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A Prelude to a Third Dimension of the Periodic Table: Superatoms of Aluminum Iodide Clusters

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A Prelude to a Third Dimension of the
Periodic Table:
Superatoms of Aluminum Iodide Clusters

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in Chemical Physics at Virginia Commonwealth University.

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Abstract

A PRELUDE TO A THIRD DIMENSION OF THE PERIODIC TABLE:
SUPERATOMS OF ALUMINUM IODIDE CLUSTERS

By Naiche Owen Jones, Ph.D.

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Physics at Virginia Commonwealth Virginia.

Virginia Commonwealth University, 2006

Director: Shiv N. Khanna, Professor, Department of Physics

Calculations have been carried out to investigate the stability and electronic structure of aluminum iodide clusters using first principles gradient-corrected density functional theory. Analysis of $\text{Al}_{13}\text{I}_x^-$, $\text{Al}_{14}\text{I}_x^-$, and $\text{Al}_7\text{I}^-$ clusters reveals that their stability is governed by the geometrically unperturbed $\text{Al}_{13}^-$, $\text{Al}_{14}^{2+}$, and $\text{Al}_7^+$ units, respectively, that are demonstrated to constitute the compact cores of the clusters upon significant iodine content. The compact, icosahedral $\text{Al}_{13}$, icosahedral-like $\text{Al}_{14}$, and capped square bi-pyramid $\text{Al}_7$ superatom structures of the stable aluminum cores have an analogous electronic configuration to that of halogen, alkaline-earth, and alkaline atoms, respectively. Novel chemistry is demonstrated in superatoms, arising from two primary sources. Firstly, the calculations demonstrate the preference to break molecular $\text{I}_2$ bonds in favor of iodine atoms individually adsorbing onto the aluminum sites of the central aluminum core surface. Secondly, the calculations show that observations of
alternating stability trends dependent on the number of iodine ligands are connected to the formation and quenching of active sites. The significance of the induced active centers on aluminum iodide clusters upon association to alkenes is addressed, demonstrating a method towards predicting the location and extent of binding hydrocarbons. The novel chemistry of superatoms allows for a host of possible applications that integrate their unique properties in original ways and some key examples are described. Superatoms are the analogs to atoms and subsequently, just as the periodic table of elements lists atoms that can assemble into molecules and lattice structures, there exists the fathomable possibility to incorporate superatoms into extended structures such that they maintain their unique properties and result in a new class of materials. Initiation of such cluster-materials insinuates that a cluster-mediated periodic table may be a proper extension to allow for a simple means for conveying fundamental information about clusters.
Chapter 1. Introduction

1.1 Motivation

The properties and nature of bulk systems are scrupulously described by condensed matter physics. Upon the reduction of the dimensional size of bulk solids, the realm of molecules is then encountered. Within an intermediate region between that of numbers of atoms corresponding to those present in molecules and the bulk crystal, one also finds that clusters of atoms exist as a phase of matter. There are distinctions that arise between the basic characteristics of molecules and clusters. Molecules such as O$_2$ and NH$_3$ are generally stable, whereas clusters are generally metastable. Molecules are produced by nature and restricted in size and composition, whereas clusters can be custom-tailored to a wider variety of compositions and sizes. These fundamental differences put clusters of atoms in a league that distinguishes them from molecules and bulk and have made them interesting and exciting to investigate for many years.

A strong surge of advancement and insight into the field of atomic clusters during the last two decades has pushed it to the forefront of modern science [1-6]. Clusters have unique electronic, magnetic, chemical, and optical properties that delicately depend on size and composition that are often inherently different from that of their bulk counterparts. For example, clusters of non-magnetic solids (Rh) can be magnetic [7, 8], clusters of inert solids like Au can be good catalysts [9], and the reactivity can change by orders of magnitude with size. The diversity available in clusters through interactions
between atoms and a higher fraction of exposed surface area relative to the bulk material introduces a family of materials that have novel properties. The properties are governed by effects due to the special electronic and geometrical configurations of the free clusters that test the limits of even our most basic understanding of science. Additionally, clusters have been found to form stable entities [1-2], introducing the concept of custom-tailored materials that offer new kinds of useful properties. Extreme cases of stability present in a cluster species are coined as 'superatoms,' paraphrasing their tendency to exhibit properties similar to that of the elemental atoms, such as the case of the superhalogen Al$_{13}$ [10]. The maintenance of stability in the clusters when assembled as building blocks to form extended structures such as cluster chains, rings, towers, layered and three-dimensional materials is just beginning to be realized both experimentally and theoretically [11-13]. The activity in the field coincides with the need to introduce an outline for a third dimension to the periodic table that has traditionally arranged elements as a two-dimensional array of rows and columns. Consideration of the electronic configuration of superatoms and that of atoms shows analogous behavior between the two and this relationship suggests that the construction of an extension to the periodic table of elements would be appropriate to classify the unique and fascinating properties of superatoms.

Over the years, rapid growth in both experimental and theoretical developments has helped attribute to an expansion of knowledge about clusters. Investigations into clusters have improved on the experimental side due to advances in the characterization and synthesis of clusters. Highly developed multi-photon processes and spectroscopic
methods used in examining atoms, ions, and clusters have aided in research among the fields of science, including physics, chemistry, biology, and materials science and have revealed an unprecedented wealth of information about clusters whose size and composition can now be selected. Advances in high performance computing have allowed computer simulations to model larger, increasingly complex materials that are now the same size scale as those studied in experiments. The use of computer modeling and clever theoretical techniques allows an interpretation of features such as geometrical configurations and electronic construction. Furthermore, theoretical models can be found to give insight into the details about many additional fundamental properties of the observed materials on both the macroscopic and microscopic scale and beyond. The founding of theoretical interpretations induces innovations into all fields of science that outline the importance of understanding the nature of clusters and other materials. The development in raw computational power has allowed theory to help guide and reveal the significance of experimental observations. The current growth trend in computer power and availability of computer resources has allowed the option of replacing some experiments with a computer simulation of the material. Experiment and theory work best in unison and the result of such an effort has the potential to create an explosion of opportunities that were previously unrealized. One such concept is that of introducing new materials with properties that can be utilized towards the synthesis of stable clusters that may serve as the building blocks in forming extended structures with desired characteristics. In such a case, the clusters would be analogous to the atoms and their location within space or in a lattice.
Design of systems that emulate the behavior of atoms in some form has been considered in another modern development. Use of molecular beam epitaxy in sandwiching a material between two layers of another material with a larger band gap (GaAs sandwiched between AlAs layers) forms a quantum well. Electrons confined in such a well can now occupy discrete energy levels and begins to mimic the quantum configuration of electrons in the atomic orbitals surrounding an atom. Furthering the concept of mimicry of an atom is in small regions of one material deposited inside another material with a higher band gap, forming a quantum dot. Quantum dots have been referred to as artificial atoms in the sense that the discrete energy levels are formed in all three dimensions. Clever insertion of the proper materials into another material can result in the confinement of electrons within the dot at a desired potential depth. Changes in the size and shape of the quantum dot allows the spacing and grouping of the discrete energy levels to be controlled, and in addition to the control of the potential depth, the quantum dot can be designed to resemble an atom's electronic structure. Hence, quantum dots can form artificial atoms that have traits that are reminiscent of atoms [14]. The quantum dot, though, inherently requires a material in which it can be imbedded.

However, clusters are often metastable in the gas phase and found to conglomerate when exposed to a material, losing all reference to the initial clusters that formed it. Only selected clusters are stable enough to resist the forces requiring a reconstruction of the cluster geometry to that which more resembles the lattice configuration of the bulk solids. One such example is the fullerene class of structures, including the $C_{60}$ [1,2] and
another example is met-cars [15]. Molecular beam experiments conducted by Kroto and colleagues showed an intense magic peak for clusters containing sixty carbon atoms [1]. They discovered that in addition to graphite and diamond, C\textsubscript{60} is an allotrope of carbon

![C\textsubscript{60} Cluster]

**Figure 1.1:** The geometrical structure of the C\textsubscript{60} cluster.

and forms a hollow spherically shaped network of carbon atoms. A truncated icosahedron structure, containing twelve pentagonal and twenty hexagonal faces leaving sixty vertices that map the carbon atom locations (Figure 1.1). C\textsubscript{60} is known for its marked stability not only in a gas phase cluster chamber but even upon exposure to air, as it is also present in the outdoor environment. Additionally, no two pentagons share an edge within the cluster, thus reducing strain and enhancing its stability due to the \( \text{sp}^{2.28}/\text{s}^{0.09} \) p nature of hybridization. The discovery of fullerenes gave rise to the introduction of carbon nanotubes [3-4], which are also chemically inactive, but can have a high electrical conductivity and tensile strength as well. Many ideas have been proposed that use fullerenes as the model concept, including medicinal delivery, promises of superconductivity, and other nanotechnological applications [16]. Use of
high-energy collision processes have also allowed atoms to be contained within fullerenes in addition to substitution of the carbon atoms with other elements, allowing cage structures with novel properties to ensue [17]. Fullerites, the crystal form of fullerenes, can be formed and are governed by Van der Waals forces that weakly bond the clusters together (Figure 1.2). Although bonding between C$_{60}$ molecules occurs through induced dipole interactions and is inherently weak, the exceptional stability of this molecule and its resistance to reorganization of its geometrical structure upon exposure to air give hope to a class of structures that go beyond allotropes of carbon and may provide a means to realizing novel cluster-assembled materials.

![Image of C$_{60}$ molecules in face centered cubic (fcc) crystal structure](image)

**Figure 1.2:** C$_{60}$ can form a face centered cubic (fcc) crystal structure where bonding between the C$_{60}$ molecules is governed by Van der Waals forces.

The idea of utilizing stable clusters as building blocks in the design of solids can be a daunting task, first proposed by Khanna and Jena [18]. Challenges include the production of mass quantities of clusters in experiments that has become much easier than before due to advancements in cluster synthesis. Additionally, the tendency of
clusters to coalesce upon assembly into a cluster matrix must be reduced in order for the novelty in their properties to be maintained. This involves the identification of a detailed analysis of candidate clusters that are stable enough in their electronic and geometric structure to resist a rearrangement of their geometrical structure in coalescing to a larger complex upon assembly to form a crystal, but are not inert to the point that the only lattice structures that can be formed are those that resemble interactions between the inert gases. A mass spectra experiment conducted over two decades ago by Knight and colleagues found that small sodium clusters produced large peaks at particularly 2, 8, 20, 40, 58, and 92 numbers of Na atoms [19]. The enhanced nature of the peaks is attributed to the electronic shell structure of the Na atoms. Each Na atom has one 3s valence electron and at the peaks corresponding to 2, 8, 18, 20, 40, ... there is a shell closing of s, p, d, ... character, fully explaining the enhanced nature of these peaks in the experiments by use of the jellium model.

The jellium model [20] provides a simple way that considers the free electron picture to look at how the system generally behaves. The model is used to best describe characteristics of spherically symmetric metal clusters. In such a model, a spherically symmetric uniform background potential well of positive charge is used to approximate the effects of the nuclei and innermost electrons present within the metal cluster. The valence electrons of the cluster are then subject to such a potential and form stable configurations for particular numbers of electrons. The highly stable configurations correspond to 2, 8, 18, 20, 34, 40, ... electrons that reveal the magic clusters for the filled energy levels and indicate shell closures and 1s², 1s²1p⁶, 1s²1p⁶1d¹⁰, 1s²1p⁶1d¹⁰2s²,
$1s^21p^61d^{10}2s^21f^{14}$, $1s^21p^61d^{10}2s^21f^{14}2p^6$, ..., which are notably different from the atomic shell closure series. At the shell closures, the electronic character of the cluster closely resembles that of an inert gas atom and could be described as a superatom. In the case of the sodium clusters, Knight et al. found that the jellium model best represented the mass spectra data where the nuclei of the Na atoms in the cluster are regarded as the background potential upon which interaction occurs with the 3s free electrons left in the valence state of the cluster (Fig 1.3). Other experiments have been done that verify the results of Knight et al. in other metal cluster systems [21-22].

![Mass spectra of sodium clusters](image)

**Figure 1.3:** A.) Mass spectra of sodium clusters as conducted by Knight et al. [19]. B.) Peaks corresponding to closed shell orbitals within the jellium model [19].
In addition to filled electronic shells, the consideration of close atomic packing in the geometrical configuration can further enhance the stability of a cluster [18]. The mass spectra experiments by Martin and co-workers [23] on Naₙ clusters for n≤1500 atoms show that there are intense peaks that appear and are attributed to the species of filled electronic shells and for clusters containing up to 22000 atoms, the peaks are attributed to the stability induced by the structure. The highly stable systems arranged in such a manner tend to be of the icosahedral or cuboctahedral geometries [23].

**Figure 1.4:** Figure illustrating the analogous behavior between the electronic shell structure of clusters and those of atoms.
While clusters with filled electronic and geometric shells exhibit enhanced stability, it was Castleman and co-workers [21] who first showed that the electronic shells also govern the chemical behavior of clusters. Clusters of atoms that incorporate both geometrical ideality and a closure in the electronic shell structure are thus predicted to be of the highest order of stable entities in the cluster field and give rise to the notion of superatoms. Figure 1.4 illustrates a comparison that can be made between the atomic and jellium energy levels. Indeed Al_{13}^{-} is found to have an electron affinity comparable to a Cl atom, making it a superhalogen.

Al_{13}^{-} is one such example of a cluster that has both a closed electronic shell and close atomic packing [24]. Mass spectra experiments were carried out to examine the stability of anionic aluminum clusters by etching them with oxygen [21]. When the pure clusters were reacted with a high concentration of oxygen (100ccm), there are two peaks that clearly remain in the spectra, the more intense peak of Al_{13}^{-} and that of Al_{23}^{-}. This experiment clearly shows that the Al_{13}^{-} and Al_{23}^{-} species are resistant to reacting with oxygen molecules. Each Al atom has 3 valence electrons in the configuration 3s^{2}3p^{1}, yielding a total 40 electrons for the Al_{13}^{-} cluster and 70 electrons for the Al_{23}^{-} cluster, including the extra charge of the anions. The jellium model is a useful tool in giving a simple picture of the detailed electronic structure within the actual cluster and it does have its limitations, but it has repeatedly been successful in giving a general description of its features. The jellium model can explain the remarkable stability and resistance to oxygen attack by both clusters where both 40 electrons and 70 electrons correspond to a shell closure. Additionally, the Al_{13}^{-} cluster has an icosahedral geometry that further
enhances its stability (Figure 1.5) and allows it to behave like an inert gas atom, and hence makes it a superatom.

Figure 1.5: Depiction of the ground state geometry of the A$_{13}^-$ cluster.

