1^N; \epsilon). \] (24)

II.2. \textit{Ab Initio} Quantum Chemistry Method.

Precise quantitative results can be obtained using quantum chemistry. The simple picture of electrons occupying orbitals provides the basis for the Hartree-Fock (HF) approximation. HF theory provides the starting point for most of the more advanced quantum chemistry techniques. The HF method involves solving the Schrödinger equation (Eq. 25) self-consistently where \( H \) is the Hamiltonian, \( \psi \) is the wave function, and \( \epsilon \) is the energy.

\[ H\psi = \epsilon\psi \] (25)

The Hamiltonian (Eq. 26), expressed in atomic units, consists of terms representing the kinetic energy operator for the electrons, the kinetic energy operator for the nuclei, the Coulomb attraction between the electrons and the nuclei, the Coulomb repulsion between the electrons, and the Coulomb repulsion between the nuclei.

\[ H = \sum_{i=1}^{N} \frac{\nabla_i^2}{2} + \sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \] (26)
By applying the Born-Oppenheimer approximation, we can eliminate the second term in the Hamiltonian, corresponding to the kinetic energy of the nuclei, and replace the fifth term, corresponding to the Coulomb repulsion between nuclei, with a constant. Thus, the electronic Hamiltonian (Eq. 27) which describes the motion of the N electrons in the constant field of M point charges is written:

\[ H = - \sum_{i=1}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{iA}}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}. \]  

(27)

The total energy (Eq. 28) of the system is therefore the sum of the electronic energy and the energy due to the repulsion of the nuclei.

\[ E_{\text{tot}} = E_{\text{elec}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{AA}Z_{BB}}{R_{AB}}. \]  

(28)

*Ab initio* programs, such as Gaussian 92, GAMESS, and MOLCAS, calculate the self-consistent-field (SCF) molecular wave function. We begin by guessing an antisymmetrized determinant of spin orbitals. We improve these orbital guesses, associated with each of the electrons, simultaneously, until no further improvement is obtained (i.e. self-consistency is reached). The resulting wave function is called the SCF wave function. Roothaan proposed in 1951 that Hartree-Fock (HF) orbitals can be represented as linear combinations of a complete set of functions called basis functions. In practice, we must use a finite number of basis functions. A common choice is a set of Gaussian orbitals.

In order to obtain more accurate energies, the instantaneous correlation between the electrons, especially between electrons of opposite spin, must be fully taken into account. One way to do this is called configuration interaction (CI), which can be performed in several ways. The most accurate way involves doing full CI in which the wavefunction \( \psi \) is written as a linear combination of not only the HF (ground state) determinant but also all the possible substituted (excited state) determinants. The HF determinant is made up of all the occupied orbitals while the substituted determinants are
obtained by replacing one or more of the occupied orbitals in the HF determinant with an unoccupied virtual orbital.

In quantum mechanics it is possible for any state to exist, requiring full CI to be done. However, it is impossible to solve the resulting determinantal equations for systems of any but the smallest size. Fortunately, the majority of the wave function can be accounted for by doing what is called limited configuration interaction. In limited CI, only the most important excited state configuration functions are considered. Most routines consider single and double excitations, but higher excitations including triples and even quadruples can be mixed into the wave function as well. A single excitation is one in which an electron from an occupied orbital is excited to an unoccupied virtual orbital. A double excitation involves moving two electrons to virtual orbitals, a triple involves moving three and so on. Thus, the CI wave function (Eq. 29) is expressed as a linear combination of many important HF states.

$$\psi = \sum_i c_i \varphi_i$$  \hspace{1cm} (29)

The $c_i$'s are varied until $\psi$ is minimized (like in the variation method in quantum mechanics). The determinant equation (Eq. 30) must then be solved.

$$\det(H_{ij} - ES_{ij}) = 0$$ \hspace{1cm} (30)

Performing CI considerably improves the wave function, but it is still only as good as the quality of the basis set. Any set of wave functions can be used to obtain the CI energy. Geometry optimizations are typically done at the HF level of theory. CI is then used to find the correlated energy of the HF optimized structure.

II.3. REFERENCES.


CHAPTER III: THEORETICAL MODELS

III.1. INTRODUCTION.

Our studies of sodium metal clusters have focused on determining the electronic structure as a function of cluster size. The valence electronic structure is especially important, and we have made various attempts at developing a model that is simple enough so that it is computationally feasible for larger sodium clusters (Na\textsubscript{9}-Na\textsubscript{30}) yet sophisticated enough so that it correctly determines quantities, such as the minimum geometry, vertical and adiabatic ionization potentials, and electron affinities.

Path integral calculations have shown that neutral sodium clusters are planar up to six atoms, while eight atom sodium clusters have a three-dimensional structure.\textsuperscript{39-41} In the planar structures, the valence electrons are paired in the centers of triangles while in the 3-D structure for Na\textsubscript{8} the electrons are paired in the centers of tetrahedra. Figure III.1. shows the dominant correlated electronic configurations as seen from the path integral studies.\textsuperscript{39-41} Note the locations of the electron pairs in the centers of triangles and tetrahedra.

Despite the success of the path integral studies for these small clusters, there are problems associated with them that make it difficult to extend the path integral approach to clusters larger than Na\textsubscript{8}. Most of the difficulty comes from the difficulty in treating fermions. Large error bars occur when using Fermi-Dirac statistics because of the large cancellations between negative and positive regions of the probability density wave functions. Fermi-Dirac statistics involve using a wave function that is anti-symmetric with respect to exchange. This problem can be overcome,\textsuperscript{42} but it is difficult to distinguish close energy isomers such as those for Na\textsubscript{7} because the path integral calculations take a long time to converge. The location of electron pairs seen in the path integral studies\textsuperscript{39-41} suggests that a model to study sodium clusters should allow for this valence electron density to be in areas between atoms.
Figure III.1. Dominant valence electron configurations as determined from path integral Monte Carlo calculations.
III.2. **Boson Model.**

We have made several attempts to develop a model to treat sodium clusters that is simple enough so that the calculations can be done quickly yet sophisticated enough so that it will give the correct electronic structure. Our first attempt was the boson model. In it, we paired two electrons, which are fermions, with opposite spin as one boson. This was accomplished by trapping the paired electrons within a certain distance of each other to make bosons. Because we are using a model boson Hamiltonian and Bose-Einstein statistics, the difficulties involved in doing path integrals on problems governed by Fermi statistics that occur when treating exchange due to the anti-symmetry of the wave function have been eliminated. The boson wave function is symmetric with respect to exchange so there are no negative weights to cause problems as there are in Fermi-Dirac statistics. This method did not give the correct geometry for Na$_4$ which is a D$_{2h}$ rhombus. Rather than favoring the planar structure, the model predicted that the most stable isomer for Na$_4$ is a 3-D tetrahedral structure. The tetrahedron is the structure expected when close packing is the dominant factor in determining the optimum geometry. Jahn-Teller effects prevent the close-packed tetrahedron and force the planar rhombus. Jahn-Teller distortions occur in systems with partially filled shells and degenerate one-electron energy levels. These distortions lower the symmetry of the system and thereby remove the degeneracy. Distortions cannot occur in closed systems (e.g. Na$_8$) because all the degenerate levels are filled. In order to determine why the tetrahedral structure is preferred over the planar one in the boson model and find out what is missing from our boson Hamiltonian that is present in the exact path integral method, we looked at the difference in radial distribution functions between the correct path integral Monte Carlo results and the boson results. Radial distribution functions are plots showing the distribution of electron-electron distances.$^{40}$ As can be seen in the radial distribution plot shown in Figure III.2., the potential between like-spin electrons for the boson case is not as repulsive as it is in the path integral one, i.e., the electron
pairs are getting too close and the planar structure is not favored over the tetrahedral one.

![Figure III.2](image)

**Figure III.2.** Plot of electron-electron distance distribution from the boson studies and the path integral studies.

We have tried many different ways of correcting the potential between like-spin electrons. One such attempt was to introduce an effective attraction between electrons paired as bosons. Another attempt was using various forms of what we refer to as like-spin electron repulsive potentials (lerpots), such as linear potentials, step potentials, and infinitely repulsive potentials to introduce an effective repulsion between like-spin electrons. We also tried fitting the differences in radial distribution functions for Na$_4$ and Na$_6$ to logarithmic functions of the form $c \ln(1.-\exp(br^2)) - a$, where $a$, $b$, and $c$ are the
fitting parameters and \( r \) is the distance between electrons. Eventually a form of an infinitely repulsive potential in which the center of mass of like-spin electrons are prevented from getting within 6.5 au of each other \( (V(r)=0, \ r \geq 6.5; \ V(r)=\infty, \ r < 6.5) \) was found that gave the correct geometry (a planar \( D_{2h} \) rhombus) for \( \text{Na}_4 \) but failed when extended to \( \text{Na}_6 \).

III.3. NON-ATOM-BASED GAUSSIAN S ORBITALS.

These results prompted us to change the approach of our research. We abandoned the boson idea and proceeded to search for the best form of a non-atom-based Gaussian s orbital to represent the valence electron density. A non-atom-based orbital is an orbital that is placed at a single site in the space between atoms rather than on atoms. It allows some of the electron density to be centered at sites other than atomic sites. After solving the necessary one- and two-electron integrals analytically using the Gaussian s functions, a Hartree-Fock Monte Carlo program was written to solve the self-consistent-field (SCF) wave function. Calculations were done on the \( \text{Na}_2 \)-\( \text{Na}_8 \) neutral clusters as well as the corresponding cationic and anionic clusters. During the Monte Carlo calculations, both the nuclei and the Gaussian s orbitals were allowed to move.

Most of the results (geometries and energies) for these clusters were qualitatively correct, but some difficulties occurred with the geometry of \( \text{Na}_7 \) and with the anions. Shown in Figures III.3.-III.9. are the average structures obtained for the neutral Na clusters with 2-8 atoms from the Monte Carlo Hartree-Fock simulations using Gaussian s orbitals at the NAB sites. The bond lengths are given in au where \( 1 \text{ au} = 0.5292 \ \text{Å} \). The minimum structure obtained for \( \text{Na}_7 \) should have been pentagonal bipyramidal instead of planar. SCF energies (au) were obtained in 2000 pass Monte Carlo Hartree-Fock simulations with \( \beta = 2000 \) \( (T \approx 150 \text{ K}) \) for the following clusters: \( \text{Na}_4, E=-0.6899; \text{Na}_5, E=-0.8622; \text{Na}_6, E=-1.0524; \) and \( \text{Na}_8, E=-1.4147 \).
Figure III.3. The structure of Na$_2$ obtained using s Gaussian functions at the NAB sites, which are denoted by X.

Figure III.4. The structure of Na$_3$ obtained using s Gaussian functions at the NAB sites, which are denoted by X.

Figure III.5. The average optimized structure of Na$_4$ obtained using s Gaussian functions at the NAB sites, which are denoted by X.

Figure III.6. The average optimized structure of Na$_5$ obtained using s Gaussian functions at the NAB sites, which are denoted by X.
Figure III.7. The average optimized structure of Na$_6$ obtained using $s$ Gaussian functions at the NAB sites, which are denoted by X.

Figure III.8. The structure of Na$_7$ obtained using $s$ Gaussian functions at the NAB sites, which are denoted by X.
Figure III.9. The average optimized structure of Na₈ obtained using s Gaussian functions at the NAB sites, which are denoted by X.

The anionic cluster energies were higher (less stable) than the corresponding neutral cluster energies. Thus, the extra electron on the cluster was not bound. These results suggested the need for some p-like character in our shell orbitals because the s-like character of the orbital was inadequate to represent the directional nature of the bonding. Adding orbitals with higher angular momentum than required to treat the ground state of a sodium atom, allows the molecular orbitals of the cluster to take on a different shape which may be necessary to properly describe other states of the cluster such as an excited state or an ionic state. The orbitals in clusters do not necessarily hybridize. The molecular orbitals may be s-like or p-like with little or no mixing. The problem with the anion indicates that diffuse functions may also be necessary because they would allow the orbitals to increase in size so that the extra electronic charge can extend farther into space. Diffuse functions are usually added to the basis sets when using standard \textit{ab initio} quantum chemistry programs to do calculations involving anions.

III.4. REFERENCES.


CHAPTER IV: NON-ATOM-BASED ORBITAL BASIS SET

IV.1. NAB BASIS SET DEVELOPMENT.

Based on the partial success of our Monte Carlo calculations using non-atom-based (NAB) s Gaussian functions, we wanted to test the validity of using NAB s and p Gaussian functions. In doing so, we could also determine the best values for the exponents of the s and p Gaussian functions which make up the NAB Gaussian orbitals that would correctly model the valence electron density of the sodium clusters. To accomplish this, we used standard quantum chemistry programming packages including GAMESS, Gaussian 92, and MOLCAS and performed all-electron calculations. These are ab initio methods in which the self-consistent-field (SCF) wave function is obtained at the Hartree-Fock (HF) level of theory. Configuration interaction (CI) was done to include the effects of electron correlation. Electron correlation is needed to get a good value for the energy of sodium clusters.

Two basis sets were used in our calculations. To develop our basis set, we started with the basis set B (13s8p1d) of Bonacic-Koutecký et al. which will be referred to as the B1 basis set. We used GAMESS to test and perturb this basis set in an effort to determine which orbitals accounted for different aspects of the electron density. We ran a series of calculations on the Na\textsubscript{4} cluster removing various orbitals from the basis set and adding others to determine the importance and role of each basis function. We saw that three s functions and two sets of p functions were responsible for the valence electron density as well as one set of d functions. The d orbital was found to only be necessary to achieve quantitative agreement with experiment so it was removed to speed up the calculations. The basis set B1 without the d orbital will be referred to as the B2 basis set.

By determining which orbitals were responsible for the valence electron density, we could begin to develop and test a basis set made up of NAB Gaussian functions. The
set of Gaussian functions placed at a single site in place will be referred to as a NAB group. As a first guess, these NAB groups were placed at the same locations as the pairs of electrons seen in our earlier path integral calculations.\textsuperscript{47-49} To obtain this basis set, we started with the B2 basis set and modified it by removing the s and p orbitals, (s(0.024617), s(0.010), p(0.060), and p(0.020)), which account for most of the valence electron density from the atoms and placing them at the sites of our non-atom-centered groups. An additional s and set of p functions were also placed at each of the non-atom-centered group sites. The exponents of these functions were optimized using GAMESS for Na\textsubscript{4} and Na\textsubscript{6} and were found to be s(0.065) and p(0.040). One s orbital, s(0.058065), was left on each atom to account for electron density remaining on the atoms. The molecular orbitals obtained were shown to have only minor contributions from this orbital. In Na\textsubscript{4}, the largest contribution from any atom-based s orbital was 7.0%. This new basis set with both atom-based and non-atom-based functions will be known as the non-atom-based (NAB) basis set. The NAB basis set contains fewer basis functions than the B2 basis set as shown in Table IV.1.

IV.2. GEOMETRY OPTIMIZATION PROCEDURE.

We used the following procedure to optimize the exponents and geometries of the neutral four and five atom clusters. The geometries of these clusters were optimized at the SCF level with GAMESS\textsuperscript{43} using the B2 basis set. The optimizations were done using the B2 basis set to ensure that any lowering of energy obtained was due entirely to the change in basis set. As a check, optimizations using the NAB basis were done on the smaller clusters (Na\textsubscript{4} and Na\textsubscript{5}) and similar structures were obtained. The geometries were the same, but the bond distances differed slightly. Initial NAB group positions were chosen to be the centers of triangles, based on previous path integral calculations.\textsuperscript{48} The exponents of the added s and p orbitals were optimized using the TRUDGE algorithm included with the GAMESS quantum chemistry package. Next, the positions of the NAB groups were optimized at the SCF level using the scan option in Gaussian 90.\textsuperscript{50}
Table IV.1. QCISD(T) Energies (au) for Na Clusters at their Optimized Neutral and Cationic Geometries Obtained with the NAB and B2 Basis Sets. \(N_{\text{val}}\) is the Number of Valence Basis Functions and \(N_{\text{group}}\) is the Number of NAB Groups.

<table>
<thead>
<tr>
<th></th>
<th>QCISD(T) NAB basis</th>
<th>(N_{\text{val}}) ((N_{\text{group}}))</th>
<th>QCISD(T) B2 basis</th>
<th>(N_{\text{val}})</th>
<th>Energy Difference QCISD(T) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutral</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
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<td>-647.4342</td>
<td>36</td>
<td>2.89</td>
</tr>
<tr>
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<td>7.09</td>
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</table>

The collection of NAB orbitals at each spatial location (a single NAB group) was moved together. The SCF energy was insensitive to small changes in the positions of the NAB groups, so further optimization was performed at the QCISD(T) level. For Na₄, NAB group positions moved 0.57 au farther away from the center of the cluster as a result of this higher level of optimization. While this is a large difference for nuclei to move in an atom-based orbital optimization, this difference is relatively small on the scale of the bond lengths and may just be a reflection of not optimizing all the exponents of the NAB groups, but just the extra s and p orbital exponents (see below). As a check for consistency, the exponents were again optimized at the SCF level using the TRUDGE algorithm in GAMESS, but only a very small improvement in energy resulted. A full
geometry optimization including sodium atoms and NAB groups at the SCF level for \( \text{Na}_4 \) with the NAB basis led to insignificant changes in atom positions. A similar procedure was followed for the sodium pentamer with three NAB groups, each located at the center of one of the three triangles shown in Figure IV.1. The optimized s and p exponents of the extra s and p orbitals of the NAB groups for the \( \text{Na}_4 \) and \( \text{Na}_5 \) CI optimized cluster geometries were similar so we set them to \( s(0.065) \) and \( p(0.040) \) for all calculations using the NAB basis set.

We used these optimized exponents and the optimized geometries obtained with the B2 basis in our further studies of \( \text{Na}_4, \text{Na}_5, \text{Na}_6, \) and \( \text{Na}_8 \). The NAB group positions were optimized at the SCF level with the scan procedure in Gaussian 90 for \( \text{Na}_6, \text{Na}_8, \text{Na}_4^+, \text{Na}_5^+, \text{Na}_6^+, \) and \( \text{Na}_8^+ \). The NAB orbital positions were varied by hand to determine the minimum QCISD(T) energy. We note that the manual determination of NAB group positions is not essential for studies of larger clusters. In the larger clusters it will be necessary to use methods from statistical mechanics (such as Monte Carlo or molecular dynamics) to properly locate and statistically weight the different isomers that are possible with increasing cluster size. The same statistical procedures can be used to locate the NAB positions without significant additional effort. Figure IV.1. and Figure IV.2. show the optimized locations of the NAB groups.

We judge the two basis sets by comparing the total energies and the ionization potentials of all the clusters as well as the electronic absorption spectrum for the four-atom cluster. If the smaller NAB basis reproduces experimental results as well as the larger B2 basis, then the NAB orbitals can be useful in studying sodium clusters. Vertical and adiabatic ionization potentials for \( \text{Na}_4, \text{Na}_5, \text{Na}_6, \) and \( \text{Na}_8 \) were calculated with Gaussian 90, and the absorption spectrum for \( \text{Na}_4 \) was calculated with MOLCAS.\(^{45}\) Further analysis of the basis sets includes an examination of the molecular orbital coefficients and the Löwdin density; these provide a way to determine the amount of
electron density residing on the NAB groups and, thereby, the physical relevance of these orbitals.

IV.3. RESULTS.

The QCISD(T) energies are shown in Table IV.1. Energies calculated using the NAB basis set are more stable than those calculated using the B2 basis by 2-8 kcal/mol. This is despite having fewer orbitals in the NAB basis than in the B2 basis. For comparison, we note that the original B1 basis used approximately 55% more basis functions than the B2 basis to gain 6-15 kcal/mol in energy\(^46\) relative to the B2 basis. The NAB basis set uses up to 35% fewer basis functions, yet still gains 2-8 kcal/mole in energy relative to the B2 basis. This suggests that the NAB groups provide a representation of the exact electronic structure similar to the larger atom-based B1 and B2 bases. It is also possible that the NAB groups provide some effective d character to the molecular orbitals as they are not located on the atoms. The difference in energies of the B2 and the NAB basis set is not simply a unitary transformation of molecular orbitals; if it were, the energies and other physical properties would be identical when calculated using both basis sets. Note that placing an extra NAB group in the center of each of the Na\(_6\) and Na\(_8\) clusters provides increased stability due to the larger number of basis functions. Still, it is an easy calculation to do, and there are the same or fewer basis functions than with the B2 basis set.