The concept of the superatom is founded first on the similarity between shell closings pertaining to stable numbers of valence electrons in the jellium model and those shell closings observed in actual atoms that are organized in the periodic table of elements. As shown in the case of A$_{13}^-$, this cluster’s behavior resembles mostly that of an inert gas atom and shows resemblances in chemical character to the inert gases allowing classification of A$_{13}^-$ as a krypton atom. This introduces the notion that there exist stable clusters that behave similarly to atoms that have the same number of electrons needed to fill an electronic orbital. The stable clusters may serve as constituents in an assembled matrix that is similar to the construction of a lattice or other
extended structure by atoms. Hence, cluster-dimers, cluster-molecules, cluster-chains, cluster-rings, and three-dimensional structures built from clusters may be potentially formed to remain stable upon assembly and resistant to oxygen attack. This seems to be a valid direction in further advancing atomic cluster science. Perhaps the field of clusters has evolved such that it is reasonable to consider introducing a third dimension to the periodic table of elements that provides a compilation of the useful information about clusters that behave similarly to their elemental atom counterparts.

In this work, we demonstrate how the characterization of new superatoms provides a wealth of novel chemistry that can be used towards a greater understanding of science. First we will cover the unique behavior of two families of aluminum cluster anions, $\text{Al}_{13}\text{I}_x^-$ and $\text{Al}_{14}\text{I}_x^-$, contrasted with the conventional polyhalide formations that are found naturally. Next, a discussion into the nature of a highly stable neutral and anionic $\text{Al}_7\text{I}^-$ is carried out and introduces for the first time a jellium compound. Finally, we will discuss the extension of the aluminum iodide cluster research towards revealing the nature of including a superhalogen in a reaction with a model hydrocarbon, propene. All of the contributions offered herein provide new insight into superatoms and the novel chemistry that they offer.
Chapter 2. Experimental Procedure

Since the present thesis relies on a synergism between theory and experiment, we first briefly review the experimental procedure. Mass spectrometry is the method referred to within this paper that is used to generate and analyze cluster ions [25]. The mass spectrometer has three main parts, including the ion source, the mass analyzer, and the detector (Fig. 2.1). The ion source is where the clusters are created, the mass analyzer separates the ions by the mass to charge ratio, and the detector allows for detection of the ions there. The experiment allows control of cluster size and temperature. Generation of a spectrum with details on the mass to charge ratio of the ions is the end result that can be used in determining the composition of clusters. It can be used to study ions in the gas phase and allows addition of reactants and analysis thereof.

Clusters are created within a cluster source. There is a rotating sample disk that consists of the material that will be formed into clusters. The disk is struck with a pulsed laser beam (figure 2.2) via the Laser Vaporization (LaVa) technique that will result in forming ions. This happens as refrigerated helium or other inert gas is released into the chamber where the laser beam collides with the rotating drum in order to cool the clusters. The impact of the laser with the drum creates a plume of vapor that contains metal clusters that will be observed. The clusters are allowed a few milliseconds to cool to equilibrium with the helium. This allows the temperature of the clusters to be
calculated. The mixture of the inert gas and metal clusters then seeps out of a nozzle due to a pressure gradient and forms a molecular beam of clusters.

![Diagram]

**Figure 2.1:** A detail of the experimental apparatus used to create mass spectra. The carrier gas is introduced through H, and J shows the flow tube. B is the chamber that holds the quadrupole analyzer and A is the detection chamber. The apparatus allows tweaking of cluster size and temperature [25].

The beam is collimated through a series of small slits on the order of a millimeter wide. As the beam passes the first slit, a chopper is located behind it (figure 2.i). The chopper is a rotating disk that contains a slit along its radius. It rotates about 100 times per second [26]. As the disk rotates, it chops the beam into a small packet about a centimeter long. The clusters are later deflected within a mass analyzer. The deflection occurs in a tube about 1 meter long.
Clusters are deflected in one direction as they go through the magnets. This is due to their finite inertia and an angular momentum. Thus the clusters act as a paramagnetic atom in a sense and are deflected in one direction due to the net force created from the applied magnetic field. There is a deflection distance that is measured for each cluster, with the less massive ions deflecting more than the larger ions. Next, the detector determines the deflection and finds the mass to charge ratio and the final mass spectra can then be created. This requires that the clusters have a charge to be observed; thus neutral clusters cannot be observed.

![Diagram of cluster creation chamber](image)

**Figure 2.2:** Schematic of the cluster creation chamber [26].

Current experimental techniques cannot reveal the geometric structure of the clusters created in the chamber. This brings us to considerations on theoretical methods that can reveal the spatial orientations of the atoms amongst a host of other possibilities.
Chapter 3. Theoretical Method

3.1 Electronic Structure Calculations

The discovery of the electron in 1897 by J. J. Thomson as an elementary particle initiated a revolution in physics and chemistry due to its nature in forming the basic underlying electromagnetic interactions present in the matter that we interact with on an everyday basis. The introduction of the electron at that time as a fundamental constituent of matter raised questions that tested the classical interpretation of how physics behave around us. Niels Bohr made important contributions to describing the stability of atoms and molecules by quantum mechanics that introduced the quantization of discrete energy levels that electrons may occupy on the atomic scale for which he achieved the Nobel Prize in Physics in 1922. Contributions from experiments rigorously tested the theory of quantum mechanics in the following years and increased confidence in the importance of quantum theory of the electronic structure of matter in how it provides a basis upon which further advancements can occur in describing electronic structure.

The need for numerical approximations to aid in theoretical research in clusters of atoms has developed since their initiation to take account for the electron-electron interactions that take place in a many-body system. Any system that includes electron-electron interactions is impossible to solve exactly. Theoretical methods that simplify this problem have been developed in the past and continue to be developed. The jellium
model became well known for its simplicity in spreading the electrons uniformly throughout a volume, but the requirement of more detailed calculations was evident. Current theoretical methods rely on a self-consistent field approximation (SCF), which reduces the problem to a single electron interacting with an average field of the other electrons and nuclei. The Hartree-Fock and density functional methods use the approach of converging the resultant ground state energy by a sequence of SCF cycles.

Electronic structure calculations on matter begin with use of the Schrödinger equation that explains the space and time dependence of quantum mechanical systems. The time-dependent Schrödinger equation is

\[ H(t)|\psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle. \]

In this equation, \( H(t) \) is the time-dependent Hamiltonian operator, \( \psi(t) \) is the associated time-dependent wavefunction, \( t \) denotes the time evolution, and the Dirac notation is adopted. Each state of an instantaneous time element of the system can be mapped into a unit vector element of the complex Hilbert space. Hence the time-dependent Schrödinger equation describes the rate of change of the time-dependent state vector of the Hilbert space.

What is most interesting is that the complexity of the time-dependent Schrödinger equation can be reduced upon the non-inclusion of the time-dependence. Time-independent calculations are of interest herein where the energy distribution remains constant with evolving time. The time-independent Schrödinger equation for a free N-electron system without any relativistic effects can be written as the famous equation
\[ H\psi = E\psi. \]

Here, \( H \) is the time-independent Hamiltonian operator, \( E \) is the electronic energy, and \( \psi = \psi(\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_n) \) is the electron wave function. The coordinates \( \bar{x}_i = \bar{r}_i s_i \) are composed of the discrete electron spin \( s_i \) and spatial coordinates \( \bar{r}_i \). The wavefunction must be a well behaved function and continuous through any boundary conditions. It must also properly decay to zero towards approach of an infinite distance from the particle. Considering molecular electronic interactions, we must account for the kinetic energy in such a system, the attraction experienced between the positively charged nucleus and the negatively charged electrons, as well as any repulsion experienced between electrons due to their like charges. It is also worth noting that \( E \) is the electronic energy and does not include the repulsion experienced between different nuclei. Inclusion of this energy can be considered in the substitution of \( E \) for the total energy \( W = E + V_{nn} \) where \( V_{nn} \) is the potential experienced between the nuclei. This term can be added to the electronic energy at the end of the calculation. Continuing on, the time-independent Hamiltonian operator can be separated into three parts, written as

\[ H = T + V_{ne} + V_{ee}. \]

\( T \) denotes the kinetic energy operator, the nucleus-electron attraction energy operator is \( V_{ne} \), and the electron-electron repulsion operator is \( V_{ee} \). The kinetic energy operator can be written as

\[ T = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2. \]
Now consider an external potential acting on the \( i^{th} \) electron. We are considering the interaction of molecules and atoms, so this external potential can be written as

\[
V_{\text{ext}}(\vec{r}) = v(\vec{r}) = -\sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha}},
\]

where \( Z_{\alpha} \) denotes the atomic number of the nuclei under consideration for \( \alpha \) nuclei in the system. This potential acts on each electron of spin \( \alpha \) or \( \beta \) at the particular spatial coordinate. It is important to note that atomic units are adopted here to facilitate the interpretation of the important variables in the equation. The resulting operator that takes into account the nuclear and electronic attraction takes into account the electrostatic potential each electron experiences due to the nucleus of the atoms,

\[
V_{\text{ne}} = \sum_{i=1}^{N} v(r_i).
\]

The electron-electron repulsion term can be written as

\[
V_{ee} = \sum_{i<j}^{N} \frac{1}{r_{ij}}.
\]

Here, the electron repulsion experienced between electrons of spin up or spin down is accounted for without over-counting by use of the very familiar electrostatic potential. The Hamiltonian operator can thus be conveniently written as

\[
H = -\sum_{\alpha=1}^{N} \frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N} v(\vec{r}_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}.
\]

Inclusion of spin in such a Hamiltonian requires the introduction of a factor of two in the counting to take into consideration the assumption in such a system that the two spin states of the electron are degenerate. Developments in solving the Schrödinger equation
have proceeded throughout the years and require numerical methods to approximate key interactions that simultaneously enable a calculation to complete in a reasonable amount of time and provide accurate final results. Solving the equation allows determination of the electronic energy $E$ and adding to that the repulsion energy between nuclei results in the total energy $W$ of the system. This small amount of information regarding a system can provide an outstanding amount of information on the details of the system in relation to the geometrical configuration that constructs the spatial orientations of the atoms and electronic configuration.

Our focus is to find the true ground state configuration of the system and its resulting energy $E_0$. Now let’s consider the calculation of the electronic energy in determining the ground state energy, where this energy can be determined by the formula

$$E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \int \Psi^* H \Psi \, d\vec{x}.$$ 

Now let’s use the calculation of variartions to expand the wavefunction $\Psi$ into a linear combination of the eigenfunctions of the Hamiltonian transformation operator $H$ such that the orthogonal and normalized $\Psi = \sum_i c_i \psi_i$. Now we can write the energy functional by the following equation,

$$E[\Psi'] = \frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2},$$

where $E_i$ is the energy of the $i^{th}$ eigenvalue of $H$. The absolute ground state of the system $E[\Psi_0] = E_0$ and the other states beyond $i = 0$ are higher in energy. Further proof
of this is shown through the variational principle and use of Lagrange multipliers yielding \( \delta E[\Psi] = \delta \left[ \langle \Psi | H | \Psi \rangle - E \langle \Psi | \Psi \rangle \right] = 0 \) [27]. Numerical procedures follow in solving of this equation for the wavefunction \( \Psi \) as a function of \( E \) and then adjust \( E \) until normalization is realized and the final ground state energy is found. Thus, for a system in the guessed state \( \Psi \), the energy is greater than or equal to the ground state energy, i.e., \( E_0 \leq E[\Psi] \). This means that minimization of the energy functional \( E[\Psi] \) for the allowable \( \Psi \) states will allow for determination of the ground state energy \( E_0 \) that corresponds to the ground state wavefunction \( \Psi_0 \), for only at this point will \( E[\Psi] = E_0 \).

The density functional formalism is used in the convergence of the results presented later, but there have been developments of the many-body systems that also deserve some attention. Hartree had the intuition that a many electron system may be dealt with by interacting a single electron with the combination of the approximating factor of the electrostatic field produced from the averaged charge density of other electrons and the field produced by the nuclei [28] and now we move on to some concepts found in the Hartree-Fock approximation.
3.2 Hartree-Fock

The Hartree-Fock method was first used in 1930 by Fock and uses an approximative procedure to determine the ground state wavefunction and the corresponding ground state energy of many-body systems of various atomic constituents. The beauty of this approximation begins with the notion to write the wavefunction of a many-body system of N electrons as an antisymmetrized determinant known as the Slater determinant and to neglect the contributions due to the spin-orbit interaction. The application of the variational principle allows for the derivation of N equations that describe the behavior of the N electrons involved in the calculation. The Hartree-Fock approximation was implemented to allow for an approximate method via numerical procedure to solve for the ground state of a many-body system by use of the self-consistent field theory. The neglection of electron correlation effects led to improvement of this theory in post Hartree-Fock implementations by use of perturbation theory. The beauty of the approach is that it provided a decent approximative method for its time that used well-established laws of physics without any empirical treatment or models and is known as a true ab-initio code.

The Hartree method follows by minimizing over all N-electron wave functions \( \psi_i \), with a spin and orbital coordinate \((\vec{r}_i, s_i)\), of the form [29]

\[
\Psi_1 (\vec{r}_1, s_1, \vec{r}_2, s_2, ..., \vec{r}_N, s_N) = \psi_1 (\vec{r}_1, s_1) \psi_2 (\vec{r}_2, s_2) ... \psi_N (\vec{r}_N, s_N).
\]
Notice that this equation does not take into account the antisymmetric property of the electrons due to their characterization as fermions. Additionally, it assumes that there is no correlation between electrons. This product of one electron levels represents the Hartree equations,

\[-\frac{\hbar^2}{2m} \nabla^2 \psi_i(\vec{r}) + U^{\text{ion}}(\vec{r}) \psi_i(\vec{r}) + \left[ e^2 \sum_j \int d\vec{r}' \left| \psi_j(\vec{r}') \right|^2 \frac{1}{|\vec{r} - \vec{r}'|} \right] \psi_i(\vec{r}) = \varepsilon \psi_i(\vec{r}).\]

These are the same as those discussed above except that now the Hamiltonian operates on the product of one-electron levels $\psi_i(\vec{r})$. Here the simplification using atomic units is not addressed to show how some of the fundamental constants are placed throughout the equation. The kinetic energy term is found by operating $-\frac{\hbar^2}{2m} \nabla^2$ on each electron wave function $\psi_i(\vec{r})$. The potentials of the ions is embedded in $U^{\text{ion}}$. In the Hartree equations, each electron denoted by $i$ interacts with the average distribution of the other electric field. The potential energy of the interacting electron in their field is given by the term in brackets, which will be denoted by

\[U^{e} = e^2 \sum_j \int d\vec{r}' \left| \psi_j(\vec{r}') \right|^2 \frac{1}{|\vec{r} - \vec{r}'|}.\]

Calculations of the nonlinear wave functions and energies are carried out by use of iterations. A form of $U^{e}$ is guessed and the Hartree equations are solved using the guessed form. The resulting wave functions are used in the next iteration, when an updated form of $U^{e}$ is used. Now the Hartree equations are solved again and this
process repeats until there is a convergence in the energy of the system, which signifies that further iterations will not provide an appreciable change in the potential $U^<$. The Hartree method developed into a wonderful basis for theoretical investigations into many electron interacting systems. It worked well for low atomic number, closed shell systems. It did have shortcomings, although, that were a result of the exclusion of taking into account the antisymmetry of the electrons, the neglect of the Pauli exclusion principle, and no presence of an exchange term.