We now examine whether the NAB orbitals are contributing significantly to the total electron density. The results of this analysis are shown in Figure IV.3. and Figure IV.4., where the total valence electron charge density (via Löwdin analysis) is shown for both atoms and NAB groups. As can be seen, a significant amount of the electron density of the valence electrons has moved from the sodium atoms onto the NAB groups. The fraction of the electron density that can be accounted for using the NAB groups ranges from 70-86%, clearly demonstrating the importance of the NAB basis set.
Figure IV.1. The geometries of the Na₄, Na₅, Na₆, and Na₈ neutral clusters optimized at the SCF level using the B2 basis set. The NAB groups are denoted by X. Distances are given in angstroms.
Figure IV.2. The geometries of the Na₄, Na₅, Na₆, and Na₈ cationic clusters optimized at the SCF level using the B2 basis set. The NAB groups are denoted by X. Distances are given in angstroms.
Figure IV.3. The Löwdin electron densities of the atoms and the NAB groups are shown for the Na₄, Na₅, Na₆, and Na₈ neutral clusters. The numbers in parentheses are the Löwdin electron densities for the sodium clusters without NAB groups obtained using the B2 basis.
Figure IV.4. The Löwdin electron densities of the atoms and the NAB groups are shown for the Na₄, Na₅, Na₆, and Na₈ cationic clusters. The numbers in parentheses are the Löwdin electron densities for the sodium clusters without NAB groups obtained using the B2 basis.
The structures of the cations are shown in Figure IV.2, and the energies from the different basis sets are shown in Table IV.1. Note the extra stabilization obtained using the NAB basis set. The vertical and adiabatic ionization potentials are shown in Table IV.2. The ionization potentials obtained with the NAB basis set are similar to those obtained with the B2 basis set. Both the B2 and the NAB basis sets agree qualitatively with experiment, neither demonstrating a better fit. The addition of a fourth or fifth NAB group to the inner triangle of the Na₆ or the inner tetrahedron of the Na₈ cluster, respectively, causes the vertical ionization potential to change by only 0.01 eV.

Table IV.2. Vertical and Adiabatic Ionization Potentials (eV) for Na₄, Na₅, Na₆, and Na₈ Using the NAB and B2 Basis Sets.

<table>
<thead>
<tr>
<th></th>
<th>Vertical IP NAB basis</th>
<th>Vertical IP B2 basis</th>
<th>Adiabatic IP NAB basis</th>
<th>Adiabatic IP B2 basis</th>
<th>Experimental IP⁵¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₄</td>
<td>4.07</td>
<td>4.08</td>
<td>4.01</td>
<td>4.02</td>
<td>4.24</td>
</tr>
<tr>
<td>Na₅</td>
<td>3.87</td>
<td>3.98</td>
<td>3.64</td>
<td>3.69</td>
<td>3.99</td>
</tr>
<tr>
<td>Na₆</td>
<td>4.29</td>
<td>4.32</td>
<td>4.00</td>
<td>4.09</td>
<td>4.23</td>
</tr>
<tr>
<td>Na₈</td>
<td>4.13</td>
<td>4.18</td>
<td>3.89</td>
<td>3.97</td>
<td>4.22</td>
</tr>
</tbody>
</table>

A final test for the two basis sets is their ability to predict the absorption spectrum for a given cluster. We calculated the absorption spectrum for Na₄ using MOLCAS.⁴⁵ Shown in Table IV.3 are the ground and excited states of the four-atom cluster using both basis sets, along with their excitation energies. The excited states found with the NAB basis are purer than those found with the B2 basis at least for the configuration with the largest coefficient. A comparison with experiment and previous results using the B₁ basis and those of Poteau et al., who used a large non-atom-based basis, centered at the origin of the cluster, is given in Table IV.4 for the visible states of the Na₄ cluster. We include their results for the 4s, 4p, 4d + 2s/atom basis (P1). Unfortunately, the quantum chemical package we used did not allow us to calculate the transition moments for the
experimentally visible transitions. Even so, it is clear that the NAB basis set is far superior to the B2 basis set, both in absolute absorption frequency and in relative spacing of frequencies. In addition, with the exception of the highest energy excitation ($^{1}\text{B}_{1u}$), the NAB basis set performs about as well as the B1 and P1 basis sets, despite having only half as many valence orbitals. It is thus clear that the much smaller NAB basis can be used to predict accurately the properties of these small clusters.

IV.4. CONCLUSIONS.

A non-atom-based orbital scheme was used to study the electronic structure of small sodium clusters. Previous path integral results motivated this study. Using NAB groups located near the centers of simple geometric structures, we obtain excellent agreement with experiment and previous quantum chemical studies which used much larger basis sets. Our procedure has some similarities with the calculations of Poteau and Spiegelmann.53

Studies of larger clusters are hindered by the need to identify and properly statistically weight the different possible isomers. As cluster size is increased, the number of possible local energy minima representing different isomers dramatically increases and it becomes necessary to use statistical mechanics methods to sample the available phase space. Using a small set of NAB groups for valence electrons and a pseudopotential for core electrons along with a Monte Carlo procedure makes the determination of minimum geometries for larger clusters feasible.

The results of our calculations suggest that the electronic structure of alkali clusters may be viewed as electron density located between atoms rather than on them as is the case for conventional molecules. This is what one should expect given the low ionization potentials of these atoms and the fact that they exist as metals in the bulk.
Table IV.3. Ground and Excited State Energies of Na₄ for the Optimized Ground State Neutral Geometry from MOLCAS. Also Shown Are the Coefficients of the Major Contributing Molecular Orbital Configurations.

<table>
<thead>
<tr>
<th>State</th>
<th>E(MRCI) (au)</th>
<th>Excitation energy (eV)</th>
<th>Major Configurations and Coefficients</th>
<th>E(MRCI) (au)</th>
<th>Excitation energy (eV)</th>
<th>Major Configurations and Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹A₂</td>
<td>-647.4404</td>
<td></td>
<td>.904(aₑ²b₃u¹)</td>
<td>.905(aₑ²b₃u²)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>³B₁₀e</td>
<td>-647.4192</td>
<td>0.577</td>
<td>.877(aₑ²b₃u¹b₂u¹)</td>
<td>-647.4199</td>
<td>0.432</td>
<td>.838(aₑ²b₃u¹b₂u¹)</td>
</tr>
<tr>
<td>³B₃₁u</td>
<td>-647.4069</td>
<td>0.911</td>
<td>.817(aₑ²a₈¹b₂u¹)</td>
<td>-647.4046</td>
<td>0.848</td>
<td>.779(aₑ²b₃u¹b₁u¹)</td>
</tr>
<tr>
<td>¹B₁₀e</td>
<td>-647.4048</td>
<td>0.967</td>
<td>.876(aₑ²b₃u¹b₂u¹)</td>
<td>-647.4068</td>
<td>0.788</td>
<td>.833(aₑ²b₃u¹b₂u¹)</td>
</tr>
<tr>
<td>³B₂₀u</td>
<td>-647.3979</td>
<td>1.157</td>
<td>.672(aₑ¹b₃u²b₂u¹) +.524(aₑ²b₃u¹b₁u¹)</td>
<td>-647.3957</td>
<td>1.090</td>
<td>.636(aₑ¹b₃u²b₂u¹) +.526(aₑ²b₃u¹b₁u¹)</td>
</tr>
<tr>
<td>³B₂₁u</td>
<td>-647.3966</td>
<td>1.190</td>
<td>.858(aₑ²b₃u¹b₁u¹)</td>
<td>-647.3970</td>
<td>1.057</td>
<td>.884(aₑ²b₃u¹b₁u¹)</td>
</tr>
<tr>
<td>³B₂₀u</td>
<td>-647.3808</td>
<td>1.621</td>
<td>.672(aₑ²a₈¹b₂u¹) -.472(aₑ²b₃u¹b₁u¹)</td>
<td>-647.3820</td>
<td>1.464</td>
<td>-.517(aₑ²a₈¹b₂u¹) +.492(aₑ²b₃u¹b₁u¹)  +.304(aₑ²a₈¹b₁u¹)</td>
</tr>
<tr>
<td>³A₁₀e</td>
<td>-647.3807</td>
<td>1.624</td>
<td>.532(aₑ²b₃u¹b₃u*¹) +.504(aₑ¹a₈¹b₃u²) +.442(aₑ²b₃u¹b₁u¹)</td>
<td>-647.3825</td>
<td>1.450</td>
<td>-.501(aₑ¹a₈¹b₃u²) +.482(aₑ²b₃u¹b₃u⁺¹) -.443(aₑ²b₃u¹b₃u⁺¹)</td>
</tr>
<tr>
<td>¹B₂₀u</td>
<td>-647.3799</td>
<td>1.646</td>
<td>.583(aₑ²a₈¹b₂u¹) -.423(aₑ²b₃u¹b₁u¹) -.326(aₑ²b₃u²b₂u¹)</td>
<td>-647.3826</td>
<td>1.447</td>
<td>.528(aₑ¹a₈¹b₂u¹) -.398(aₑ²b₃u¹b₁u¹) +.343(aₑ¹b₃u²b₂u¹)</td>
</tr>
<tr>
<td>¹B₃₁u</td>
<td>-647.3729</td>
<td>1.837</td>
<td>.863(aₑ²a₈¹b₁u¹)</td>
<td>-647.3747</td>
<td>1.662</td>
<td>.833(aₑ²a₈¹b₁u¹)</td>
</tr>
<tr>
<td>¹B₃₁u</td>
<td>-647.3663</td>
<td>2.017</td>
<td>.765(aₑ²a₈⁺¹b₃u¹)</td>
<td>-647.3736</td>
<td>1.694</td>
<td>.688(aₑ²a₈⁺¹b₃u¹) -.383(aₑ¹a₈⁺¹b₃u¹) -.262(aₑ²b₃u⁰b₁u¹)</td>
</tr>
<tr>
<td>¹B₁₀u</td>
<td>-647.3586</td>
<td>2.226</td>
<td>-.527(aₑ²a₈¹b₁u¹) +.527(aₑ²b₃u¹b₂u¹)</td>
<td>-647.3730</td>
<td>1.707</td>
<td>.521(aₑ²a₈¹b₁u¹) +.495(aₑ²b₃u¹b₂u¹)</td>
</tr>
<tr>
<td>¹B₂₀u</td>
<td>-647.3458</td>
<td>2.573</td>
<td>-.692(aₑ²b₃u²b₂u¹) +.472(aₑ²b₃u¹b₁u¹)</td>
<td>-647.3439</td>
<td>2.500</td>
<td>.679(aₑ²b₃u²b₁u¹) +.525(aₑ¹b₃u⁰b₂u¹)</td>
</tr>
<tr>
<td>¹B₁₀u</td>
<td>-647.3299</td>
<td>3.006</td>
<td>-.615(aₑ²b₃u¹b₂u¹) +.569(aₑ²b₃u²b₁u¹)</td>
<td>-647.3311</td>
<td>2.848</td>
<td>-.501(aₑ²a₈¹b₁u¹) +.474(aₑ²b₃u²b₁u¹)  +.233(aₑ¹a₈⁺¹b₁u¹)</td>
</tr>
</tbody>
</table>

* Refers to the third orbital of that particular symmetry.
# Refers to the fourth orbital of that particular symmetry.
Table IV.4. Comparison of the Energies (eV) of the Visible Excited States that Comprise the Vertical Spectrum for Na4. The Number of Valence Basis Functions in Each Basis Set Is 28 (NAB), 36 (B2), 56 (B1), and 44 (P1).