Fock decided to take account for the antisymmetry of the electrons in developing the Hartree-Fock formalism by use of the Slater determinant [29],

$$\Psi(\vec{r}_1 s_1, \vec{r}_2 s_2, ..., \vec{r}_N s_N) = \frac{1}{(N!)^2} \begin{vmatrix} \psi_1(\vec{r}_1 s_1) & \psi_1(\vec{r}_1 s_2) & \cdots & \psi_1(\vec{r}_1 s_N) \\ \psi_2(\vec{r}_2 s_1) & \psi_2(\vec{r}_2 s_2) & \cdots & \psi_2(\vec{r}_2 s_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\vec{r}_N s_1) & \psi_N(\vec{r}_N s_2) & \cdots & \psi_N(\vec{r}_N s_N) \end{vmatrix}.$$

This replaces the wave function used before that wrote the Hartree equations by use of the product of single electron orbitals. Now, upon the inclusion of Fock’s developments, the $\psi_i(r_i, s_i)$ spin-orbitals are a product of a function of the spatial orientation and spin. The inclusion of the Slater determinant provides compatibility with the Pauli exclusion principle, which states that no two electrons may have the same quantum state. Now we have the correction in the Hartree approach that imposes the fundamental sign change as a result of interchanged arguments within the wave function in order to realize the antisymmetric nature of the electrons. Hence,

$$\Psi(\vec{r}_1 s_1, ..., \vec{r}_j s_j, ..., \vec{r}_N s_N) = -\Psi(\vec{r}_1 s_1, ..., \vec{r}_j s_j, ..., \vec{r}_N s_N).$$
By use of the calculus of variations and the incorporation of Lagrange multipliers, the Hartree-Fock equations are found to be [28-31]

\[
H\psi_i^\sigma(\vec{r}) = \left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\vec{r}) + \sum_{j,\sigma_j} d\vec{r}' \psi_j^{\sigma_j^*}(\vec{r}')\psi_j^{\sigma_j}(\vec{r}') \frac{1}{|\vec{r}' - \vec{r}|}\right] \psi_i^\sigma(\vec{r}) - \ldots
\]

\[
\ldots - \sum_j \int d\vec{r}' \psi_j^{\sigma_j^*}(\vec{r}')\psi_i^\sigma(\vec{r}') \frac{1}{|\vec{r}' - \vec{r}|} \psi_j^{\sigma_j}(\vec{r}) = E_i^\sigma \psi_i^\sigma(\vec{r})
\]

Here, we have reverted back to atomic units for clarity. The one-electron orbitals \(\psi_i^\sigma\) remain as such and note the explicit inclusion of spin \(\sigma\). Fock introduces the last term, the nonlinear, nonlocal exchange term, which is an integral operator that is a direct result of using the Slater determinant in place of the one-electron wave functions. Now, when \(i = j\), the exchange term cancels with the self-interaction term since the antisymmetry of the electrons has been taken into account. This prevents an electron from interacting with itself, and subsequently adds a correction to the Hartree equations. Note that only electron correlations as a result of the Pauli exclusion principle are included in the exchange term. Numerical calculations based on the Hartree-Fock method can be carried out in a self-consistency loop as in the original Hartree method. Results of the Hartree-Fock approach are ideal for atoms and molecules of various types. It is not as well implemented in systems with a much higher quantity of electrons to deal with [30]. This allows for another method to take precedence, the density functional theory.
3.3 Density Functional Theory

3.3.1 Introduction

Many-body systems that have been discussed to this point towards solving electronic structure problems in quantum chemistry and physics use the electron wavefunction as the underlying framework that construct the developments in the Hartree-Fock method. For an N electron system and consideration of the three spatial coordinates, the many-body electron wavefunction is dependent on 3N variables. Fundamentally, density functional theory (DFT) allows for the extraction of physical properties in a system through primarily an analysis of the ground state electron density $n_0(\vec{r})$. With the density functional theory, the 3N variables that construct the many electron distribution wavefunction can be replaced by the electron density, a function of just 3 variables; one for each spatial coordinate $\vec{r}$. The result of this is extensive computational simplifications that still allow for reasonable accuracy in the results.

Originally, the density functional theory is a method proposed in 1927 by Thomas and Fermi. Further developments allowed density functional theory to take off after Hohenberg and Kohn illustrated that there is indeed an existence of one-to-one mapping between the ground state of the electron density and the ground state of the wavefunction of a many-body system. The theorem that they proposed showed that the ground state electron density has a direct correlation to the ground state energy of the many-body system. The studies by Hohenberg and Kohn provided a strong foundation for DFT in
showing that the ground state density can be used to form functionals of it that reveal the characteristics of all properties in a system [32], but only provided existence proofs and functionals carried out on one-electron systems, leaving much to be desired for practical, many-electron use. Kohn and Sham followed up the work, and their contributions allow for a practical use towards understanding the physics of real-world problems through the introduction of approximate methods to finding the ground state functionals of the density in many-electron systems. Kohn and Sham simplified the many-body problem of interacting electrons subjected to an external potential to that of non-interacting electrons moving through an effective potential through clever use of a slowly varying electron density [33]. Contributions in the past few decades have increased the accuracy of DFT calculations through advancements in better approximative measures of modeling the exchange and correlation contributions to the total energy of the system. Regardless of the popularity of DFT, it does have some drawbacks. The van der Waals forces of interacting closed shell systems are not accurately described by DFT. A result of this is that DFT cannot be accurately used in calculations on many biochemistry related problems. There is research that is being carried out during the present day that considers the inclusion of additional terms in the functional to allow for a better description of the behavior of such systems.
3.3.2 Thomas and Fermi Contributions

Conceptually, the density functional theory originated with the work done by Thomas and Fermi [31, 34, 35]. In their work, the kinetic energy of the many-particle system was approximated by use of the electron density as the functional in combination with a classical treatment of the electron-electron and nuclear-electron interactions. The kinetic energy as a functional of the density is written as

\[ T_{TF}(n(\vec{r})) = C_1 \int n(\vec{r})^{5/3} d\vec{r}, \]

where \( C_1 \) is a constant. The Thomas and Fermi contributions did not take into consideration the exchange or correlation of the electrons, but Dirac later added this in 1930 [36]. The energy formula for electrons in an external potential \( V_{ext} \) is the result and given by the following,

\[ E_{TF}[n(\vec{r})] = C_1 \int d\vec{r} n(\vec{r})^{5/3} + \int d\vec{r} V_{ext}(\vec{r}) n(\vec{r}) + ... \]
\[ ... + C_2 \int d\vec{r} n(\vec{r})^{4/3} + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} \]

Note that this is written only in terms of the electron density \( n(\vec{r}) \). The first term is the local approximation to the kinetic energy, the second term considers the active behavior of the external potential, the third term is the local exchange term approximation, and the fourth and final term is the electrostatic energy similar to what is found in the Hartree equations.
Minimizing the energy functional \( E_{TF}[n(\vec{r})] \) yields the ground state density and corresponding ground state energy of the system provided that the constraint of finding the total number of electrons \( N \) by integrating the over the density. The method of Lagrange multipliers yields the solution to this as minimization of the following functional which arises from the variational principle for small variations in the density,

\[
\delta \left\{ E_{TF}[n] - \mu_{TF} \left( \int n(\vec{r}) d\vec{r} - N \right) \right\} = 0.
\]

The \( \mu_{TF} = \frac{\delta E_{TF}[n(\vec{r})]}{\delta n(\vec{r})} \) is the Lagrange multiplier and corresponds to the Fermi energy. This forms the Euler-Lagrange equation that can be written of the form,

\[
\frac{1}{2} (3\pi^2)^{2/3} n(\vec{r})^{2/3} + V(\vec{r}) - \mu_{TF} = 0.
\]

The \( V(\vec{r}) = V_{ext}(\vec{r}) + V_{Hartree}(\vec{r}) + V_{exchange}(\vec{r}) \) term is the total potential. The result in this equation can be solved under the constraint proposed above that the total electrons \( N \) as a functional of the density is equal to the integration over the density for all spatial coordinates. The electron density found in this manner can then be used in the relation to solve for the energy of the system as given by \( E_{TF}[n] \).

The Thomas-Fermi method can yield reasonable results for atoms, but upon considering larger systems leading up to molecules, the basic premise of the theory falls short of expectations. It shows that the system of \( 3N \) degrees of freedom found in the Hartree approach can be reduced to 3 degrees of freedom by use as the density as a functional. But the model is oversimplified due to the neglect of electron correlation and
inaccuracies in the exchange energy that was used leaving a result that does not provide a realistic interpretation of real-world problems.

### 3.3.3 Hohenberg and Kohn Theorems

This brings us to a discussion of the contributions that Hohenberg and Kohn realized in developing their theorems. The framework of density functional theory is based on the two theorems that they proved in their paper [32]. Theorem I states that “The external potential $v(\vec{r})$ is determined, within a trivial additive constant, by the electron density $n(\vec{r})$ [31, 32].” The density $n(\vec{r})$ can allow for the determination of the number of electrons $N$ in a system by

$$N = N[n(\vec{r})] = \int d\vec{r} n(\vec{r}),$$

thus as a direct result of this, the ground state energy $E_0$ of the system can be determined by the corresponding ground state electron density $n_0$ and is also a direct relation to the ground state many-electron wavefunction. Subsequently, all electronic properties can be determined from the electron density.

Hohenberg and Kohn show the proof of the first theorem through contradiction. Consider two potentials $V_1$ and $V_2$ that differ by more than a constant and each give the same density $n$ such that there would also be two Hamiltonians $H_1$ and $H_2$ that also have the same ground state densities. By use of the result found by the variational principle that shows $E_0 \leq E[\Psi]$ we find that the following relations ensue,
\[ E_0^1 < \langle \Psi' | H_1 | \Psi' \rangle = \langle \Psi' | H_2 | \Psi' \rangle + \langle \Psi' | H_1 - H_2 | \Psi' \rangle = E_0^2 + \int d\vec{r} n(\vec{r}) \left[ v_1(\vec{r}) - v_2(\vec{r}) \right] \]

and
\[ E_0^2 < \langle \Psi | H_1 | \Psi \rangle = \langle \Psi | H_2 | \Psi \rangle + \langle \Psi | H_1 - H_2 | \Psi \rangle = E_0^1 - \int d\vec{r} n(\vec{r}) \left[ v_1(\vec{r}) - v_2(\vec{r}) \right]. \]

The ground state energies of \( H_1 \) and \( H_2 \) are \( E_0^1 \) and \( E_0^2 \), respectively. Adding these two equations and rearranging results in \( E_0^1 + E_0^2 < E_0^2 + E_0^1 \) which is an invalid, contradictory statement. Thus, there cannot be two different potentials \( V_1 \) and \( V_2 \) that differ by more than just a constant that give the same ground state density \( n_0 \). Thus, for any system of interacting potentials, the second Hohenberg-Kohn theorem holds and can also be extended to show that given the ground state electron density, all properties of the system can be determined.

Now let’s consider the second Hohenberg-Kohn theorem, that states “For a trial density \( n(\vec{r}) \), such that \( n(\vec{r}) \geq 0 \) and \( \int d\vec{r} n(\vec{r}) = N, \ E_0 \leq E_v[n] \) [31, 32].” Also,
\[ E_v = T[n] + V_{\text{ex}}[n] + V_{\text{es}}[n]. \]

This theorem states that under the constraints considered, the electron density as a functional of the energy can be written, and the ground state electron density subsequently is a functional of the global minimum energy of the system for any external potential. Now let’s consider how Hohenberg and Kohn set forth to prove their second theorem. Consider each property of a system of particles, including the Hohenberg-Kohn energy, as a functional of the electron density \( n(\vec{r}) \) such that
\[ E_{\text{HK}}[n] = T[n] + E_{\text{int}}[n] + \int d\vec{r} V_{\text{ext}}(\vec{r}) n(\vec{r}) + E_{\text{el}}. \]

The \( F_{\text{HK}} \) term includes all internal energies and kinetic energies of the interacting electrons present in the system of particles. Now consider the ground state electron
density $n^i_0(\vec{r})$ for an external potential $V^{i}_{eo}(\vec{r})$. The resulting Hohenberg-Kohn energy functional is the expectation value of the Hamiltonian corresponding to the ground state, and for a wavefunction $\Psi^i$ we have $E^i = E_{HK} [n^i_0] = \langle \Psi^i | H | \Psi^i \rangle$. For another density, it immediately follows that the subsequent energy of the next state will be greater in energy than $E^1$ and subsequently, $E_0 < E_1 < E_2$, just as the second theorem states. It is also worth noting that if complete knowledge of the kinetic and internal energies are known, exact determination of the fundamental properties, the ground state density and energy, would be possible. Now we move on to the developments by Kohn and Sham in providing a density functional theory that can be used in calculations for complex many-particle systems.

3.3.4 Insight of Kohn and Sham

The approach by Kohn and Sham in 1965 has allowed density functional theory to take precedence as one of the most popular methods for electronic structure calculations today. The formulation of the resulting equations provided a means to evaluate the ground state energy, density, and other parameters of a many-body system such that the inaccuracies only form as a result of the necessary approximations made to the exchange-correlation energy functional. We shall now begin our journey towards briefly showing the existence of the Kohn-Sham equations.
The density functional theory uses the electron density $n(\vec{r})$ as a variational parameter, developed by the work of Hohenberg, Kohn, and Sham. We may begin by writing out the electron density, dependent on the spatial and spin $\sigma$ coordinates, as

$$n(\vec{r},\sigma) = \sum_{\sigma} \sum_{i=1}^{N^\sigma} |\psi_i^\sigma(\vec{r})|^2.$$  

$N = N^a + N^b$ represents the number of electrons in the system and $\psi_i$ are the one-electron orbitals. We must find solutions to the density dependent Schrödinger equation, for the one-electron spin orbitals that are self-consistent in the electron density.

The total energy of the system, as derived by Kohn and Shom, has the form [31]

$$E_{KS} = T_s [n(\vec{r})] + \int d\vec{r} V_{\text{ext}}(\vec{r}) n(\vec{r}) + E_{\text{Hartree}} + E_{\Pi} + E_{xc}[n(\vec{r})].$$  

$E_{\Pi}$ is the energy due to the interactions between nuclei and $V_{\text{ext}}$ is the external potential due to the nuclei. The kinetic energy term is $T_s$ and is given by

$$T_s = -\frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N^\sigma} \langle \psi_i^\sigma | \nabla^2 | \psi_i^\sigma \rangle = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N^\sigma} \int d\vec{r} |\nabla \psi_i^\sigma(\vec{r})|^2.$$  

The Hartree energy is simply the following formula,

$$E_{\text{Hartree}} = \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|}.$$  

The exchange and correlation effects are included in the $E_{xc}$ term that is dependent on the electron density. The exchange and correlation effects takes into account the Pauli Exclusion Principle, forbidding electrons with the same spin from occupying the same state, as well as providing a Coulombic repulsion between electrons. The Hartree-Fock theory neglects the correlation effects from Coulomb repulsion between the electrons,
and here DFT carefully analyzes them within the description of the energy of the system. The $E_{xc}$ term can be conveniently written as

$$E_{xc}[n] = \langle T \rangle - T_{s}[n] + \langle V_{in} \rangle - E_{Hartree}[n].$$

This form of the exchange correlation shows the explicit dependence on the spatial and spin coordinates of the density functional term. Also, we can see here that exchange-correlation term is the difference between the kinetic and internal energies of the real system and that of the modeled versions for these, where $E_{Hartree}$ provides information about the electron-electron repulsion. Furthermore, this shows that if we can have an exact formulation of the exchange energy term, the exact ground state electron density may also be known, and through mapping the results there, the exact ground state energy and other properties may also be found. This, however, is not possible, due to the complex nature of the exchange-correlation term and leaves us to make approximations to this term for calculations.

Further analysis shows that the following relations can be determined [31],

$$\frac{\delta T_s}{\delta \psi_i^{\sigma}(\vec{r})} = -\frac{1}{2} \nabla^2 \psi_i^{\sigma}(\vec{r}) \text{ and } \frac{\delta n_i^{\sigma}}{\delta \psi_i^{\sigma}(\vec{r})} = \psi_i^{\sigma}(\vec{r}).$$

The constraint imposed by orthonormalization, $\langle \psi_i^{\sigma}(\vec{r}) | \psi_i^{\sigma}(\vec{r}) \rangle = \delta_{\sigma,\sigma} \delta_{i,i}$, can be treated by method of Lagrange multipliers towards deriving the following Kohn-Sham Schrödinger relations via the above equations with eigenvalues as $\epsilon_i$,

$$H_{KS}^{\sigma} \psi_i^{\sigma}(\vec{r}) = \epsilon_i^{\sigma} \psi_i^{\sigma}(\vec{r}).$$

The Kohn-Sham Hamiltonian $H_{KS}$ can be determined by [31, 33]
\[ H_{KS}^{\sigma}(\tilde{r}) = -\frac{1}{2} \nabla^2 + V_{KS}(\tilde{r}) \text{ where} \]

\[ V_{KS}^{\sigma}(\tilde{r}) = V_{\text{ext}}(\tilde{r}) + V_{\text{Hartree}}(\tilde{r}) + V_{\text{xc}}^{\sigma}(\tilde{r}). \]

The Hartree and exchange-correlation potentials may be written as

\[ V_{\text{Hartree}}(\tilde{r}) = \frac{\delta E_{\text{Hartree}}}{\delta n(\tilde{r})} \] and \[ V_{\text{xc}}^{\sigma}(\tilde{r}) = \frac{\delta E_{\text{xc}}}{\delta n(\tilde{r})}. \]

The Kohn-Sham equations coupled with the Hohenberg-Kohn theorems provided an important leap towards density functional theory becoming the widely used tool that it is today. Their method of separating out the kinetic energy and Hartree energy terms, subsequently allowing for the development of methods of finding the exchange-correlation energy through local approximations of the electron density is attributed to the great merit of their theory. Further insight into the behavior of the exchange-correlation energy allowed derivation of more accurate approximate methods of solving for this term.

DFT iterations are carried out by solving the density dependent, many-body, DFT Schrödinger equation by first guessing a value of the electron density \( n(\tilde{r}) \). The calculations are carried out, formulating a new Schrödinger equation where a new electron density may be obtained. This is continued until there is no appreciable variance in the electron density through the self-consistent field approach. From here, the total energy may be calculated to obtain the ground state energy of the system by use of the eigenvalues found in the converged DFT wave equations.
3.4 NRLMOL Code

Within the framework of the density functional theory, the NRLMOL (Naval Research Laboratory Molecular Orbital Library) code was developed by M. R. Pederson et al [37-39]. This code was used to provide the calculations presented here. It makes calculations by determination of an accurate and efficient charge density integration mesh that incorporates the atomic sites and interstitial regions. The atomic site regions are included by use of an atomic sphere integration mesh. The accuracy of the integration mesh increases exponentially as the radial mesh points on the atomic spheres are incremented. Gaussian functions are the basis sets centered at the atomic sites in the calculation and accurately express the electronic orbitals. The electron spin density atomic spheres are integrated over to yield the local magnetic moment at each atomic site.

Concerning all of the calculations discussed within this document, first-principles calculations were conducted within the density functional theory framework by use of the NRLMOL set of codes [37-39], which calculates the molecular orbitals by using a linear combination of atomic orbitals that are created by Gaussian functions that are centered on atomic sites. PBE generalized gradient approximations were included as gradient corrections to allow for the exchange and correlation contributions to be included [40] in the potential and energy. The NRLMOL code creates a mesh of points that is numerically integrated over to obtain the Hamiltonian matrix elements. The basis set for Al atoms had 6s, 5p, and 3d Gaussians and the I atoms had 8s, 7p, and 5d Gaussians. A
d Gaussian function was chosen to supplement the chosen basis [37-39]. Geometrical optimization was carried out on all clusters by calculating Hellmann-Feynman forces and moving the atoms in the direction of the forces after each self-consistent loop until the forces drop below a threshold of 0.001 Hartree/bohr. When this state has been reached, the program converges and the final geometrical configuration is given as output for the ground state of the cluster. The program requires various initial geometrical configurations for each cluster to be submitted until the final ground state structure is obtained.
Chapter 4. The Al\textsubscript{13}I\textsuperscript{−} Cluster

4.1 Al\textsubscript{13} – A Superhalogen

A cluster derives its stability from two factors. First, a geometric contribution in that clusters with compact geometries are more stable. Secondly, clusters that have electronic arrangements that form a closed electronic shell are more stable. Al\textsubscript{13}\textsuperscript{−} is a cluster that satisfies both these criteria, namely that it has an icosahedral geometrical structure and filled electronic structure according to the jellium model. Its closed electronic shell allows it to behave as an inert entity. More importantly, it has a shell structure of 1s\textsuperscript{2}p\textsuperscript{6}d\textsuperscript{10}2s\textsuperscript{2}1f\textsuperscript{4}2p\textsuperscript{5} that is analogous to halogen atoms. Indeed it has an adiabatic electron affinity (AEA) of 3.4eV [41] and from experiments the AEA is measured to be 3.57eV [42]. Of all of the halogens on the periodic table, the AEA of Al\textsubscript{13} by the experimental results is closest to that of a chlorine atom, which has an AEA of 3.61eV [43] and by comparison with the theoretical calculation, the AEA is closest to that of Br, with 3.36eV [44]. This presents the question as to what happens when interaction takes place between Al\textsubscript{13}, an extra electron, and a halogen with a large atomic radius of about 140pm, such as an iodine atom that has an electron affinity of 3.06eV [45]. There are many features that will be of importance in such an investigation. Of main importance is whether the presence of the I atom distorts in any way the geometry of the Al\textsubscript{13} cluster and how is the extra electronic charge in the highest occupied molecular orbital (HOMO) distributed about the cluster. Bergeron et al. carried out
investigations into probing the very essence of the characteristics that entail in acid etching experiments that revealed the $\text{Al}_{13}\Gamma$ cluster [10, 46].

Experiments were carried out analyzing the reaction of Al clusters with HI in various flow rates (Figure 4.1.1) [10, 46]. As the volumetric flow rate is increased to 200 standard cubic centimeters per minute (sccm) of 10% HI seeded in He, there are four intense peaks that remain in the spectra, labeled as $\text{Al}_{13}\Gamma^-$, $\text{Al}_{13}\Gamma$, $\text{Al}_{13}\Gamma^-$, and $\text{Al}_{14}\Gamma$ (Figure 4.1.1C). The mere presence of these four peaks in such high concentrations of HI indicates their nonreactive tendency with HI. Of the four “magic” peaks, the most intense is that belonging to the $\text{Al}_{13}\Gamma$ cluster, showing that it can be easily produced and that it is highly stable with regards to etching with HI. Supplemental oxygen etching experiments were done that showed an increase in intensity in the molecular beam upon increasing the volumetric flow rate of oxygen, finalizing the verdict of outstanding stability in the $\text{Al}_{13}\Gamma$ cluster [10, 46]. Theoretical first-principles calculations concluded that the icosahedral structure of $\text{Al}_{13}\Gamma^-$ remained intact (Fig 4.1.2). Remarkably, the extra electronic charge in the HOMO orbital was shown to be concentrated mainly about the $\text{Al}_{13}$ cluster in a position about the vertex opposite of the on top site location of the iodine atom (Fig 4.1.3). This introduced evidence that suggests the $\text{Al}_{13}$ core resembles that of a halogen atom, and acts as a superhalogen in the complex. Thus the stability of the cluster is due to the maintenance of its geometry and the 40-electron shell closure within the jellium model that corresponds to $\text{Al}_{13}\Gamma^-$ due to the extra electronic charge that is still situated mainly about the aluminum cluster.
Figure 4.1.1: Mass spectra details showing the reaction of the A.) pure aluminum clusters with B.) 25sccm and C.) 200sccm of 10% HI in He. The y-axis is the peak intensity [10].
**Figure 4.1.2:** The ground state geometry of the $\text{Al}_{13}\Gamma$ cluster [10].

**Figure 4.1.3:** Highest occupied molecular orbital (HOMO) charge density map of the $\text{Al}_{13}\Gamma$ cluster[10].
4.2 Thoughts Revolving around Al$_{13}$I$^-$

That which remains to be seen is the nature of stability in the other clusters present in the spectra. The staying power of Al$_{13}$I$^-$ within the mass spectra experiments was not surprising since its highly stable nature and nonreactive behavior have been carefully studied and concluded. Of particular interest is the Al$_7$I$_3^-$ and Al$_{14}$I$_3^-$, both of which are present as magic peaks. Further analysis of Al$_7$I$_3^-$ must be taken into consideration in identifying the reasoning behind its stability. The Al$_7$ cluster on the surface may appear to be accurately represented as a species where there are 3 free electrons from the 3s$^2$ 3p$^1$ configuration of the valence electrons. Al$_7$ has six fewer Al atoms contributing to its characteristics as Al$_{13}$ and considerations into the extent of sp mixing must be taken into consideration, given that the 3s$^2$ orbital is completely occupied and may not provide the necessary overlap within the cluster to allow the two electrons found there to be considered as free electrons in a model representative of a confined nearly free electron gas such as the jellium model. So it is necessary to address this in a calculation and consider each atom within the small cluster to contain one free electron that may be used in a simpler model to grasp a general picture to account for the stability of such a cluster as Al$_7$I$_3^-$. It was found that if the Al$_7$I$^-$ cluster can be looked at within such a model where there are eight free electrons present including one due to the anionic charge. This description allows the pure anionic cluster to be classified as stable within the jellium description since there is a shell closure present at 8 electrons [47]. For the case at hand here, this could give a nice picture of the Al$_7$I$_3^-$ cluster if one were to assume
that the electronic charge were to remain in a cloud mostly on the Al\textsubscript{7} cluster. The problem with such an assumption is that the Al\textsubscript{7} cluster has a much lower electron affinity than Al\textsubscript{13} and indeed also lower than that of an iodine atom. Additionally, the geometric structure of the Al\textsubscript{7}\textsuperscript{-} is that closest resembling a capped octahedron. This is a far cry from the compact geometry in the icosahedral structure of Al\textsubscript{13}\textsuperscript{-}. This suggests that a single iodine atom may take the charge in order to fill its 5p orbital, leaving a possibly less stable Al\textsubscript{7} core. Under the presence of multiple iodines, it may be preferable by such a model described here to dissociate the cluster into Al\textsubscript{II} and pure Al\textsubscript{I} parts or to induce a perturbation to the Al\textsubscript{7} core. The jellium model best describes shell-closures within a spherically symmetric potential, although a wider range of potentials such as the square well and three-dimensional harmonic oscillator potentials also produce closings at 2, 8, 18, 20, 34, 40,... electrons. A possible problem here is that the geometry of the Al\textsubscript{7} cluster could become distorted to an extent that the use of the jellium model would not be an accurate representation. Even if the structure of Al\textsubscript{7}I\textsubscript{3}\textsuperscript{-} were to be maintained upon adsorption of three I atoms, it does not appear likely that reasoning according to a nonexistent mixing of s-p states could provide a completely explanatory picture as to the nature of the Al\textsubscript{7}I\textsubscript{3}\textsuperscript{-} cluster that would be representative of the stability witnessed in the experiments.

It is then natural to propose another possibility that may be more evident upon a detailed investigation. Ionized mass spectra experiments producing cationic aluminum clusters have shown Al\textsubscript{7}\textsuperscript{+} to be highly stable [48]. Although the structure of the Al\textsubscript{7}\textsuperscript{+} cluster is a face-capped octahedron and is not completely spherical in nature, it is still
possible to use the jellium model as a brief description of such a cluster. Considering that there could be substantial mixing in the s-p states (which would require a detailed investigation into the density of states of the geometrically optimized cluster) of each Al atom, we can conclude that there would be 21 free electrons that can be modeled by the jellium picture corresponding to Al$_7$ and 20 electrons including the ejected electron to form the free electron gas representation in Al$_7^+$. Twenty electrons correspond to an electron shell closing by the jellium model and help to fathom some reasoning behind the enhanced stability seen within the experiment. This introduces the question regarding whether the Al$_7$ core in Al$_7$I$_3^-$ can closely resemble that of Al$_7^+$ in some form. Or is it the case that Al$_7^-$ has stability that hinges on some feature in the bonding or electronic levels that extends into the neutral cluster and is further enhanced by the presence of iodine atoms?

A measurement of the energy gap, the difference between the HOMO and lowest unoccupied molecular orbital (LUMO), gives some insight into the stability of such a cluster. A high HOMO-LUMO gap indicates a highly stable nature of the molecule under observation since its levels more closely resemble that of an inert gas atom. Furthermore, there is the possibility that clusters such as Al$_7$I$_3$ are indeed highly stable as neutrals where the Al$_7^{3+}$ core is formed, corresponding to a shell-closure at 18 electrons, and there is electron transfer in a direction towards the iodines. Maybe this would suggest that such stable neutral molecules are the true entities that harness the stability and are simply resistant to a geometrical transformation after the process of negative ionization occurs and can show up in the experimental spectra that are limited to
displaying charged species. This introduces the notion that there may be a complete series of $\text{Al}_7\text{I}_3^-$ clusters that pivot on the maintenance of a stable cationically charged $\text{Al}_7$ core that corresponds to a shell closing within the jellium model as iodine atoms decorate the surface of the $\text{Al}_7$ core with minimal perturbation of its geometry. There could also be an interesting nature to the dipole moments formed in the cluster due to charge transfer that would take place from the $\text{Al}_7$ core to the iodines that can be explained in a simple model within the framework of a greater all-encompassing theory. This provides a reasonable network of ideas considered throughout the investigation into the nature of this highly stable cluster. Any or none of these ideas could have potentially been a valid interpretation but it is useful to consider a variety of possibilities before setting off to complete the work. All of these details were analyzed by use of density functional theory methods to allow for a conclusive solution to this problem.