<table>
<thead>
<tr>
<th>State</th>
<th>NAB basis</th>
<th>B2 basis</th>
<th>B1 basis</th>
<th>P1 basis</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>1B2_u</td>
<td>1.65</td>
<td>1.45</td>
<td>1.57</td>
<td>1.60</td>
<td>1.63</td>
</tr>
<tr>
<td>1B3_u</td>
<td>1.84</td>
<td>1.66</td>
<td>1.74</td>
<td>1.86</td>
<td>1.80</td>
</tr>
<tr>
<td>1B3_d</td>
<td>2.02</td>
<td>1.69</td>
<td>1.92</td>
<td>2.00</td>
<td>1.93</td>
</tr>
<tr>
<td>1B1_u</td>
<td>2.23</td>
<td>1.71</td>
<td>2.12</td>
<td>2.27</td>
<td>2.18</td>
</tr>
<tr>
<td>1B2_d</td>
<td>2.57</td>
<td>2.50</td>
<td>2.52</td>
<td>2.57</td>
<td>2.50</td>
</tr>
<tr>
<td>1B1_d</td>
<td>3.01</td>
<td>2.85</td>
<td>2.80</td>
<td>2.91</td>
<td>2.77</td>
</tr>
</tbody>
</table>

IV.5. REFERENCES.


CHAPTER V: AB INITIO HARTREE-FOCK MONTE CARLO STUDIES

V.1. INTRODUCTION.

After the testing of the NAB groups was completed and they were shown to be effective in describing the electronic structure in sodium clusters, we needed to incorporate the possibility of p functions into our quantum chemistry Monte Carlo program. This required the solution of all the integrals involving both s and p Gaussian functions. The types of integrals included the one-electron integrals for the overlap energy, the kinetic energy, and the potential energy and the two-electron integrals for the Coulomb and exchange energies. The Hamiltonian used is

\[ H_{\text{elec}} = \sum_i \left( -\frac{1}{2} \nabla_i^2 + \sum \sum \left( \frac{Q}{|r_{ic} - R_c|} - \frac{A}{|r_{ic} - R_c|} e^{-\alpha|r_{ic} - R_c|^2} + B e^{-\beta|r_{ic} - R_c|^2} \right) + \sum \frac{1}{|r_i - r_j|} \right) \]

where \( \nabla_i^2 \) is the Laplacian and the three terms inside the parentheses are a pseudopotential used to describe the ionic sodium nucleus. The pseudopotential allows the replacement of the core electrons of the sodium atoms with a mathematical function so that only the valence electrons have to be treated with the Hartree-Fock theory reducing the number of electrons per sodium atom from 11 to 1. The results of the solution of the 1-electron and 2-electron integrals for all cases involving s and p Gaussian orbitals are shown in the Appendix. The 1-electron integrals are solved analytically while the 2-electron integrals require a numerical solution based on the Rys quadrature method using the weighting factor from Chebyshev-Gauss quadrature.

The program is fairly versatile. It solves the wave function self-consistently at the Hartree-Fock (HF) level of theory. Electron correlation can be included in the calculation by mixing in various excited state configurations. The molecular orbitals are obtained through a self-consistent diagonalization of the resulting matrix. Many parameters can be varied such as the temperature of the simulation (related to \( \beta \)) and
some optimized using Monte Carlo\textsuperscript{56} including the positions of the sodium centers, the positions of the NAB groups and the exponents of the NAB s and p functions. Moves can be proposed in a random direction or according to the normal modes of the cluster vibrations. Moves attempted in random directions will be referred to as regular moves.

\textbf{V.2. CALCULATIONS.}

Calculations were performed on the small clusters with 4-8 atoms allowing for full optimization of the geometry and the exponents of the orbitals. NAB basis sets were used where each NAB group consisted of only one s and one set of p Gaussian functions which is a much smaller basis set than the quantum chemistry NAB basis set made up of 3 s and 3 sets of p functions per NAB group. Geometries usually converge within 2000 Monte Carlo passes. Optimizations were performed at two different temperatures, $T=150$ K ($\beta=2000$) and $T=300$ K ($\beta=1000$). The higher the temperature the more the cluster moves.

The clusters considered were the neutral and the cationic sodium clusters. We compared the optimized exponents from the small cluster calculations. The exponents were similar for all the small neutral clusters so we set them to the average values ($s(0.03), p(0.06)$). For the cationic clusters, the exponents were not as consistent. We set them to the same values as the neutrals and for the 4- and 5-atom cations, these exponents gave the literature geometries. For the larger clusters with 9, 10, 13, 18, and 20 atoms, an initial run was done using only s orbital functions to obtain a reasonable starting geometry. The more accurate calculations using both s and p functions could then be started in this geometry reducing the overall computational time. However, the calculations for these larger clusters and also Na$_7$ and Na$_8$ take a long time to converge to a geometry. Because of this, we realized we needed to find a way to speed up the program. We need to make the sampling more efficient, and we need to reduce the time the program takes to complete one Monte Carlo pass. During one Monte Carlo pass, one move of each NAB and each sodium center is attempted.
The average cluster geometries from the optimizations were minimized by performing what is known as a quench. A quench is a Monte Carlo simulation done at a very low temperature (~0 K) in which only moves that are downhill in energy are accepted. Small steps are taken and eventually the cluster geometry changes very little. The minimized geometry is then averaged according to symmetry considerations and single point CI energy calculations are done to obtain the correlated electronic energy.

The energies are used to calculate quantities which can be compared to experimental values. For example, the vertical IP is the difference in CI energies of n-atom neutral and cationic clusters, both at that cluster's optimized neutral geometry. To obtain adiabatic ionization potentials, one needs the optimized cationic structure as well. There is a question of the proper basis set one should use in treating cationic clusters. For neutral clusters, a minimal basis set is used. That is, one s and set of p functions is used for each NAB group site and one site or orbital is needed for each pair of electrons. The problem occurs in the case of odd cluster sizes. For example, Na₅ requires three NAB group sites while Na₅⁺, which has four valence electrons, needs only two NAB groups. However, to maintain basis set consistency, Na₅⁺ should be given three NAB groups. (See discussion of specific clusters.) Next, the CI energy of the optimized neutral cluster and the optimized cationic cluster are calculated and the difference between the two CI energies is the adiabatic ionization potential. Electron affinities are found in a similar way using the optimized anionic cluster energies but were not obtained. Optimizations on anionic clusters are a little more difficult to do because the anions usually require more diffuse basis sets in quantum chemistry calculations, and in calculations for even cluster sizes, a NAB group has to be added. To obtain the electron affinities, more needs to be learned about the correct basis set to use, and how the number of basis functions affects the geometry of the cluster. This can be studied using the Na₇ and Na₇⁺ clusters because of the five-fold symmetry of the pentagonal bipyramidal structure.
V.3. RESULTS.

The optimized geometries for the small neutral clusters obtained with the Hartree-Fock Monte Carlo program with the exception of Na$_7$ agree qualitatively with the geometries in the literature. The structures obtained are shown in Figure V.1. - Figure V.4. The energies from these calculations are shown in Table V.1. Note that the locations of the NAB groups for these optimized clusters are typically farther from other NABs and closer to the nearest sodium atom than they were in the ab initio quantum chemistry optimizations. We performed studies on Na$_7$ starting in the pentagonal bipyramidal structure. The cluster moved out of this geometry but had not converged to another geometry yet. A quench on the pentagonal structure was performed for Na$_7$, but the energy obtained was 14 kcal/mol higher than the unconverged geometry. The NAB basis set may need a fifth site to represent the five-fold symmetry of the electron density correctly or atom-based orbitals may need to be added.

![Figure V.1](image.png)

Figure V.1. The optimized symmetrically averaged structure of Na$_4$ obtained using the Hartree-Fock Monte Carlo program with s and p Gaussian functions at the NAB sites. The + indicates the location of a NAB group.
Figure V.2. The optimized symmetrically averaged structure of Na$_5$ obtained using the Hartree-Fock Monte Carlo program with s and p Gaussian functions at the NAB sites. The + indicates the location of a NAB group.

Figure V.3. The optimized symmetrically averaged structure of Na$_6$ obtained using the Hartree-Fock Monte Carlo program with s and p Gaussian functions at the NAB sites. The + indicates the location of a NAB group.
Figure V.4. The optimized symmetrically averaged structure of Na₈ obtained using the Hartree-Fock Monte Carlo program with s and p Gaussian functions at the NAB sites. The + indicates the location of a NAB group.
Table V.1. Hartree-Fock and Configuration Interaction Energies (au) for Neutral and Cationic Sodium Clusters Using the Quantum Monte Carlo Program.

<table>
<thead>
<tr>
<th></th>
<th>Hartree-Fock Energy</th>
<th>Configuration Interaction Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_4)</td>
<td>-0.7075</td>
<td>-0.7150</td>
</tr>
<tr>
<td>Na(_5)</td>
<td>-0.8772</td>
<td>-0.8838</td>
</tr>
<tr>
<td>Na(_6)</td>
<td>-1.0639</td>
<td>-1.0700</td>
</tr>
<tr>
<td>Na(_8)</td>
<td>-1.4453</td>
<td>-1.4507</td>
</tr>
<tr>
<td>Na(_4^+)</td>
<td>-0.5764</td>
<td>-0.5878</td>
</tr>
<tr>
<td>Na(_5^+)</td>
<td>-0.7586</td>
<td>-0.7660</td>
</tr>
<tr>
<td>Na(_5^+) (3 orbs)</td>
<td>-0.7585</td>
<td>-0.7667</td>
</tr>
<tr>
<td>Na(_6^+)</td>
<td>-0.9462</td>
<td>-0.9522</td>
</tr>
<tr>
<td>Na(_8^+)</td>
<td>-1.3198</td>
<td>-1.3244</td>
</tr>
</tbody>
</table>

The Na\(_4^+\), Na\(_5^+\), Na\(_6^+\), and Na\(_8^+\) geometries are shown in Figure V.5. - Figure V.11. Some differences were found in the optimized geometries of the cations obtained with the Hartree-Fock Monte Carlo program using NAB orbitals and the geometries from the literature. For Na\(_4^+\), the geometry obtained (Figure V.5.) agrees with the quantum chemistry geometry.

For Na\(_5^+\), we obtained a twisted bow-tie structure. (Figure V.6.) Quantum chemistry gives a planar bow-tie structure as the lowest energy isomer. (Figure V.7.) The twisted bow-tie structure is the same as the planar bow-tie structure but with two of the atoms rotated 90° out of the plane. The optimized twisted bow-tie has two NAB groups. We studied this difference in geometries using Gaussian 92\(^5\) and found the barrier to rotation to be very small using only two NAB groups. In fact, there is almost free rotation about the central atom. The Hartree-Fock and the QCISD(T) energies are shown in Table V.2. For this comparison, the optimized bow-tie geometry of the atoms found in the quantum chemistry study was used. The B2 basis set was used to optimize
the positions of the atoms, and the NAB basis set was used to obtain the positions of the NABs. To obtain the twist geometry, the bond lengths were left unchanged but two atoms were rotated 90° out of the plane. Note that the NAB basis set is at least 0.0056 au (3.5 kcal/mol) more stable than the B2 basis set, and the twisted bow-tie is about 0.0008 au (0.5 kcal/mol) more stable than the planar bow-tie. If, however, as discussed above a third NAB group is added to Na₅⁺, the structure doesn't rotate as freely. It still rotates out of the plane, and the average structure obtained is the twisted bow-tie. (Figure V.8.) The third NAB group is positioned almost 6 Å away from the bow-tie and prevents free rotation about the central atom.

For Na₆⁺, we obtained a C₂ᵥ geometry shown in Figure V.9, rather than the Cₛ tent-like structure (Figure IV.2.) seen in the quantum chemistry studies. The C₂ᵥ geometry was studied using Gaussian 92.⁵⁷ The geometry of the atoms was optimized using the B2 basis set. The coordinates of the atoms were frozen, and the positions of the NAB sites were determined in an optimization using the quantum chemistry NAB basis set. The HF and CI energies were calculated for both the C₂ᵥ and the Cₛ isomers and are listed in Table V.2. Note that the C₂ᵥ geometry is lower in energy than the Cₛ geometry at each level of theory and with each basis set and that the NAB basis set is lower in energy than the B2 basis set at each geometry and at both levels of theory. At the CI level, the C₂ᵥ structure is 0.002 au (1.3 kcal/mol) more stable than the Cₛ structure with the B2 basis and 0.005 au (3.0 kcal/mol) more stable with the NAB basis. The NAB basis set is about 0.008 au (5 kcal/mol) more stable than the B2 basis for each isomer of Na₆⁺.

Our preliminary calculations of Na₈⁺ gave a tetrahedral structure (Figure V.10.) similar to the Na₈ neutral structure (Figure V.4.). For the Na₈⁺ cluster, the bonds are longer than the bonds in the Na₆ cluster. This is in contrast to the C₂ᵥ Na₈⁺ structure (Figure IV.2.) found in the quantum chemistry studies. The stereoview of the Na₈⁺ tetrahedral structure is shown in Figure V.11.
Figure V.5. The optimized symmetrically averaged structure of Na$_4^+$ obtained using the Hartree-Fock Monte Carlo program with s and p Gaussian functions at the NAB sites. The + indicates the location of a NAB group.

Figure V.6. The optimized symmetrically averaged structure of Na$_5^+$ with two NAB groups obtained using Hartree-Fock Monte Carlo with s and p Gaussian functions at the NAB sites. The + indicates the location of a NAB group.
**Figure V.7.** The Na$_5^+$ optimized twist geometry shown in the planar bow-tie configuration. The + indicates the location of a NAB group.

**Figure V.8.** The optimized symmetrically averaged structure of Na$_5^+$ with three NAB groups obtained using Hartree-Fock Monte Carlo with s and p Gaussian functions at the NAB sites. The + indicates the location of a NAB group.
Table V.2. Hartree-Fock (HF) and QCISD(T) Energies (au) for Two Low-Energy Isomers of Na$_5^+$ and Two Low-Energy Isomers of Na$_6^+$ Determined from Gaussian 92 Calculations Using the NAB and the B2 Basis Sets.

<table>
<thead>
<tr>
<th></th>
<th>Hartree-Fock Energy</th>
<th>Hartree-Fock Energy</th>
<th>Configuration Interaction Energy</th>
<th>Configuration Interaction Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B2 basis</td>
<td>NAB basis</td>
<td>B2 basis</td>
<td>NAB basis</td>
</tr>
<tr>
<td>Na$_5^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar</td>
<td>-809.1161</td>
<td>-809.1149</td>
<td>-809.1634</td>
<td>-809.1690</td>
</tr>
<tr>
<td>Bow-tie</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_5^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Twisted</td>
<td>-809.1166</td>
<td>-809.1157</td>
<td>-809.1640</td>
<td>-809.1698</td>
</tr>
<tr>
<td>Bow-tie</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_6^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>-970.9674</td>
<td>-970.9696</td>
<td>-971.0233</td>
<td>-971.0308</td>
</tr>
<tr>
<td>Na$_6^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_{2v}$</td>
<td>-970.9679</td>
<td>-970.9697</td>
<td>-971.0254</td>
<td>-971.0335</td>
</tr>
</tbody>
</table>
Figure V.9. The optimized symmetrically averaged structure of Na$_6^+$ with three NAB groups obtained using Hartree-Fock Monte Carlo with $s$ and $p$ Gaussian functions at the NAB sites. The + indicates the location of a NAB group.
Figure V.10. The optimized symmetrically averaged structure of Na$_8^+$ with three NAB groups obtained using Hartree-Fock Monte Carlo with s and p Gaussian functions at the NAB sites. The + indicates the location of a NAB group.

Figure V.11. The stereoview of the Na$_8^+$ tetrahedral structure. The + signs represent the locations of the NAB sites.
The vertical and adiabatic ionization potentials are given in Table V.3. and are compared with the experimental values. The values follow the same trend as the experimental values. They are larger for even clusters and smaller for odd clusters.

Table V.3. Vertical and Adiabatic Ionization Potentials (eV) for Na₄, Na₅, Na₆, and Na₈ Using the Quantum Monte Carlo Program.

<table>
<thead>
<tr>
<th># of NABs for cation</th>
<th>Vertical IP</th>
<th>Adiabatic IP</th>
<th>Experimental IP⁵⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₄</td>
<td>2</td>
<td>3.665</td>
<td>3.461</td>
</tr>
<tr>
<td>Na₅</td>
<td>2</td>
<td>—</td>
<td>3.205</td>
</tr>
<tr>
<td>Na₆</td>
<td>3</td>
<td>3.499</td>
<td>3.186</td>
</tr>
<tr>
<td>Na₇</td>
<td>3</td>
<td>3.804</td>
<td>3.205</td>
</tr>
<tr>
<td>Na₈</td>
<td>4</td>
<td>3.608</td>
<td>3.437</td>
</tr>
</tbody>
</table>

V.4. NEW PROGRAM.

Changes were made in the program to speed it up and to test the assumption that the electronic structure is the dominant factor determining the geometry of the lowest energy isomer. This was done by freezing the orbital positions and then allowing the nuclei to move to their preferred positions based on the location of the orbitals. Some preliminary testing of this program showed that it takes about 10 passes for the atom positions to equilibrate to a particular NAB orientation. It takes more passes if the nuclei are far from their preferred positions. The program was then modified so the orbital moves were attempted during every 10th pass of a Monte Carlo simulation.

V.5. REFERENCES.


CHAPTER VI: CONCLUSION

VI.1. RESULTS.

We have shown that NAB groups provide the correct physical attributes needed to model the electronic structure of sodium clusters. The electronic structure of sodium clusters is very different physically from more traditional molecules which are modeled successfully using only atom-based basis sets. This idea of non-atom-based basis sets can therefore be very useful in studying many different metallic systems.

The success of the NAB basis set in the comparison with quantum chemistry results suggests that it does describe the electronic structure in alkali clusters and can be used in simple numerical calculations to study larger clusters. The results of these calculations have shown that the NAB basis set provides the correct physical picture of the electron density in sodium clusters. It is a much smaller basis set than traditional atom-based basis sets and can therefore be used to study larger clusters than is possible with programs using these larger basis sets.

Monte Carlo quantum chemistry studies have been performed using a program that we have written and modified to include s and p Gaussian orbitals. It uses pseudopotentials to represent the core electrons and s and p Gaussian functions placed at NAB sites to represent the valence electrons. We studied Na₅ clusters ranging in size from 4 to 6 and 8 atoms. Preliminary work was also done on Na₅ clusters with 7, 9, 10, 13, 18 and 20 atoms but the geometries had not converged so no results are reported. These calculations are currently underway.

VI.2. FUTURE DIRECTIONS.

In order to extend these studies to larger clusters more work will have to be done to make the program more efficient. With the current version of the program, Na₁₈ and Na₂₀ calculations with p functions cannot be done on the IBM RS6000 computers in a reasonable amount of CPU time. However, simulations using only s functions are
possible. More work is also needed on Na$_7$, Na$_7^+$, Na$_8^+$, Na$_9$, and Na$_9^+$. We have made the simulations faster by not moving the positions of the NAB groups on every pass through the program. However, this method needs further testing with more cluster sizes to see how often the moves of the NAB groups need to be attempted. The idea is to let the nuclei adjust to the positions of the NABs between NAB moves. The efficiency of the sampling is also in question. One way to improve this is to move the Na centers and the NAB groups according to their normal modes of vibration rather than in random directions. Possibilities for improving the efficiency of the program are currently being tested on Na$_8^+$ and will then be used to extend the calculations on the Na$_7$ and Na$_9$ neutral and cationic clusters.
APPENDIX

The subroutines which solve the one- and two-electron integrals involving s and p primitive Gaussian functions and an electronic Hamiltonian are given. The Hamiltonian is

\[ H_{\text{elec}} = \sum_i \frac{1}{2} \nabla_i^2 + \sum_i \sum_c \left( -\frac{Q}{|r_i - R_c|} - \frac{A}{|r_i - R_c|} e^{-\alpha_i R_{c1}^2} + Be^{-\beta_i R_{cl}^2} \right) + \sum_{ij} \frac{1}{|r_i - r_j|}. \]

The three terms in the parentheses are the pseudopotential of Preuss et al.,\textsuperscript{59} which represents the core electrons of the sodium atoms. For the one-electron integrals, there are three parts of the Hamiltonian whose matrix elements have to be considered including the overlap energy term, the kinetic energy term, and the three potential energy terms.

1. The overlap integrals are given by
   \[ \langle \phi_A | \phi_B \rangle \] where \( \phi_A \) and \( \phi_B \) represent primitive s or p Gaussians.

2. The kinetic energy integrals are given by
   \[ \langle \phi_A | \hat{T} | \phi_B \rangle \] where \( \hat{T} = -\frac{1}{2} \Delta \).