There is also the case of the $\text{Al}_{14}\text{I}_3^-$ presence in the molecular beams. There are a variety of reasons that one can imagine that help begin a more detailed explanation into the nature of this cluster. In oxygen etching experiments, $\text{Al}_{14}^-$ does not appear as an intense peak in the mass spectra [21] upon exposure to oxygen, whereas the significant $\text{Al}_{13}^-$ remains. R. L. Johnston et al. conducted a search using model potentials and a genetic algorithm to narrow down the number of structures that can pertain to a closer representation of a possible ground state of aluminum clusters [49]. These resultant low energy clusters found by use of the classical potentials are generally cage-like and spherical, being adequate candidates for an investigation using the jellium model. Additionally, the geometry of $\text{Al}_{14}$ could be simply described by that of an icosahedral
Al_{13} unit with an Al atom capping one of the triangular faces. An investigation into
many other structures, including a distorted dodecahedron-like structure was carried out
to determine the true ground state of the Al_{14} cluster and its anionic counterpart.

Nonetheless, one can deduce the free valence electron count within an Al_{14} cluster to be 43. It is likely that the additional Al atom bonded to the Al_{13} cluster would
perturb the geometry of both the anion and the neutral and reduce the high AEA of the
Al_{13} cluster, allowing Al_{14} to become a charge donor in the presence of a highly
electronnegative species such as iodine. Thus the Al_{14}I_{3}^{-} cluster could prefer an Al_{14}^{2+}
core decorated in some manner by iodine atoms about the core, which accumulate charge
to fill their outermost orbital by charge transfer. Such a core would be in agreement with
a shell closure of forty electrons in the jellium picture and could help explain the stability
of such a cluster. A detailed analysis within the DFT framework of the electronic
structure and geometrical configuration, even an inclusion of spin-polarized effects must
be conducted to determine the exact nature of the stability in this cluster. An inclusion of
calculations on other clusters that may give more clues, including Al_{14}I^{-}, Al_{14}I_{2}^{-}, Al_{14}I_{3}^{-},
Al_{13}I_{2}^{-}, Al_{13}I_{3}^{-}, and Al_{14}I_{4}^{-} must also be considered. The determination of the ground
states of these clusters were concluded only after a very thorough investigation into
possible structures, some of which include cage-like behavior and distorted shapes, with
I_{n} bonds intact and broken, etc. Everything must be taken into consideration in order to
determine if there is any possibility of an Al_{14}^{2+} core.

The presence of such a core is of significance in introducing the possibility that
there may be something more present in the mass spectra of the positively charged
aluminum cluster ions [48] that the experiment would not be able to differentiate. Within the mass spectra experiment, upon contact with the detector, the mass to charge ratio can be deduced. It is not impossible that the ion source could doubly ionize some clusters, including Al$_{14}$, which would lead to the presence of Al$_{14}^{2+}$ in the beams as part of the intense peak present for Al$_7^+$ due to the same mass to charge ratio. It would be interesting if firm reasoning can be found that would allow an investigation into this possibility as well. The many fascinating possibilities ensuing from the observations in the aluminum iodide clusters brings us to a complete theoretical analysis of oxygen etching experiments on an entire series of stable entities that may arise under such conditions, leading us to the impact of the theoretical work centered on Al$_{13}$I$_x^-$ and Al$_{14}$I$_x^-$ clusters.
Chapter 5. The Nature of Aluminum Iodide Clusters

5.1 $\text{Al}_{13}\text{I}_x^-$ (x=1-12)

Calculations were carried out in order to pinpoint the most interesting characteristics of the novel behavior of the aluminum iodide clusters and describe the inner-workings of the nature that produces such results within a simple model [50, 51]. A precursor to a detailed investigation of the aluminum iodide clusters requires an independent study on the stability present in the Al$_{13}$I$^-$ cluster. A variety of structural compositions of the aluminum cluster moiety were performed, including dodecahedral, icosahedral, and non-cage-like structures. In agreement with previous results, it was found that the neutral Al$_{13}$ cluster has an electron affinity of 3.35eV and the geometrical structure is icosahedral in its ground state with an Al-Al bond length of 2.80 angstroms. Next, a detailed analysis considering a multitude of initial geometrical configurations was optimized with the NRLMOL code for the Al$_{13}$I$^-$ cluster. The most interesting structures investigated include various configurations of I about the bridge, on top, and triangular face sites. Upon optimization of the geometry, the on top orientation of the Al$_{13}$I$^-$ cluster was found, in agreement of the previous results [10, 46]. Also in agreement is the HOMO charge density of Al$_{13}$I$^-$ indicating an accumulation of the negative charge cloud in the HOMO occupation about the Al atom at the vertex opposite to the position
of the Al atom upon which I adsorbs as in figure 4.1.3. The HOMO-LUMO gap is 0.7eV and the dissociation energy of a neutral I atom is found to be 2.48eV.

Next, calculations were carried out simulating a host of structures for the Al$_{13}$I$_2^-$, Al$_{13}$I$_3^-$, and Al$_{13}$I$_4^-$ clusters. The most interesting results of some of the various isomers are tabulated in figure 5.1.1. Note that the ground state, indicated by GS in the figure, maintains an icosahedral Al$_{13}$ core for all cases. The question regarding the nature of binding of the iodine atoms can be answered here. The traditional arrangement of iodine molecules in polyiodides consists of branching chain geometries [52] with building blocks of I, I$_2^-$, and I$_3^-$ forming the series of I$_{2n+1}^-$ (n=0,1,2,...) for extended molecules. Thus it is interesting to carry out an investigation into this with the introduction of a single Al$_{13}^-$ cluster as a replacement for one of the iodine atoms in the chain structures found in nature for the I$_{2n+1}^-$ series. This allows for a comparison to what we know about I$_{2n+1}^-$ chain construction. The calculations leading to the structures shown in figure 5.1.1 show that the preservation of the molecular iodine is not maintained upon its adsorption. The I$_2$ bond is broken to form Al-I bonds within the structure as indicated by the lower energy geometries shown in figure 5.1.1 that have intact Al-I bonds. The energies of the isomers with intact I$_2$ configurations are higher in energy than the ground state by 2.13eV for Al$_{13}$I$_2^-$ and 1.73eV for Al$_{13}$I$_3^-$. Additionally, the geometry optimized isomer containing an I$_2$ unit for Al$_{13}$I$_4^-$ is 2.21eV higher in energy than the ground state. This preponderance of Al-I bonds within the ground state structures of these four clusters provides a convincing argument to the formation of the stable series of aluminum clusters by etching larger clusters according to the reaction
\[ \text{Al}_n^+ + I_2 \rightarrow \text{Al}_{n+1}I + \text{Al} \]

This simple chemical reaction equation is in agreement with the observation that most of the clusters are formed by additively adsorbing a single I atom without noticeable presence of I\(_2\) units in the series. This does not provide any information about the reason for preference in the addition of single iodine atom units within the series. Also, there must be an explanation for why the clusters in the series that have an even number of iodine atoms are more stable than those clusters having an odd number of iodine atoms.

It is best to start as simple as possible in order to fulfill a more thorough analysis regarding the lack of I\(_2\) units present in the clusters due to preference to form Al-I bonds. Let's begin the argument considering the energetics in simple units of I\(_2\), All, and All\(_3\). The I\(_2\) molecule has an atomization energy (AE) of 2.21eV and the All molecule has an AE of 3.83eV, both detailed in table 5.1.1. This shows that All bonds are inherently stronger than I-I bonds at the molecular level. Also consider the stable entity of All\(_3\), which has an AE of 8.75eV such that the average bond strength of the Al-I units is 2.92eV. Again, this shows that Al-I bonding is stronger than that of I-I bonding. Energetically, the favorability of breaking I\(_2\) bonds and forming All bonds is clear starting from the most basic molecular comparison. This general claim does indeed continue for all clusters within the Al\(_{13}\)I\(_x^+\) series.
<table>
<thead>
<tr>
<th>Cluster</th>
<th>Atomization Energy (AE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I₂</td>
<td>2.21eV</td>
</tr>
<tr>
<td>AlI</td>
<td>3.83eV</td>
</tr>
<tr>
<td>AlI₃</td>
<td>8.75eV</td>
</tr>
</tbody>
</table>

*Table 5.1.1: Atomization energies (AE) of simple molecules.*

Consider a comparison between the Al₁₃I₄⁻ cluster and the branching I₅⁻ cluster. The I₅⁻ molecule has two similarly shaped structures, a V-shaped conformer where two iodine molecules are coordinated by an apical iodide in a [(I⁻)·2I₂] configuration and an L-shaped conformer where a triiodide ion is coordinated with an iodine molecule in a [(I₃⁻)·I₂] configuration [52]. Note that both of these structures require intact I₂ molecular bonding. This reveals that neither of the pentaiodide configurations exhibits similarity to the ground state structure of the Al₁₃I₄⁻ cluster shown in figure 5.1.1. Particularly, the pentaiodide molecule sums up the building blocks of polyiodides that are found most stable corresponding to I, I₂, and I₃⁻ and assemble to form the extended structures in the stable I₂n+1⁻ series. The analogs to these clusters within the aluminum iodide cluster framework are Al₁₃⁻, Al₁₃I, and Al₁₃I₂⁻, which are all stable entities. If the Al₁₃⁻ cluster were strictly acting as elemental iodine, I₂ molecules can be added upon these core clusters to form superpolyhalides where the nature of molecular iodine is maintained. Aluminum iodides do indeed have stable cores that are used as foundations for larger clusters, however it is found that I₂ bonds are broken in favor of forming the Al-I bonds.
that are shown in the ground state structures of Figure 5.1.1. Within the experiment that was conducted it is reasonable to note that the kinetic conditions are sufficient to provide enough energy to climb the energy barrier that would otherwise prevent I\textsubscript{2} dissociation into its atomic units.

The case at hand is more related to the character of fluorohalides such as the BrF\textsubscript{x}\textsuperscript{-} series. Bromine fluorohalides are shown to have a central halogen with a larger atomic radius decorated with smaller fluorine atoms [53]. An example is the octahedral (O\textsubscript{h}) geometry of the BrF\textsubscript{6}\textsuperscript{-} ion and the D\textsubscript{4h} symmetry of the BrF\textsubscript{4}\textsuperscript{-} ion. Within the bromine fluorohalide series, the total number of halogen atoms must be odd to allow for an existing stable anion, just as is the case for the multiple iodine chains and also the aluminum iodide case currently considered where Al\textsubscript{13}\textsuperscript{-} takes the place of a halogen atom. The electron affinity of a fluorine atom is greater than that of a bromine atom, whereas in the aluminum iodide series, the electron affinity of the Al\textsubscript{13}\textsuperscript{-} cluster is greater than that of the iodine atoms that surround it. Due to the remarkable difference in the electron affinity in the aluminum iodide series of clusters, electron transfer occurs from the surrounding fragments towards the central cluster and induces a bond polarity dynamic that for the first time has been witnessed to occur in an interhalogen system. This is discussed further in section 5.1.1, pertaining to the electron transfer of Al\textsubscript{13}I\textsubscript{x}\textsuperscript{-} clusters, 5.1.1. Overall, this is attributing to a truly unique system with novel characteristics, considering how the Al\textsubscript{13}\textsuperscript{-} cluster remains relatively unperturbed in the cluster.
Now we turn to additional details of the research that are required in order to make any more conclusions about the nature of the stable aluminum iodide clusters. A more comprehensive explanation regarding the reasoning behind even numbers of iodine atoms yielding stable clusters in the experiment after the introduction of oxygen etching in the Al\textsubscript{13}I\textsubscript{x}^- series can only be deduced upon a study detailing the entire series of clusters. Figure 5.1.2 suggests that there is a role played by considering the occupation of the charge centers indicated by arrows in the HOMO charge density plots by I atoms for Al\textsubscript{13}I\textsuperscript{-} and Al\textsubscript{13}I\textsubscript{3}^- that form more stable even clusters of Al\textsubscript{13}I\textsubscript{2}^- and Al\textsubscript{13}I\textsubscript{4}^-, respectively. Notably in the figure is the presence of a tendency towards forming a σ bond between the Al\textsubscript{13} moiety and the I atoms for Al\textsubscript{13}I\textsuperscript{-} and Al\textsubscript{13}I\textsubscript{3}^- and a change to π bonding present for even numbers of iodine atoms. This could also be a reason for the stability present in the even numbers of iodine atoms for the Al\textsubscript{13}I\textsubscript{x} series, but further discussions involving the larger clusters will put this and other observations to the test. That which is being discovered suggests that these clusters are a new class of superpolyhalides that have been formed with a core that remains Al\textsubscript{13}^-, and construction that is different from that of conventional polyhalides.

Of considerable interest is also to what extent does the Al\textsubscript{13}^- core remain intact geometrically upon extensive iodine adsorption. Now we shall consider the entire series of Al\textsubscript{13}I\textsubscript{x}^- clusters, including high quantities of iodine atoms present. A large study was conducted regarding converging many geometries and spin multiplicities of the larger clusters as well. Only the most interesting and relevant to discussion are depicted in Figure 5.1.3. Within this figure, there is a comparison between aluminum iodide clusters
with an intact icosahedral $\text{Al}_{13}^-$ core that contains an interior Al atom completing the $I_h$ symmetry, decorated by up to twelve iodine atoms and labeled as $I_n$, and two other competing families including an elongated cage (EC) and distorted spherical cage (DSC) class of structures. Relative energies are shown to indicate stability with respect to a comparison with the $I_h$ family of geometries. The positive values indicate less stable clusters with respect to the $I_h$ series and the negative values indicate more stable clusters with respect to the $I_h$ family of structures. Additionally, bond lengths of the clusters are on the order of the same magnitude as those present in the smaller $\text{Al}_{13}I_n^-$ clusters shown in Figure 5.1.1, typically Al-Al bond lengths are $\sim 2.8$ angstroms and Al-I bond lengths are $\sim 2.6$ angstroms.

Starting with $\text{Al}_{13}I^-$, the icosahedral $\text{Al}_{13}^-$ core remains intact and one iodine atom decorates the pure aluminum core in an on top site, in agreement with previous results [10]. The EC and DSC structures are 1.16eV and 0.63eV less stable than the compact $I_h$ geometry. The difference in stability between the compact $I_h$ cluster motif and the cage-like clusters is greater than 0.30eV, favoring the more stable compact $I_h$ core to build upon up to and including six iodine atoms present about the $\text{Al}_{13}^-$ cluster. The structure of $\text{Al}_{13}^-$ remains unperturbed for such an abundance of iodine atoms, further highlighting the superpolyhalide nature of these remarkable clusters. Additionally, for up to six iodine atoms present in the series, there are no competing isomers that can be found. However, upon the addition of one more iodine atom to $\text{Al}_{13}I_6^-$, the two cage structures and compact $I_h$ geometry become competing isomers. According to the calculations, the EC structure is 0.06eV more stable than the $I_h$ cluster and the DSC is 0.02eV more stable
than the compact structure. The energy differences in such clusters are less than ~0.10eV and can be considered as true isomers. Al_{13}I_{8}^{-} has two isomers, one of the I_{h} motif and one of the EC cluster type. For Al_{13}I_{8}^{-}, the DSC style cluster is 0.21eV less stable than the I_{h} cluster.