3. The three different potential energy integrals are given by
   \[ \langle \phi_A | \hat{V}_1 | \phi_B \rangle \] where \( \hat{V}_1 = -\frac{Q}{|r - R|} \),
   \[ \langle \phi_A | \hat{V}_2 | \phi_B \rangle \] where \( \hat{V}_2 = -\frac{A}{|r - R|} e^{-\alpha_i R_{c1}^2} \), and
   \[ \langle \phi_A | \hat{V}_3 | \phi_B \rangle \] where \( \hat{V}_3 = B e^{-\beta_i R_{c1}^2} \).

The normalized s Gaussian is

\[ \phi_A = |s\rangle = N_A e^{-\alpha_i R_{c1}^2}, \text{ where } N_A = \left( \frac{8\pi^3}{3} \right)^{\frac{1}{4}}. \]

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The normalized $p_x$ Gaussian is

$$\phi_A = \langle p_x \rangle = N_A x e^{-gA r^2}, \text{ where } N_A = \left(\frac{128(gA)^5}{\pi^3}\right)^{1/4}.$$ 

Similar equations exist for the $p_y$ and $p_z$ Gaussians. $N_A$ is the normalization constant for a Gaussian function centered at $R_A = (X_A, Y_A, Z_A)$ which is a vector representing the coordinates of center $A$, and $r = (x, y, z)$ which are the variables of integration.

There are 20 different cases possible of 1-electron integrals to solve. There are four different combinations of $s$ and $p$ functions for each of the five terms in the Hamiltonian. (i.e. Four are overlap integrals, four are kinetic energy integrals, and twelve are potential energy integrals.) A special case exists in the potential energy integrals when either the term $RPC=0.0$ or $RPCp=0.0$ which are defined in the FORTRAN function POTEN.

The 2-electron integrals are calculated by the function EE. The 2-electron integrals represent the Coulomb and exchange integrals. These integral are calculated numerically using the Rys quadrature method. The weighting function from the Chebyshev-Gauss quadrature is used instead of the one given in the Rys quadrature method.

In the following functions, $RA$ is an array where the coordinates of the positions of orbital $A$ are stored, $RB$ is for orbital $B$, $RC$ is for orbital $C$, and $RD$ is for orbital $D$. In the function POTEN, $RC$ is an array storing the coordinates of a sodium center not an orbital. The exponents of the Gaussian functions are $g1$ for the Gaussian function at the site of orbital $A$, $g2$ for the one at site $B$, $g3$ for the one at site $C$, and $g4$ for the one at site $D$. $l1$, $l2$, $l3$, and $l4$ are parameters indicating the type of Gaussian function (i.e. $l1=0$ for an $s$, $l1=1$ for a $p_x$, $l1=2$ for a $p_y$, $l1=3$ for a $p_z$).

C FUNCTION TO CALCULATE THE OVERLAP INTEGRAL
C
function S(RA,RB,g1,g2,l1,l2)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
dimension RA(3),RB(3)
real*8 NA,NB

calculate constants needed for equations

PI=DACOS(-1.d0)
c=g1*g2/(g1+g2)
c1=(dsqrt(PI/(g1+g2)))**3
RAB2=((RA(1)-RB(1))**2+(RA(2)-RB(2))**2+(RA(3)-RB(3))**2)
d1=g1+g2
exp1=exp(-c*RAB2)

initialize variables

if(ll .eq. 0) then
else
endif

endif

endif

s=NA*NB*ts
return
end

FUNCTION TO CALCULATE THE KINETIC ENERGY

function T(RA,RB,g1,g2,l1,l2)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
dimension RA(3),RB(3)
real*8 NA,NB
c calculate constants needed for eqs
PI=DACOS(-1.d0)
c=g1*g2/(g1+g2)
c1=(PI/(g1+g2))**1.5
RAB2=((RA(1)-RB(1))**2+(RA(2)-RB(2))**2+(RA(3)-RB(3))**2)
d1=g1+g2
exp1=dexp(-c*RAB2)
c initialize variables
tt=0.d0
if(l1.eq.l2) then
  if(l1.eq.0) then
    print*,'<sls>'
    NA=(2.d0*g1/PI)**.75
    NB=(2.d0*g2/PI)**.75
    tt=c1*exp1*c*(3.d0-2.d0*g1*g2*RAB2/d1)
  else
    print*,'<pxls>'
    NA=(128.d0*g1**5/PI**3)**.25
    NB=(128.d0*g2**5/PI**3)**.25
    tt=c1/d1*exp1*$
    $  (2.d0*((g1*g2)/d1)**3*(RA(l1)-RB(l1))**2*RAB2
    $ -7.d0*(g1*g2/d1*(RA(l1)-RB(l1)))**2
    $ -(g1*g2/d1)**2*RAB2 + 2.5d0*g1*g2/d1)
  endif
else
  if(l1.eq.0) then
    print*,'<spxl>'
    NA=(2.d0*g1/PI)**.75
    NB=(128.d0*g2**5/PI**3)**.25
    tt=c1*exp1/d1*(RB(l2)-RA(l2))*$
    $ (-5.d0*g1*g2/d1 + 2.d0*(g1*g2/d1)**2*g1*RAB2)
  else if(l2.eq.0) then
    print*,'<pxls>'
    NA=(128.d0*g1**5/PI**3)**.25
    NB=(2.d0*g2/PI)**.75
    tt=c1*exp1/d1*(RA(l1)-RB(l1))*$
    $ (2.d0*(g1*g2/d1)**3*(RA(l1)-RB(l1))**2+RAB2
    $ -7.d0*(g1*g2/d1**2)*RAB2 + 2.5d0*g1*g2/d1)
  endif
end if
$ -5.0 \cdot g1 \cdot g2 / g2 \cdot d1 + 2.0 \cdot (g1 \cdot g2 / d1)^2 \cdot g2 \cdot RAB2$

else

print', '<pxlpy>

NA = (128.0 \cdot g1 / PI)^2 \cdot 0.25
NB = (128.0 \cdot g2 / PI)^2 \cdot 0.25

tt = c1 / d1 \cdot exp1

$ -7.0 \cdot (g1 \cdot g2 / d1)^3 \cdot (R1 - R2)^2 \cdot (R1 - R2) \cdot RAB2$
$ + 7.0 \cdot (g1 \cdot g2 / d1)^2 \cdot (R1 - R2)^2 \cdot (R1 - R2)$

endif
endif
t = NA \cdot NB \cdot tt
return
end

FUNCTION TO CALCULATE PSEUDOPOTENTIAL FOR
THE ELECTRON-SODIUM CORE

function poten(RC,RA,RB,g1,g2,l1,l2)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
dimension RC(3),RA(3),RB(3),RP1(3),RP2(3)
real*8 NA,NB

c DATA FOR SODIUM

DATA Q,A,ALPHA,B,BETA,RCUT /1.0d0,.077d0,.090d0,

$ 4.504d0,.920d0,.55d0/

c calculate the constants needed for the potential energy equations

P1=DACOS(-1.d0)
c = g1 / (g1 + g2)
d1 = g1 + g2
d2 = g1 + g2 + alpha
d3 = g1 + g2 + beta

c1 = -Q * (PI / d1) ** 1.5
c2 = -A * (PI / d2) ** 1.5
c3 = -B * (PI / d3) ** 1.5

RAB2 = ((RA(1) - RB(1))^2 + (RA(2) - RB(2))^2 + (RA(3) - RB(3))^2)
RAB = dsqrt(RAB2)
RAC2 = ((RA(1) - RC(1))^2 + (RA(2) - RC(2))^2 + (RA(3) - RC(3))^2)
RAC = dsqrt(RAC2)
RBC2 = ((RB(1) - RC(1))^2 + (RB(2) - RC(2))^2 + (RB(3) - RC(3))^2)
RBC = dsqrt(RBC2)
RPX = (g1 * RA(1) + g2 * RB(1)) / d1
RPY = (g1 * RA(2) + g2 * RB(2)) / d1
RPZ = (g1 * RA(3) + g2 * RB(3)) / d1
RPXP = (g1 * RA(1) + g2 * RB(1) + alpha * RC(1)) / d2
RPYP = (g1 * RA(2) + g2 * RB(2) + alpha * RC(2)) / d2
RPZP = (g1 * RA(3) + g2 * RB(3) + alpha * RC(3)) / d2
\[ \text{RPC2} = ((Rpx-RC(1))^2 + (Rpy-RC(2))^2 + (Rpz-RC(3))^2) \]
\[ \text{RPCp2} = ((Rpxp-RC(1))^2 + (Rpyp-RC(2))^2 + (Rpzp-RC(3))^2) \]
\[ \text{RPC} = \text{dsqrt}(\text{RPC2}) \]
\[ \text{RPCp} = \text{dsqrt}(\text{RPCp2}) \]
\[ \exp1 = \text{dexp}(-c*\text{RAB2}) \]
\[ \exp2 = \text{dexp}((-g1*g2*\text{RAB2} - g1*\alpha*\text{RAC2} - g2*\alpha*\text{RBC2})/d2) \]
\[ \exp3 = \text{dexp}((-g1*g2*\text{RAB2} - g1*\beta*\text{RAC2} - g2*\beta*\text{RBC2})/d3) \]
\[ \text{erf1} = \text{erf}(\text{dsqrt}(d1)*\text{RPC}) \]
\[ \text{erf2} = \text{erf}(\text{dsqrt}(d2)*\text{RPCp}) \]
\[ \text{RP1}(1) = Rpx \]
\[ \text{RP1}(2) = Rpy \]
\[ \text{RP1}(3) = Rpz \]
\[ \text{RP2}(1) = Rpxp \]
\[ \text{RP2}(2) = Rpyp \]
\[ \text{RP2}(3) = Rpzp \]