Additionally, by simply comparing the final, converged appearance of the isomeric Al_{13}I_{7}^{-} and Al_{13}I_{8}^{-} clusters, the EC and DSC clusters appear to possibly be a result of migration of the central Al atom in the compact I_{h} structure towards the surface. There could be a variety of explanations to this, but one to consider is that it may be a result of the denial of charge to the iodine due to a higher electron affinity of Al_{13} than the iodine atom and the extensive charge buildup on the central cluster from a high amount of iodine ultimately weakens the Al-Al bonding on the central Al atom in favor of Al-I bonding that can be found at the surface of the cluster. It seems that as we approach saturating the cluster with an I:Al on a 1:1 ratio, the preference of Al-I bonds becomes more and more necessary to result in a stable cluster, even at the energy cost required to migrate the central Al atom towards the outside of the cluster. Could it be that the ultimate nature of fully saturated clusters are simply forming units of neutral AlI (which cannot be detected in an experiment due to the requirement of a real value for the mass to charge ratio)? Returning to the mass spectra in figure 5.3.1C, it is shown that there is a notable decrease in the intensity of the peak for Al_{13}I_{8}^{-} after the oxygen etching takes place. This could indeed be due to having two competing isomers for this cluster and hence two pathways of cluster formation at this point, whereas the Al_{13}I_{x}^{-} clusters for x ≤ 6 have only one stable configuration, that of a stable, fully intact and unperturbed Al_{13}^{-}.
cluster constructing the core upon which these clusters are built. Hence the prominent peak intensities for Al$_{13}$I$_x^-$ clusters containing six or less iodine atoms.

Starting with Al$_{13}$I$_9^-$, structures of the cage variety are more stable. This seems to suggest that the Al$_{13}$I$_7^-$ and Al$_{13}$I$_8^-$ clusters act as a turning point from the highly stable compact I$_h$ core structures to the cage structures found to be more stable from 9 to 12 iodine atoms. It is also worth noting that the mass spectra shown in Figure 5.3.1C shown after oxygen etching takes place and noting that none of the clusters with nine or more iodine atoms are present as prominent features in the spectra for the Al$_{13}$I$_x^-$ series. It is entirely possible that the cage-like structures, though fascinating, may be easily susceptible to dissociation into fragments, likely including Al-I and even AlI$_3$ units, due to the absence of the Al$_{13}$I$_7^-$ to govern and enhance stability in these clusters. Determination of the role of the cage structures requires further treatment to come to a conclusion.

There is a pronounced trend in the mass spectra of Figure 5.3.1 that shows the clusters with even numbers of iodine atoms have greater stability than those with odd numbers of iodine atoms for the Al$_{13}$I$_x^-$ series. This notable pattern of stability can be accounted for within the reach of theoretical studies. First consider the change in energy $\Delta E_x$ such that

$$\Delta E_x = E(\text{Al}_{13}\text{I}_x^-) - E(\text{Al}_{13}\text{I}_{x-1}^-) - E(\text{I})$$

which corresponds to the gain in energy as successive iodines are added to the system. The $E(\text{Al}_{13}\text{I}_x^-)$ term is the total energy of the Al$_{13}$I$_x^-$ cluster, $E(\text{Al}_{13}\text{I}_{x-1}^-)$ is the total energy of the Al$_{13}$I$_{x-1}^-$ cluster with one less iodine and $E(\text{I})$ is the total energy of the iodine atom.
The results are conveniently plotted for the system under observation in figure 5.1.4 and Table 5.1.2 details the numerical values. Only the ground state structures were considered in the figure and table and the compact icosahedral core was chosen to be representative for those structures that have isomers. The clusters with odd $x$ are shown in figure 5.1.4 to require approximately $-0.9\text{eV}$ less gain in energy for I atom adsorption than the clusters of even $x$ for $x$ less than nine. This assures that the energy gain is more favorable towards inducing a higher stability in the clusters of even $x$ than of odd $x$ and can be visualized in the alternating pattern shown in figure 5.1.4. The pattern continues as such for the cage like structures also.

Consider the charge density of the HOMO level of the icosahedral core and cage structures shown in figure 5.1.5 to further account for the physical origin of the pronounced stability in the clusters of even $x$ for the $\text{Al}_{13}\text{I}_x^-$ motif. First consider those geometries of the $I_h$ variety. There is the overwhelming presence of an accumulation of charge about the Al atom opposite to the Al site upon which the odd iodine is adsorbed in the HOMO charge distribution for those clusters of odd numbers of iodine atoms. These sites are coined as ‘active centers’ and are denoted by an arrow in the figure. Furthermore, consider a single iodine atom added to the (odd) $\text{Al}_{13}\text{I}_x^-$ cluster. As the iodine approaches the cluster, the active center provides a large accumulation of charge upon which it can attempt to fill the last electron in its $p$ orbital and hence fill the active site, forming a stable cluster with an even number of iodine atoms. The introduction of another iodine atom upon an even cluster generates an active site that is then subsequently quenched upon occupation by another iodine atom to it. The generation
and annihilation of active centers in the system provides a graphical and physical origin to the variations in peak intensities and the quenching is marked by a large gain of $\Delta E_x$, leading to clusters of even numbers of iodine atoms being more stable than those of odd numbers of iodine atoms throughout the spectra for the $\text{Al}_{13}I_x^-$ series.

The EC structures obey the same criteria as the $I_h$ family of structures in generating the active sites in that the on top I atom generates an active center upon the Al site opposite to the Al atom in which it binds. The active sites only present for odd numbers of iodine atoms and are also indicated by arrows. For the DSC family of geometries, an active site is generated adjacent to the odd iodine atom that is introduced to the system. These sites are also quenched upon further iodine addition found in clusters of even $x$. Hence all clusters with odd numbers of iodine atoms have induced active centers and behave in such a manner that adsorbing a single additional I atom to the surface quenches the active site. Thus it is within the nature of these clusters that the even and odd alternation in the number of iodine atoms in regards to stability is fundamentally present within the physical properties of the system, notably the active site creation and occupation and the energy gain of adding subsequent iodine atoms to the system for the $\text{Al}_{13}I_x^-$ clusters.

Now consider one more tool at our disposal for further probing these clusters via theoretical means in order to finalize our concepts. An additional marker of stable systems is a large HOMO-LUMO gap at shell closings when considering the jellium framework [13, 54]. Figure 5.1.6 depicts the HOMO-LUMO gap in the $\text{Al}_{13}I_x^-$ clusters and how it compares to varying numbers of iodine atoms. It is indeed found that the
clusters with even numbers of iodine atoms have a large HOMO-LUMO gap and is indeed also larger than those clusters with odd numbers of Al atoms. This provides us with ample proof to conclude two things, one that the jellium model is indeed sufficient to provide a simple picture to describe the behavior of the aluminum iodide clusters, and secondly that the gaps that are present in the figure are in complete agreement with the trends in stability found in the experiments.

Theoretical analysis of the Al$_{13}$I$_x$$^-$ clusters has illuminated several key points about the nature of these clusters. The iodine atoms in these clusters do not bind as molecular iodine of the form I$_2$ but instead as I atoms. The even and odd stability patterns can be attributed to the physical nature of the formation of active centers for odd $x$ and their subsequent quenching upon occupation by an additional iodine atom. Of greatest importance is that for the most intense peaks in the spectra, for $x \leq 8$, there is a unperturbed Al$_{13}^-$ upon which the cluster is built and forms a superhalogen core upon which larger extended structures are built.
5.1.1 Electronic Charge on Al\textsubscript{13}I\textsuperscript{−} Clusters.

The iodine atoms form covalent bonds with the aluminum atoms upon which they bind with electronic charge building up upon the pure aluminum core of these clusters with increasing amounts of iodine doping. This bonding is present in charge accumulations between Al-I bonds in the total charge density plots. This brings us to a discussion about the electronic charge buildup on the aluminum clusters upon adding iodine atoms. The electron affinity of the Al\textsubscript{13} cluster is greater than that of the iodine atoms that surround it. This suggests that some electron transfer occurs from the surrounding fragments towards the central cluster and induces a bond polarity dynamic that for the first time has been witnessed to occur in an interhalogen system. Overall, this is attributing to a truly unique system with novel characteristics, considering how the Al\textsubscript{13} cluster remains relatively unperturbed in the aluminum iodide clusters. Further observation of the bond polarity in aluminum iodide clusters can be investigated by use of Mulliken population analysis for the extra charge.

The Al\textsubscript{13}I\textsuperscript{−} cluster has −0.63e\textsuperscript{−} Mulliken charges on the Al site and −0.37e\textsuperscript{−} charges on the I site. This suggests that the dipole moment is directed towards the site taking the least amount of the extra charge, thus towards the iodine site introducing a novel system with unique behavior. Upon adding another iodine atom in forming Al\textsubscript{13}I\textsubscript{2}\textsuperscript{−}, the two iodine atoms have Mulliken charges of about −0.36e\textsuperscript{−} each. The pure aluminum portion of the cluster carries the remainder of the charge, at −0.28e\textsuperscript{−}. This shows that the bond
polarity has now been changed and the dipole moment points towards the core aluminum cluster part. For the structures of the compact icosahedral geometry, subsequent loading of I atoms to the cluster bind and the result is between $-0.33e^-$ to $-0.37e^-$ Mulliken charge for each I atom. The Al$_{13}$ core then begins to carry a net positive charge upon increasing the number of I atoms decorating the cluster that leads to a migration of the central Al from its position in the I$_h$ geometry to the surface, forming the cage-like structures.

For the cage structures, each I atom has approximately $-0.26$ to $-0.31e^-$ Mulliken charge. The Al atoms upon which the I atoms have become bound each show a positive net charge of between $+0.2$ and $+0.35$ Mulliken charges. This indicates that a much stronger bond polarity is found, inducing a dipole moment oriented from each I atom towards Al the site upon which it becomes bound. The Al atoms gain of increasing positive charge leads to the expansion of the cluster that allows for a reduction in the activation barrier to allow the central Al to venture to the surface. Hence, the results suggest that the cage structures are more easily dissociated into Al-I fragments than the I$_h$ clusters due to the increase in like charge repulsion between Al atoms at the surface upon adding more iodine atoms. Additionally, it is found in the experimental spectra that the DSC caged clusters starting with Al$_{13}$I$_5^-$ and beyond are not as easily formed and don’t result in major peaks in the spectra.

One additional point to mention is that the I$_h$ clusters do indeed manage to maintain the geometric character of the Al$_{13}^-$ cluster as a core. The closed geometric and electronic shells of this cluster can indeed remain intact upon subsequently covalently bonding increasing amounts of iodine to the pure metal cluster.
Figure 5.1.1: Competing isomers for $\text{Al}_{13}\text{I}_2^-$. GS indicates the ground state clusters.

Note that clusters with intact I$_2$ units are higher in energy. The atomization energies (AE) are given in units of eV and bond lengths are in units of angstroms.
Figure 5.1.2: The ground state structures and HOMO charge density maps of Al₁₃Iₓ⁻ clusters. The arrows point to regions of high charge density.
Figure 5.1.3: Relative energies (eV) for the Al$_{13}$L$_x$ (x=1-12) clusters.
Figure 5.1.4: $\Delta E_x$ for the $Al_{13}I_x$ (x=1-12) clusters.
Table 5.1.2: Atomization energies (AE) and the gain in energy $\Delta E_1$ upon successive addition of I atoms for $\text{Al}_{13}\text{I}_x^-$. 

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Type</th>
<th>AE (eV)</th>
<th>$\Delta E_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_{13}\text{I}_1^-$</td>
<td>$\text{I}_h$</td>
<td>36.11</td>
<td>2.48</td>
</tr>
<tr>
<td>$\text{Al}_{13}\text{I}_2^-$</td>
<td>$\text{I}_h$</td>
<td>39.44</td>
<td>3.33</td>
</tr>
<tr>
<td>$\text{Al}_{13}\text{I}_3^-$</td>
<td>$\text{I}_h$</td>
<td>41.89</td>
<td>2.45</td>
</tr>
<tr>
<td>$\text{Al}_{13}\text{I}_4^-$</td>
<td>$\text{I}_h$</td>
<td>45.15</td>
<td>3.26</td>
</tr>
<tr>
<td>$\text{Al}_{13}\text{I}_5^-$</td>
<td>$\text{I}_h$</td>
<td>47.44</td>
<td>2.29</td>
</tr>
<tr>
<td>$\text{Al}_{13}\text{I}_6^-$</td>
<td>$\text{I}_h$</td>
<td>50.65</td>
<td>3.21</td>
</tr>
<tr>
<td>$\text{Al}_{13}\text{I}_7^-$</td>
<td>$\text{I}_h$</td>
<td>52.89</td>
<td>2.24</td>
</tr>
<tr>
<td>$\text{Al}_{13}\text{I}_8^-$</td>
<td>$\text{I}_h$</td>
<td>56.18</td>
<td>3.30</td>
</tr>
<tr>
<td>$\text{Al}_{13}\text{I}_9^-$</td>
<td>DSC</td>
<td>58.88</td>
<td>2.67</td>
</tr>
<tr>
<td>$\text{Al}<em>{13}\text{I}</em>{10}^-$</td>
<td>DSC</td>
<td>61.97</td>
<td>3.08</td>
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<tr>
<td>$\text{Al}<em>{13}\text{I}</em>{11}^-$</td>
<td>DSC</td>
<td>64.48</td>
<td>2.52</td>
</tr>
<tr>
<td>$\text{Al}<em>{13}\text{I}</em>{12}^-$</td>
<td>DSC</td>
<td>67.86</td>
<td>3.38</td>
</tr>
<tr>
<td>$\text{Al}<em>{13}\text{I}</em>{13}^-$</td>
<td>DSC</td>
<td>69.60</td>
<td>1.74</td>
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</table>
Figure 5.1.5: HOMO charge density plots for the Al$_{13}$I$_x^-$ (x=1-12) clusters.
Figure 5.1.6: HOMO-LUMO Gap for the Al$_{13}$I$_x^- (x=1-13)$ clusters.
5.2 $\text{Al}_{14}I_x^- (x=1-12)$

We now turn to the $\text{Al}_{14}I_x^-$ series, which is present in the molecular beams of the oxygen etching experiments for odd numbers of iodine atoms. Of particular interest is the $\text{Al}_{14}I_3^-$ cluster, which was also found in high abundance in the experiments considering the reaction between HI and aluminum iodide clusters [10, 46]. Thus an investigation regarding determining the major factors behind the stability of this fascinating cluster has been conducted. Additionally, this unique cluster forms the first peak within the stable series of $\text{Al}_{14}I_x^-$ clusters, further indicating that it may provide a stable core upon which the other clusters are to be formed. Upon finalizing the calculations done on the ground state of the $\text{Al}_{14}$ cluster, it is found that it has an icosahedral structure with an Al atom capping a triangular hollow site of the icosahedral shell. Additionally, the AEA of this cluster is found to be less than that of $\text{Al}_{13}$ and also less than that of an iodine atom. This suggests that upon construction of $\text{Al}_{14}I_3^-$, each iodine atom would withdraw charge from the bare aluminum cluster’s core and the extra electron. The resulting complex then has an aluminum core that can be approximated to contain 40 valence electrons, corresponding to a shell closure within the jellium model. This is indeed the result that is found. With such a case explaining the stability of $\text{Al}_{14}I_3^-$, it would be expected then, that $\text{Al}_{14}I_5^-$, $\text{Al}_{14}I_2^-$, and $\text{Al}_{14}I^-$ would all have a core structure built from pure aluminum atoms corresponding to $\text{Al}_{14}^{2+}$, $\text{Al}_{14}^+$, and $\text{Al}_{14}$ neutral, respectively. The similarity here is depicted in figure 5.2.1. The structures and bond lengths of the free clusters of neutral $\text{Al}_{14}$, $\text{Al}_{14}^+$, and $\text{Al}_{14}^{2+}$ are compared to the cores
present in the iodine rich clusters. This reveals a similarity in the trend of the bond lengths between the free cluster and the core upon which the iodine rich clusters are built for the bond length corresponding to the Al-Al distance of the Al atom that caps the hollow site of the icosahedron and the Al-Al distance of a bond contained within the triangular face of the clusters. The bond lengths increase upon successively oxidizing the Al$_{14}$ cluster in the same manner that they increase upon adding I atoms to the cluster. The ground states of the Al$_{14}$I$_3^-$ cluster and the free Al$_{14}^{2+}$ both have an Al-Al bond stretched to allow for situation of the extra Al atom to take place. Most impressive, though, is that the overall shape of the aluminum cluster core present in the Al$_{14}$I$_x^-$ (x=1-3) becomes more spherical upon adding additional iodines as well as the free cluster of Al$_{14}$ upon successively ionizing it. The tendency towards a more spherical shape allows the jellium model to be an accurate representation to describe this cluster. It is simply fascinating that the Al$_{14}^{2+}$ core of Al$_{14}$I$_3^-$ shares a similar valence to the alkaline earth atoms present in the periodic table. This, in addition to the sound compact geometric structure of the cluster may indeed allow it to act as an alkaline earthlike superatom core upon further addition of I atoms.

A large structural assessment was conducted to reveal the ground state geometry of the Al$_{14}$I$_3^-$ cluster, including an analysis of spin multiplicities. The study revealed the iodine atoms prefer an on top site orientation with regards to the aluminum atoms. Some of the more interesting isomeric structures that can in some manner be considered cluster-molecules are shown in figure 5.2.2 along with their atomization energies. Isomer A is an AlI$_3^-$-Al$_{14}$ structure, isomer B is the ground state structure of Al$_{13}$I$_3^-$ bound
to an AlI molecule, isomer C is an AlI3-I2, isomer D is a varying take on the ground state structure indicated by GS in the figure, which is an Al142+ core decorated by I ligands. Isomer C is 2.02eV less stable than the ground state cluster indicating the preference of this cluster to also dissociate I2 bonds in preference for atomic I adsorption, like that which was found for the case of the Al13Ix- cluster series. Of all of these clusters in addition to many other structures, the preferred organization of the Al14I3- cluster is that of E in the figure, again emphasizing the physical description as being most reminiscent to an alkaline earth superatom. The structure of the ground state Al14I3- cluster is best described as a closed shell Al14++ core surrounded by three I- ligands. The physical behavior of such a cluster gives theoretical reasoning behind substantial peaks not being present for Al14I- or Al14I2-, leaving the Al14I3- cluster as the first prominent peak in the spectra shown in figure 5.3.1C. More details must be accounted for within this series before an explanation to the trend of the odd numbers of iodine atoms having remarkable stability upon exposure to molecular oxygen in the Al14Ix- series for clusters beyond x=3.

The clusters in the series Al13Ix- were found to have cage-like structures that can be used as an interesting comparative tool to the ground state structures. The Al14I3- cluster can be viewed as an Al14++ core surrounded by three I- ligands. The pure Al14++ component of the cluster has the icosahedral structure of an Al13- cluster, where the Al-Al bonds of one triangular face are stretched to allow occupation and binding of one additional Al atom to form the final product of Al14I3-, including the I atoms that decorate the surface of the cluster. An exhaustive search of the possible geometries and spin
multiplicities resulted in a similar profile for the Al₁₄I₃⁻ cluster series that yielded clusters having cage-like structures as being the most relevant in comparison to the ground state structures that were found. The distorted spherical cage (DSC) structures are depicted in figure 5.2.3 and are listed according to relative energies to the compact icosahedral Iₘ geometries that were considered as well. A positive value for the relative energy indicates that the DSC structure is less stable than the Iₘ geometry for that cluster, whereas a negative value for the relative energy indicates that the DSC cage-like cluster is more stable than the Iₘ counterpart for that cluster. The DSC geometries are best described as like an Iₘ geometry with the central Al migrating to the surface of the cluster and accommodating itself there, leaving a hollow shell, and hence forming a cage.

We have realized that the Al₁₄I₃⁻ provides a remarkable stable basis that may provide a working foundation to further adsorb iodine upon this cluster. There now arise two questions regarding the series of clusters that begin with it. What is the maximum amount of iodine that can be present without resulting in a distortion of the Al₁₄I₃⁻ core if it indeed serves as a core? Also, does I₂ bond cleavage and preference of Al-I bonding remain favorable? The hollow cage structure for the Al₁₄I₃⁻ cluster is 0.11eV higher in energy than that of the Iₘ geometry that is discussed above. In fact, all of the DSC structures for x≤8 are at least 0.11eV higher in energy and hence less stable than the clusters formed from the Iₘ geometry. At large iodine content, starting with the Al₁₄I₆⁻ cluster and continuing for up to x=14, the cage-like variety become stable and at this point the cage becomes an elongated version of the initial more spherical cages that are shown for the smaller clusters. Investigations were carried out for up to x=14 and
indeed the Al$_{14}$I$_{13}^-$ and Al$_{14}$I$_{14}^-$ clusters were found to also be of the DSC type as well. Returning to the mass spectra of figure 5.3.1C, there are no remarkable peaks that can be identified beyond the Al$_{14}$I$_9^-$ cluster. Again, this suggests that as favoritism of the hollow cage-like variety of structures develops, the high quantity of iodine atoms may result in an easily fragmented cluster that is only weakly held together by Al-Al bonds. Of all of the clusters in either the cage or compact families, there is always an overwhelming presence of Al-I bonding in favor of I$_2$ bonding, just as what was found for the Al$_{13}$I$_x^-$ series of clusters. This shows that the addition of a single Al atom, although it does play a role in a variety of interesting changes to the system, has no effect on changing this. But most fascinating is that the Al$_{14}$I$_3^-$ core cluster does indeed remain intact for up to and including eight iodine atoms. Perhaps this cluster does serve as a reasonable core upon which larger clusters are built after all.

The larger clusters are formed from Al$_{14}$I$_3^-$ in the following manner. Consulting the figures showing the ground state geometries of the larger clusters and referring to figure 5.2.1 shows that the next additional I atom occupies the site at the base of Al$_{14}$I$_3^-$, labeled as A in the geometrical figure forming Al$_{14}$I$_4^-$.

The Al$_{14}$I$_5^-$ cluster has a structure where the site labeled as A remains unoccupied and the two additional iodines occupy two sites opposite to each other on the Al$_{14}$ part of the cluster. For the entire series of the compact I$_h$ style clusters, site A remains unoccupied for clusters of odd x and it becomes occupied for clusters of odd x. None of the cases behold intact I$_2$ bonds. The alternation of occupation and absence of an iodine atom at site A begins to clarify the stable nature of the clusters of odd x in this series due to the I at site A not bonding as strongly.
The HOMO charge densities of the clusters are plotted in figure 5.2.4. Note that the general picture here is a bit different from that which is found for the Al$_{13}$I$_x^-$ clusters due to the alternation in occupancy of the site A in figure 5.2.1. There is a presence of active centers in these clusters, but the mechanism is different and will be described later. Note, however, that there is a presence of a small active center at site A that is present for the cases where it remains unoccupied for odd x within structures of the I$_h$ type. However, there is merit in further confirming the similarity of the pure aluminum core of the Al$_{14}$I$_3^-$ cluster to that of Al$_{14}^{++}$ that involves the total charge densities of such clusters. This first involves the construction of the total charge density of a free Al$_{14}^{++}$ superimposed onto the total charge densities of three neutral I atoms placed at the coordinates found in the Al$_{14}$I$_3^-$ cluster. The resultant charge density is then subtracted from the total charge density of the Al$_{14}$I$_3^-$ cluster. This process was done to reveal the localization of charge due to the Al$_{14}$I$_3^-$ three additional electrons that are not included in the charge density constructed from Al$_{14}^{++}$ + 3I. The result is found that there is a preponderance of the electronic charge localized about the iodine sites of the cluster. This provides further reason towards confirmation that the core of Al$_{14}$I$_3^-$ does indeed behave as an Al$_{14}^{++}$ cluster.

Let us next consider the change in energy $\Delta E_x$ as successive iodines are added to the system,

$$\Delta E_x = E(Al_{14}I_x^-) - E(Al_{14}I_{x-1}^-) - E(I) \quad \text{for } x \geq 2 \text{ and}$$

$$\Delta E_x = E(Al_{14}I_x^-) - E(Al_{14}I_{x-1}^-) - E(I) \quad \text{for } x = 1.$$
The electron affinity of Al\textsubscript{14} is less than that of an iodine atom, hence the use of a different equation for x = 1, which describes the dissociation energy of I\textsuperscript{−} from Al\textsubscript{14}I\textsuperscript{−}. The values of ΔE\textsubscript{x} are plotted in figure 5.2.5 and the numerical values are shown in table 5.2.1. There is a profound variation found in the even-odd oscillations of figure 5.2.5 starting with the Al\textsubscript{14}I\textsubscript{3}− cluster. The reason due to beginning the oscillations at this point is due to the stable 40 electron dicaticonic Al\textsubscript{14}\textsuperscript{++} core of the Al\textsubscript{14}I\textsubscript{3}− cluster can only form after Al\textsubscript{14} is surrounded by three iodine atoms and an extra charge. The Al\textsubscript{14}I\textsubscript{4}− cluster finds the extra iodine at the only available active site as not being as strongly bound as paired iodine atoms at opposite sites, so there is a noticeable decrease in the change in energy ΔE\textsubscript{x} relative to that of the stable Al\textsubscript{14}I\textsubscript{3}− cluster. The occupation of the site A by an iodine atom plays a role in the progression of the larger clusters that are formed in that when this small active site is occupied (for all even x), ΔE\textsubscript{x} of those clusters are less than those clusters where that site remains unoccupied due to the formation of paired I atoms about the Al\textsubscript{14} portion of the cluster. Hence, the energetics described in the figure do indeed show that the ground state structures found do correspond to a higher stability present in clusters of odd x than those clusters of even x for clusters of the Al\textsubscript{14}I\textsubscript{x}− family.

The progression of the clusters of the compact icosahedral family is best illustrated in figure 5.2.6. Depicted within are the charge densities of the HOMO level and the binding energy of each added iodine atom BE(I) for each step. Beginning with the ground state of Al\textsubscript{14}I\textsubscript{4}−, an additional iodine atom would bind similarly to how it binds in the Al\textsubscript{13}I\textsubscript{x}− series and the resultant structure forms an accumulation of charge density on the Al site opposite to the Al atom upon which it adsorbs. The iodine atom binds to this
site with energy of 2.48eV. The generated active site is of the variety that was found in the Al\textsubscript{13}I\textsubscript{x} series of clusters for odd x. The iodine atom that is occupying site A of figure 5.2.1 then moves to the active site, yielding a gain of 0.58eV in energy, further stabilizing the cluster and forming the ground state of Al\textsubscript{14}I\textsubscript{5}\. Note that in the cluster formed, there is the presence of a small active site at the site where the I was previously occupied located at the triangular face of aluminum atoms the base of the Al\textsubscript{14} portion of the Al\textsubscript{14}I\textsubscript{5} cluster. The small active site will become occupied upon the adsorption of an additional iodine atom with a binding energy of 2.46eV in forming Al\textsubscript{14}I\textsubscript{6} and the process will repeat itself upon further addition of I atoms. Thus the formation and subsequent occupation of active sites plays a critical role in the formation of the clusters of the Al\textsubscript{14}I\textsubscript{x} variety. In addition, it gives a physical reasoning towards explaining the nature of these clusters to behave in such a manner that those of odd x are highly stable. Conclusively, the Al\textsubscript{14} core can be described as closely resembling the nature of the alkaline earth elements in the periodic table with a valence of 2.

In continuation of discussing the stability of the clusters of this series, let’s now consider the impact that electronic structure plays in developing their characteristics. Clusters with a large HOMO-LUMO gap are fundamentally highly stable within the jellium model. Thus a map depicting the HOMO-LUMO gap in Al\textsubscript{14}I\textsubscript{x}\textsuperscript{−} clusters is provided in figure 5.2.7. Notice that we see a similar trend of oscillatory behavior as with the gain in energy per iodine atom depicted in figure 5.2.5. Those clusters with a larger HOMO-LUMO gap are of odd numbers of iodine atoms, reassuring us of the stable nature found in these species. The gap present for Al\textsubscript{14}I\textsuperscript{−} and Al\textsubscript{14}I\textsubscript{2}\textsuperscript{−} is also indeed
smaller than that found in Al\textsubscript{14}I\textsubscript{3}⁻, again providing additional proof towards describing the remarkable stability found in this cluster. After this, the oscillations continue.

Theoretical studies have illustrated several key concepts that describe the nature of clusters of the Al\textsubscript{14}I\textsubscript{x}⁻ family. The iodine atoms in these clusters do not bind as molecular iodine of the form I\textsubscript{2} but instead prefer the formation of Al-I bonds. The odd and even stability patterns can be attributed to the physical nature of the formation and annihilation of active centers. Of greatest importance is that for the most intense peaks in the spectra, for \(x \leq 8\), there is an unperturbed Al\textsubscript{14}⁺⁺ upon which the cluster is built and plays an integral role in the formation of extended structures throughout the spectra. The Al\textsubscript{14}⁺⁺ core begs comparison of this cluster with the alkaline earth atom elements of the periodic table and introduces the notion of it behaving as an alkaline earth superatom in the series of clusters.
5.2.1 Electronic Charge on Al\textsubscript{14}I\textsubscript{x}⁻ Clusters.

Bonding occurs between the aluminum and iodine atoms upon their approach in forming the stable clusters discussed of the Al\textsubscript{14}I\textsubscript{x}⁻ family. Of other considerable interest is the charge accumulation onto the atomic sites of the cluster and revealing any type of interesting features that may play an important role in the chemistry of these systems. Hence, Mulliken population analysis is a useful tool in describing characteristics of the system under observation.