\text{c}
\text{initialize variables}
\text{c}
\text{v1} = 0.0\ d0
\text{v2} = 0.0\ d0
\text{v3} = 0.0\ d0
if(\text{l1 .eq. l2}) then
  if(\text{l1 .eq. 0}) then
    \text{print*},'<\text{sls}>'
    \text{NA} = (2.0\*g1/\Pi)^.75
    \text{NB} = (2.0\*g2/\Pi)^.75
    if(\text{RPC2} .lt. 1.0\ d-8) then
      \text{v1} = c1*\exp1*2.0\*\text{dsqrt}(d1/\Pi)
    else
      \text{v1} = c1*\exp1/\text{RPC}*\text{erf1}
    endif
    if(\text{RPCp2} .lt. 1.0\ d-8) then
      \text{v2} = c2*\exp2*2.0\*\text{dsqrt}(d2/\Pi)
    else
      \text{v2} = c2*\exp2/\text{RPCp}*\text{erf2}
    endif
    \text{v3} = c3*\exp3
  else
    \text{print*},'<\text{px}px>'
    \text{NA} = (128.0\*g1**5/\Pi**3)^.25
    \text{NB} = (128.0\*g2**5/\Pi**3)^.25
    if(\text{RPC2} .lt. 1.0\ d-8) then
      \text{v1} = c1*\exp1*2.0\*\text{dsqrt}(d1/\Pi)*(0.2\ d0*(\text{RP1(l1)}-\text{RC(l1)})^2 + 1.0\ d0/(3.0\*d1) - g1*\text{g2}*((\text{RA(l1)}-\text{RB(l1)})/d1)^2 + (-g1+g2)*((\text{RA(l1)}-\text{RB(l1)})*(\text{RP1(l1)}-\text{RC(l1)})/(3.0\ d1))
else
  v1=c1*exp1/RPC*
  $ (dexp(-d1*RPC2)/(RPC*dsqrt(PI*d1)*d1)*$
  $ (-1.5d0*(RP1(ll)-RC(ll))**2/RPC2+.5d0$
  $ +((g1-g2)*(RA(ll)-RB(ll))$
  $ -((RP1(ll)-RC(ll))*d1))$
  $ +erf1/(d1*d1)*$
  $ (.5d0*d1+.75d0*(RP1(ll)-RC(ll))**2/(RPC2*RPC2)$
  $ -.25d0/RPC2+(-g1+g2)*(RA(ll)-RB(ll))*$
  $ -(RP1(ll)-RC(ll))/(2.d0*RPC2)$
  $ -g1*g2*(RA(ll)-RB(ll))**2))$
end if
if(RPCp .lt. 1.d-8) then
  v2=c2*exp2/2.d0*dsqrt(2.d2/PI)*(0.2d0*(RP2(ll)-RC(ll))**2$
  $ +1.d0/(3.d0*d2) +$
  $ (g1*(RA(ll)-RB(ll))+alpha*(RB(ll)-RC(ll)))*$
  $ (g2*(RA(ll)-RB(ll))+alpha*(RA(ll)-RC(ll)))/d2**2$
  $ +((-g1+g2)*(RA(ll)-RB(ll))+alpha*$(
  $ ((RB(ll)-RC(ll))-(RA(ll)-RC(ll)))$
  $ *(RP2(ll)-RC(ll))/(2.d0*RPC2)$
  $ -(g1*(RA(ll)-RB(ll))-alpha*(RB(ll)-RC(ll)))*$
  $ (g2*(RA(ll)-RB(ll))+alpha*(RA(ll)-RC(ll)))/d2**2)$
end if
else
  v2=c2*exp2/RPCp*
  $ (dexp(-d2*RPC2p)/(RPCp*dsqrt(PI*d2)*d2)*$
  $ (-1.5d0*(RP2(ll)-RC(ll))**2/RPC2p+.5d0$
  $ +((g1-g2)*(RA(ll)-RB(ll))$
  $ -((RP2(ll)-RC(ll))$ $ *+erf2/(d2*d2)*$
  $ (.5d0*d2-.25d0/RPC2p$
  $ +.75d0*(RP2(ll)-RC(ll))**2/(RPC2p*RPC2p)$
  $ +(-g1*(RA(ll)-RB(ll))+alpha*(RB(ll)-RC(ll))$
  $ +g2*(RA(ll)-RB(ll))+alpha*(RA(ll)-RC(ll))$ $ *$(
  $ *(RP2(ll)-RC(ll))/(2.d0*RPC2p)$
  $ -(g1*(RA(ll)-RB(ll))$ $ *+(g2*(RA(ll)-RB(ll))$ $ +alpha*(RA(ll)-RC(ll)))))$
end if
v3=c3*exp3/d3**2*
$ ((g1*(RA(ll)-RB(ll))+beta*(RC(ll)-RB(ll)))*$
$ (g2*(RB(ll)-RA(ll))+beta*(RC(ll)-RA(ll)))+$
  $ .5d0*d3)$
else
  if(ll .eq. 0) then
    c print*, '<slpx>'
\[ \begin{align*}
\text{NA} &= (2.0 \cdot g_1/\pi)^{** 0.75} \\
\text{NB} &= (128.0 \cdot g_2^{** 5/\pi** 3})^{** 0.25} \\
\text{if } (\text{RPC}_2 \cdot \text{lt. } 1.0 - 8) \text{ then } \\
v_1 &= c_1 \cdot \exp 1 \cdot 2.0 \cdot \text{dexp}(d_1/\pi) \cdot -((\text{RP}_1(12) - \text{RC}(12))/3.0) \\
& \quad + g_1 \cdot (\text{RA}(12) - \text{RB}(12))/d_1 \\
\text{else } \quad v_1 &= c_1 \cdot \exp 1 \cdot \\
& \quad (\exp(-d_1 \cdot \text{RPC}_2 \cdot (\text{RP}_1(12) - \text{RC}(12))/\text{RPC}_2 \cdot \text{dexp}(\pi \cdot d_1)) \\
& \quad + \text{erf}_1 \cdot (g_1 \cdot (\text{RA}(12) - \text{RB}(12))/\text{RPC}_2 \cdot d_1) \\
& \quad - ((\text{RP}_1(12) - \text{RC}(12))/(2.0 \cdot \text{RPC}_2 \cdot d_1))) \\
\text{endif} \\
\text{if } (\text{RPC}_2 \cdot \text{lt. } 1.0 - 8) \text{ then } \\
v_2 &= c_2 \cdot \exp 2 \cdot 2.0 \cdot \text{dexp}(d_2/\pi) \cdot -((\text{RP}_2(12) - \text{RC}(12))/3.0) \\
& \quad + (g_2 \cdot (\text{RA}(12) - \text{RB}(12))) \cdot \alpha \cdot (\text{RB}(12) - \text{RC}(12))/d_2) \\
\text{else } \quad v_2 &= c_2 \cdot \exp 2 /\text{RPC}_2 \cdot \\
& \quad (\exp(-d_2 \cdot \text{RPC}_2 \cdot (\text{RP}_2(12) - \text{RC}(12))/\text{dexp}(\pi \cdot d_2 \cdot \text{RPC}_2))) \\
& \quad + \text{erf}_2 /d_2 \cdot \\
& \quad ((g_2 \cdot (\text{RA}(12) - \text{RB}(12)) - \alpha \cdot (\text{RB}(12) - \text{RC}(12)) - \\
& \quad \text{RP}_2(12) - \text{RC}(12))/(2.0 \cdot \text{RPC}_2))) \\
\text{endif} \\
\text{v}_3 &= c_3 \cdot \exp 3 /d_3 \cdot (g_1 \cdot (\text{RA}(12) - \text{RB}(12)) + \beta \cdot (\text{RC}(12) - \text{RB}(12))/d_3) \\
\text{else if } (l_2 \cdot \text{eq. } 0) \text{ then } \\
\text{print} \cdot ',<\text{pxls}>', \\
\text{NA} &= (128.0 \cdot g_1^{** 5/\pi** 3})^{** 0.25} \\
\text{NB} &= (2.0 \cdot g_2/\pi)^{** 0.75} \\
\text{if } (\text{RPC}_2 \cdot \text{lt. } 1.0 - 8) \text{ then } \\
v_1 &= c_1 \cdot \exp 1 \cdot \\
& \quad (\exp(-d_1 \cdot \text{RPC}_2 \cdot (\text{RP}_1(11) - \text{RC}(11))/\text{RPC}_2 \cdot \text{dexp}(\pi \cdot d_1)) \\
& \quad + \text{erf}_1 \cdot (g_2 \cdot (\text{RA}(11) - \text{RA}(11))/\text{RPC}_2 \cdot d_1) \\
& \quad - ((\text{RP}_1(11) - \text{RC}(11))/(2.0 \cdot \text{RPC}_2 \cdot d_1))) \\
\text{endif} \\
\text{if } (\text{RPC}_2 \cdot \text{lt. } 1.0 - 8) \text{ then } \\
v_2 &= c_2 \cdot \exp 2 \cdot 2.0 \cdot \text{dexp}(d_2/\pi) \cdot -((\text{RP}_2(11) - \text{RC}(11))/3.0) \\
& \quad + (g_2 \cdot (\text{RB}(11) - \text{RA}(11))) \cdot \alpha \cdot (\text{RA}(11) - \text{RC}(11))/d_2) \\
\text{else } \quad v_2 &= c_2 \cdot \exp 2 /\text{RPC}_2 \cdot \\
& \quad (\exp(-d_2 \cdot \text{RPC}_2 \cdot (\text{RP}_2(11) - \text{RC}(11))/\text{dexp}(\pi \cdot d_2 \cdot \text{RPC}_2))) \\
& \quad + \text{erf}_2 /d_2 \cdot \\
& \quad ((g_2 \cdot (\text{RB}(11) - \text{RA}(11)) - \alpha \cdot (\text{RA}(11) - \text{RC}(11)) - \\
& \quad \text{RP}_2(11) - \text{RC}(11))/(2.0 \cdot \text{RPC}_2))) \\
\text{endif} \end{align*} \]
\[ v_3 = c_3 \exp(3 \cdot (R_B(11)-R_A(11))) + \beta \exp(3 \cdot (R_C(11)-R_A(11))) / d_3 \]

else

\[ NA = (128.0 \cdot g_1 \cdot 5 / \pi \cdot 3)^{0.25} \]
\[ NB = (128.0 \cdot g_2 \cdot 5 / \pi \cdot 3)^{0.25} \]

if (RPC2 \lt 1.0 \cdot 8) then

\[ v_1 = c_1 \exp(1 \cdot 2.0 \cdot \sqrt{d_1 / \pi}) \cdot (2.0 \cdot (R_P(1(11)-R_C(11))) \]
\[ \cdot (R_P(1(12)-R_C(12))) - g_1 \cdot g_2 \cdot (R_A(11)-R_B(11)) \cdot (R_A(12)-R_B(12)) / d_1^2 \]
\[ + g_2 \cdot (R_P(1(12)-R_C(12)) \cdot (R_A(11)-R_B(11)) / (3.0 \cdot d_1)) \]

else

\[ v_1 = c_1 \exp(1 / RPC) \]
\[ \cdot \exp(-d_1 / RPC) / \sqrt{d_1 / \pi} \cdot (RPC) \]
\[ \cdot (R_P(1(11)-R_C(11))) \cdot (R_P(1(12)-R_C(12))) \]
\[ \cdot (1.0 + 1.5 \cdot d_1 / (d_1 \cdot RPC)) \]
\[ + g_2 \cdot (R_A(11)-R_B(11)) \cdot (R_P(1(12)-R_C(12))) / (2.0 \cdot d_0 \cdot RPC) \]
\[ + 0.75 \cdot d_0 \cdot (R_P(1(11)-R_C(11)) \cdot (R_P(1(12)-R_C(12))) / (RPC^2)^2) \]

endif

if (RPCp \lt 1.0 \cdot 8) then

\[ v_2 = c_2 \exp(2 \cdot 2.0 \cdot \sqrt{d_2 / \pi}) \cdot (2.0 \cdot (R_P(2(11)-R_C(11))) \]
\[ \cdot (R_P(2(12)-R_C(12))) - g_1 \cdot g_2 \cdot (R_A(11)-R_B(11)) \cdot (R_A(12)-R_B(12)) / d_2^2 \]
\[ + g_2 \cdot (R_A(11)-R_B(11)) \cdot (R_P(2(12)-R_C(12))) / (3.0 \cdot d_0 \cdot d_2) \]

else

\[ v_2 = c_2 \exp(2 / RPCp) \]
\[ \cdot \exp(-d_2 / RPCp) / \sqrt{d_2 / \pi} \cdot RPCp \]
\[ \cdot (R_P(2(11)-R_C(11))) \cdot (R_P(2(12)-R_C(12))) \]
\[ \cdot (1.0 + 1.5 \cdot d_2 / (d_2 \cdot RPCp)) \]
\[ + g_2 \cdot (R_A(11)-R_B(11)) \cdot (R_P(2(12)-R_C(12))) / (2.0 \cdot d_0 \cdot RPCp) \]
\[ + 0.75 \cdot d_0 \cdot (R_P(2(11)-R_C(11)) \cdot (R_P(2(12)-R_C(12))) / (RPCp^2)^2) \]
\[ + \text{erf(2)} / (d_2 \cdot d_2) \]
\[ \cdot (-g_1 \cdot (R_A(12)-R_B(12)) - alpha \cdot (R_B(12)-R_C(12))) \]
$ * (g_2^* (R_{A(11)} - R_{B(11)}) + \alpha^* (R_{A(11)} - R_{C(11)}))$
$ + (-g_1^* (R_{A(12)} - R_{B(12)})^*(R_{P2(12)} - R_{C(12)}))$
$ + \alpha^* (R_{B(12)} - R_{C(12)})^*(R_{P2(12)} - R_{C(12)}))$
$ + g_2^* (R_{A(11)} - R_{B(11)})^*(R_{P2(12)} - R_{C(12)}))$
$ + \alpha^* (R_{A(11)} - R_{C(11)})^*(R_{P2(11)} - R_{C(11)})) (2.0*RPCp2)$
$ + .75d0^* (R_{P2(11)} - R_{C(11)})^*(RPCp2^2))
$ end if
$ v_3 = c_3^* \exp3/(d3**2)^*$
$ (g_1^* (R_{A(12)} - R_{B(12)})^* + \beta^* (R_{C(12)} - R_{B(12)}))^*$
$ (g_2^* (R_{B(11)} - R_{A(11)})^* + \beta^* (R_{C(11)} - R_{A(11)}))$
$ end if
$ end if
$ v_{pot} = NA*NB*(v_1 + v_2 + v_3)$
$ poten = v_{pot}$
$ return$
$ end

C FUNCTION TO CALCULATE THE ERROR FUNCTION
C
function erf(x)
implicit double precision (a-h,o-z)
parameter (p=.3275911d0,a1=-.254829592d0,a2=-.284496736d0,$ a3=1.421413741d0,a4=-1.453152027d0,a5=1.061405429d0)
y=abs(x)
if(y .lt. 1.0d0) then
  PI=DACOS(-1.0d0)
  erf=2.0d0/dsqrt(pi)
$ * (y-y**3/3.0d0+0.1d0*y**5-5.0d0*y**7/42.0d0)
$ + y**9/216.0d0 - y**11/1320.0d0
$ + y**13/9360.0d0 - y**15/75600.0d0
$ + y**17/685440.0d0 - y**19/6894720.0d0)
else
t=1.0d0/(1.0d0+p*y)
  erf=1.0d0-t*(a1+t*(a2+t*(a3+t*(a4+t*a5))))*dexp(-y**2)
end if
if(x .lt. 0) erf=-erf
return
end

C FUNCTION TO CALCULATE THE 2-ELECTRON INTEGRAL
C USING RYS QUADRATURE AND CHEBSHEV-GAUSS
C QUADRATURE
C
function ee(RA,RB,RC,RD,g1,g2,g3,g4,l1,l2,l3,l4)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
dimension RA(3),RB(3),RC(3),RD(3)
REAL*8 N,NA,NB,NC,ND,IX,IY,IZ
PI=DACOS(-1.d0)
A=g1+g2
B=g3+g4
xa=(g1*RA(1)+g2*RB(1))/A
xb=(g3*RC(1)+g4*RD(1))/B
ya=(g1*RA(2)+g2*RB(2))/A
yb=(g3*RC(2)+g4*RD(2))/B
za=(g1*RA(3)+g2*RB(3))/A
zb=(g3*RC(3)+g4*RD(3))/B
rho=A*B/(A+B)
Dx=rho*(xa-xb)**2
Dy=rho*(ya-yb)**2
Dz=rho*(za-zb)**2
X=Dx+Dy+Dz
m=10
c=dsqrt(PI*rho)/dfloat(m)
NA=(2.d0*g1/PI)**.75
NB=(2.d0*g2/PI)**.75
NC=(2.d0*g3/PI)**.75
ND=(2.d0*g4/PI)**.75
if(l1.gt.0) NA=NA*2.d0*dsqrt(g1)
if(l2.gt.0) NB=NB*2.d0*dsqrt(g2)
if(l3.gt.0) NC=NC*2.d0*dsqrt(g3)
if(l4.gt.0) ND=ND*2.d0*dsqrt(g4)
N=NA*NB*NC*ND
sum=0.d0
do i=1,m
t=dcos((2.d0*dfloat(i)-1.d0)*PI/(2.d0*m))
u=dsqrt(rho*t*t/(1.d0-t*t))
n1=0
n2=0
n3=0
n4=0
if (l1.eq.1) n1=1
if (l2.eq.1) n2=1
if (l3.eq.1) n3=1
if (l4.eq.1) n4=1
IX=RIX(n1,n2,n3,n4,u,RA(1),RB(1),RC(1),RD(1),g1,g2,g3,g4)
n1=0
n2=0
n3=0
n4=0
if (l1.eq.2) n1=1
if (l2 .eq. 2) n2=1
if (l3 .eq. 2) n3=1
if (l4 .eq. 2) n4=1
IY=RIX(n1,n2,n3,n4,u,RA(2),RB(2),RC(2),RD(2),g1,g2,g3,g4)
n1=0
n2=0
n3=0
n4=0
if (l1 .eq. 3) n1=1
if (l2 .eq. 3) n2=1
if (l3 .eq. 3) n3=1
if (l4 .eq. 3) n4=1
IZ=RIX(n1,n2,n3,n4,u,RA(3),RB(3),RC(3),RD(3),g1,g2,g3,g4)
sum=sum+IX*IFY*IZ*dexp(-X*t*t)*dsqrt(1.d0-t*t)
enddo
ee=c*N*sum
return
end

FUNCTION TO DETERMINE RIX FOR FUNCTION EE

function RIX(ni,nj,nk,nl,u,xi,xj,xk,xl,ai,aj,ak,al)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
PI=DACOS(-1.d0)
A=ai+aj
B=ak+al
xa=(ai*xi+aj*xj)/A
xb=(ak*xk+al*xl)/B
rho=A*B/(A+B)
t=dsqrt(u**2/(rho+u**2))
d1=(A*B+u**2*(A+B))
ca=((A*xa+B*xb)*u**2+A*B*xa)/d1
cb=((A*xa+B*xb)*u**2+A*B*xb)/d1
Gx=ai*aj/(xi-xj)**2+ak*al/(xk-xl)**2
ci=ca-xi
cj=ca-xj
ck=cb-xk
cl=cb-xl
s1=ni+nj
s2=nk+nl
s12=s1+s2
f1=PI*dexp(-Gx)/dsqrt(A*B)
f2=t**2/(2.d0*(A+B))
if(s12 .le. 1) then
  if(s12 .eq. 0) then
\[ T_1 = f_1 \]
else
\[ T_1 = f_1 \times (n_i \times c_i + n_j \times c_j + n_k \times c_k + n_l \times c_l) \]
endif
else if \( s_{12} \geq 3 \) then
  if \( s_{12} = 4 \) then
  \[ T_1 = f_1 \times (c_i \times c_j \times c_k \times c_l \]
  \[ + (A \times c_i \times c_j + B \times c_k \times c_l)/(2 \times d_0 \times d_1) \]
  \[ + f_2 \times (c_i \times c_j + c_i \times c_k + c_j \times c_k + c_j \times c_l + c_k \times c_l) \]
  \[ + 1.0/(4.0 \times d_0 \times d_1) + 3.0 \times t^2 \times 4/(4.0 \times (A+B)^2) \]
  else
  \[ T_1 = f_1 \times ((n_i \times c_i + n_j \times c_j + n_k \times c_k + n_l \times c_l) \]
  \[ + (B \times (n_i \times n_j \times n_k \times c_k + n_i \times n_j \times n_l \times c_l) + \]
  \[ A \times (n_k \times n_l \times n_i \times c_i + n_k \times n_l \times n_j \times c_j)/((2.0 \times d_0 \times d_1) \]
  \[ + f_2 \times (n_i \times c_i + n_j \times c_j + n_k \times c_k + n_l \times c_l)) \]
  endif
else if \( s_1 = 1 \) then
  \[ T_1 = f_1 \times ((n_i \times c_i \times n_k \times c_k + n_i \times c_i \times n_l \times c_l + n_j \times c_j \times n_k \times c_k + n_j \times c_j \times n_l \times c_l)) \]
else
  \[ T_1 = f_1 \times ((n_i \times c_i \times n_j \times c_j + n_k \times c_k \times n_l \times c_l) + (n_i \times n_j \times n_k \times n_l \times A)/(2.0 \times d_0 \times d_1) + f_2) \]
endif
RlX = T1
return
end

REFERENCES.


VITA

Melissa Renee (Barnick) Prince was born in Gonzales, Texas on June 22, 1967. She completed her secondary education in Gonzales, Texas, graduating as valedictorian of Gonzales High School in 1985. She graduated summa cum laude from Texas Lutheran College with a Bachelor of Science in Mathematics and Chemistry in 1989. In August 1989, she accepted an Alumni Association Fellowship to attend graduate school at Louisiana State University, where she is presently a candidate for the degree of Doctor of Philosophy in the Department of Chemistry.
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Theoretical Studies of Sodium Metal Clusters
Title of Dissertation:

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