Unlike the case for Al\textsubscript{13}I\textsubscript{x}⁻, the stability of the Al\textsubscript{14}I\textsubscript{x}⁻ clusters are governed by a stable core reminiscent to Al\textsubscript{14}\textsuperscript{2+} providing a reasonable framework to extend through addition of increasing numbers of iodine atoms. The dependence on a positively charged core for stability and a reduced electron affinity of the Al\textsubscript{14} cluster introduces some differences in the effects seen in the Mulliken charges of these clusters. The addition of a single iodine atom to an aluminum cluster of fourteen atoms and an extra charge, forming Al\textsubscript{14}I⁻, results in \(-0.41\text{e}⁻\) Mulliken charge on the iodine and \(-0.59\text{e}⁻\) charge on the aluminum cluster. Since the doubly ionized aluminum cluster core forms the most stable orientation, the excessive accumulation of negative charge from the extra electron gives additional confirmation to the reasoning described before for the lack of stability present in the Al\textsubscript{14}I⁻ cluster. The Al\textsubscript{14}I\textsubscript{2}⁻ cluster still has a negative net charge of \(-0.24\text{e}⁻\) on the Al\textsubscript{14} portion, but following the addition of just one more I atom in forming Al\textsubscript{14}I\textsubscript{3}⁻ shows a net positive charge of \(+0.13\) Mulliken charges on the pure aluminum core. This is the first instance of the positively charged core and is more reminiscent to the free stable
dicationic cluster and forms the first stable entity of the series of Al\textsubscript{14}I\textsubscript{x}\textsuperscript{−} clusters for \(x=\text{odd}\). Also, the bond polarity in this series is directed towards the positively charged aluminum core of the cluster.

Upon increasing numbers of iodine atoms subsequently included in the calculation reveals that each I atom has a Mulliken charge of between \(-0.28\) to \(-0.34e\textsuperscript{−}\) for the icosahedral clusters. This begins a buildup of positive charge on the order of \(+0.2\) to \(+0.35e\textsuperscript{+}\) on the Al sites closest to the I atoms that are bound to the system. The buildup of positive charge on the Al atoms begins to saturate the Al surface with excess positive charge, giving rise to expansion in the system from like charge repulsion, subsequently and presumably reducing the activation barrier for migration of the central Al atom to the surface for clusters occurring at about \(x=9,10\). Upon initiation of the DSC family of structures, each iodine atom reduces the charge that it carries from the extra electron to \(-0.28e\textsuperscript{−}\) to \(-0.34e\textsuperscript{−}\) Mulliken charges each. This is in an effort to reduce the positive charge buildup on the aluminum cluster surface, but the total accumulation of net charge on the iodines is now high for the caged clusters. Also, the result reveals that a net charge of \(+0.17\) remains on each Al atom, still inducing the possibility for easy disassociation of the resulting DSC clusters into Al-I fragments. Now we turn to experimental evidence towards the formation of Al\textsubscript{13}I\textsubscript{x}\textsuperscript{−} and Al\textsubscript{14}I\textsubscript{x}\textsuperscript{−} clusters in the next section.
Figure 5.2.1: Ground state structures for $\text{Al}_{14}\text{I}^-$ and $\text{Al}_{14}^{(n-1)^+}$. Note the resemblance of the $\text{Al}_{14}$ cluster moieties to the free cluster cations.
Figure 5.2.2: The ground state cluster indicated by GS amongst competing isomers labeled (A-D). The atomization energies are in units of eV and the bond lengths are in angstroms.
\textbf{Figure 5.2.3:} Relative energies (eV) for the Al_{14}I_{x} (x=1-12) clusters.
Figure 5.2.4: HOMO charge density plots for the $\text{Al}_{14}\text{I}_x^-$ ($x=1-12$) clusters.
Figure 5.2.5: $\Delta E_x$ for the $Al_{14}I_x^-$ ($x=1-12$) clusters.
Table 5.2.1: Atomization energies (AE) and the gain in energy $\Delta E_1$ upon successive addition of I atoms for Al$_{14}$I$_n$.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Cluster</th>
<th>AE (eV)</th>
<th>$\Delta E_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_{14}$I$^-$</td>
<td>Ih</td>
<td>39.01</td>
<td>2.38</td>
</tr>
<tr>
<td>Al$_{14}$I$_2^-$</td>
<td>Ih</td>
<td>42.16</td>
<td>3.15</td>
</tr>
<tr>
<td>Al$_{14}$I$_3^-$</td>
<td>Ih</td>
<td>45.48</td>
<td>3.32</td>
</tr>
<tr>
<td>Al$_{14}$I$_4^-$</td>
<td>Ih</td>
<td>48.00</td>
<td>2.52</td>
</tr>
<tr>
<td>Al$_{14}$I$_5^-$</td>
<td>Ih</td>
<td>51.08</td>
<td>3.08</td>
</tr>
<tr>
<td>Al$_{14}$I$_6^-$</td>
<td>Ih</td>
<td>53.52</td>
<td>2.44</td>
</tr>
<tr>
<td>Al$_{14}$I$_7^-$</td>
<td>Ih</td>
<td>56.52</td>
<td>3.00</td>
</tr>
<tr>
<td>Al$_{14}$I$_8^-$</td>
<td>Ih</td>
<td>58.96</td>
<td>2.44</td>
</tr>
<tr>
<td>Al$_{14}$I$_9^-$</td>
<td>DSC</td>
<td>62.02</td>
<td>3.07</td>
</tr>
<tr>
<td>Al$<em>{14}$I$</em>{10}^-$</td>
<td>DSC</td>
<td>64.76</td>
<td>2.74</td>
</tr>
<tr>
<td>Al$<em>{14}$I$</em>{11}^-$</td>
<td>DSC</td>
<td>67.85</td>
<td>3.09</td>
</tr>
<tr>
<td>Al$<em>{14}$I$</em>{12}^-$</td>
<td>DSC</td>
<td>69.94</td>
<td>2.09</td>
</tr>
<tr>
<td>Al$<em>{14}$I$</em>{13}^-$</td>
<td>DSC</td>
<td>72.69</td>
<td>2.75</td>
</tr>
<tr>
<td>Al$<em>{14}$I$</em>{14}^-$</td>
<td>DSC</td>
<td>74.90</td>
<td>2.21</td>
</tr>
</tbody>
</table>
Figure 5.2.6: Generation and annihilation mechanism for the active sites in $\text{Al}_{14}I_x^-$. The binding energy of the additional I, $\text{BE}(I)$, is given as well as the gain in binding energy $\Delta E$ upon spatial relocation of the I atom. All energies are given in eV.
Figure 5.2.7: HOMO-LUMO Gap for the Al$_{14}$I$_x$ (x=1-14) clusters.
5.3 Mass Spectra of Al$_{13}$I$_x^-$ and Al$_{14}$I$_x^-$

The work completed in regards to Al$_{13}$I$_x^-$ and Al$_{14}$I$_x^-$ is a joint experimental and theoretical effort [50]. The experimental evidence supporting the truly stable nature of these clusters will thus be presented to suppress any doubt about the feasibility of creating such families of clusters that are discussed. Details regarding the experimental setup are described previously within this document and details are provided in the corresponding references [25, 55].

D.E. Bergeron, P.J. Roach, and A.W. Castleman, Jr. have conducted further oxygen etching experiments on aluminum iodide clusters (Fig. 5.3.1). A fast flow tube apparatus was used, equipped with a laser vaporization (LaVa) source used to produce the clusters [25]. The experiments were carried out by first laser ablation of a rotating and translating Al rod in the presence of He flowing constantly at 8000 sccm. The pure Al clusters were allowed to collisionally cool down to room temperature and then molecular iodine is sublimed and injected with He gas present. The I$_2$ was injected at the first reactant gas inlet (RGI) to produce the Al$_n$I$_x^-$ clusters. Further downstream, the O$_2$ was injected to properly analyze oxygen etching of the Al$_n$I$_x^-$ clusters. The use of two reactant gas inlets allows the Al$_n$I$_x^-$ clusters produced at the first RGI to thermalize before encountering the second RGI where molecular oxygen is introduced. A quadrupole mass spectrometer was used as the mass analyzer allowing for the experimental detection of the results.

The results for the bare Al clusters produced are given in figure 5.3.1A. After exposure to the molecular iodine vapor, there are clearly reactions that take place, shown
in figure. 5.3.1B and figure 5.3.2. The resultant Al$_n$I$_x^-$ clusters are formed and thermal equilibrium is reached through mutual interactions taking place between the elements of the reaction. The reaction that occurs can break the bond present in the I$_2$ molecules, allowing a host of products to entail. A lower concentration of molecular iodine present still produces the Al$_{13}$I$^-$ peak that was enhanced under the presence of HI [10, 46] and shown in Figure 5.3.2. But a more enhanced feature becomes present, that of Al$_{13}$I$_2^-$. Additionally, note that the low concentration regime has Al$_{14}$I$_2^-$ present as well as that of Al$_{15}$I$_2^-$. Al$_{15}^-$ was found to have increased peak intensity in the oxygen etching experiments of Leuchter et al. under the low concentrations of 7.5sccm of O$_2$ [21]. Even more interesting, at a higher concentration of molecular iodine vapor, as shown in figure 5.3.1, produces a pattern in the mass spectra that can be attributed to the series of Al$_{13}$I$_x^-$ and Al$_{14}$I$_x^-$ clusters. The Al$_{13}$I$_x^-$ series remains enhanced for up to $x=9$ and the Al$_{14}$I$_x^-$ series begins at $x=3$ and continues to $x=11$. Acid etching experiments revealed Al$_{14}$I$_3^-$ as an intense peak in the experiment that reacts HI with aluminum clusters [10, 46].

Note that figure 5.3.1B also shows an interesting trend regarding the intensity of the peaks at alterations according to even-odd numbers $x$ of iodine atoms present. For even numbers of I present in the Al$_n$I$_x^-$ series, the peak is of greater intensity corresponding to Al$_{13}$I$^-$. For the odd numbers of iodines present in the enhanced features in the mass spectra, the greater intensity peaks are of Al$_{14}$I$_x^-$ composition. Now consider the results condensed into the mass spectra given in figure 5.3.1C. This figure consists of the result after reacting the thermalized Al$_n$I$_x^-$ clusters with molecular oxygen. The results here
show convincing evidence of the even-odd alterations in the spectra. The use of oxygen etching experiments is a useful tool in examining cluster stability. The features that remain after the reaction takes place are those corresponding to even numbers of iodine atoms for the Al\(_{13}\)I\(_x\)\(^-\) series and odd numbers of iodine atoms for the Al\(_{14}\)I\(_x\)\(^-\) clusters. The peaks for odd x diminished for Al\(_{13}\)I\(_x\)\(^-\) and the peaks for even x in Al\(_{14}\)I\(_x\)\(^-\) were also diminished upon oxygen etching reactions. The experimental evidence suggests that there may be a novel description to the characteristics of aluminum iodide clusters that can only be analyzed fully by taking into consideration theoretical calculations.
**Figure 5.3.1:** Mass spectra of A.) pure aluminum cluster negatively charged ions that are B.) reacted with I₂ vapor at the first RGI and C.) etched by O₂ at the second RGI. The y-axis is the peak intensity. Green peaks correspond to clusters in the Al₁₃Iₓ⁻ family and blue peaks correspond to clusters in the Al₁₄Iₓ⁻ family [50].
**Figure 5.3.2:** Mass spectra of aluminum clusters exposed to low concentrations of I$_2$ vapor [50].
Chapter 6. A Discussion about Al$_7$I$^-$

6.1 The Pronounced Stability of Al$_7$I$^-$.

Al$_7$I$^-$ is found to be a relatively inert cluster that has a high stability that hinges on the exceptional stability found in the neutral Al$_7$I cluster [56]. The neutral cluster has a large dipole moment and reasonably high electron affinity of 2.09eV. The jellium model presents a scenario that considers the neutral cluster of seven aluminums, with three valence electrons for each, totaling 21 electrons that contribute to interacting with the positive spherically symmetric background charge. Upon approaching Al$_7$ with a single iodine atom, the presence of the extra electronegative ingredient causes an electron to be pulled from the aluminum core, leaving a situation where Al$_7^+$-I$^-$ is formed. According to the jellium model, the metallic aluminum core would then contain twenty electrons, a shell closure and indicative of high stability. Additionally, the iodine has its final orbital filled by the extra electron, yet remains bound to the cluster due to the induced dipole moment that forms upon its adsorption. The interaction between the Al$_7$ superatom and the iodine atom reveals a neutral Al$_7$I$^-$ cluster that can be regarded as a “jellium compound.” The process of creating such a cluster allows both the neutral and anionic variety of the cluster to exist with pronounced stability.

Consideration of a “jellium compound” leads down a road to test such a hypothesis to determine whether calculations can provide further insight about this and other similar clusters. Initiation of the investigation into the Al$_7$I$^g$ clusters for $\vartheta = 0, -1$ begins with a thorough, systematic study of the relative stability of clusters with approximately this
size range. Hence, an investigation towards finding the ground state geometries of neutral and anionic clusters with between \( x = 5 \) and \( 8 \) Al atoms was carried out within the Al\(_x\)I series. Various initial geometries were considered, and upon allowing the clusters to relax and optimization to take place, the clusters were compared to reveal the lowest energy structures for each cluster. All reasonable spin multiplicities were considered in addition to the geometrical optimization as well.

The results are put together in figure 6.1.1, detailing the ground state structures for the Al\(_x\)I\(^-\) clusters containing \( x = 6-8 \) aluminum atoms. The lowest possible spin multiplicity is found to be most stable for all cases. For all of the structures shown in the figure, the I atom is oriented in an on top location, bound to only one Al atom. A reinvestigation into this behavior was carried out and it was found that upon adsorbing I to a bridge site where two Al atoms are allowed to bond with the I atom, the geometrical optimization revealed that the I atom consistently moved towards the on top site upon geometrical optimization. The same was tried with initiating the calculation with bonding clearly between an I atom and three Al atoms (hence the I is placed at a hollow site). Again, it was found that optimization had no problem in cleaving the existing bonds to bind the iodine atom with a single aluminum atom in this case as well. Other bonding considerations were examined, including the possibility towards the formation of bonding four aluminum atoms with a single I within a complex that has a square face. This and all additional possibilities for bonding an I atom with more than one additional Al atom was deemed unfavorable by the calculation and were found to be higher in energy and unstable.
The explicit preference in forming Al-I bonds in this cluster shows that there may be some interesting behavior that can be gathered from this information. For each cluster depicted, the Al-I bond length is 2.64, 2.62, and 2.63 angstroms for \( \text{Al}_6\Gamma \), \( \text{Al}_7\Gamma \), and \( \text{Al}_8\Gamma \), respectively; and shows that the bond length remains relatively unchanged upon adding more aluminum atoms for the clusters considered. A free \( \text{AlI} \) molecule was calculated for comparison and found to have a bond length of 2.59 angstroms, which is similar to the bond lengths in the clusters shown in figure 6.1.1A-C. Remarkably, the free \( \text{AlI} \) bond length is nearly the same as that of the \( \text{Al}_x\Gamma \) clusters for \( x = 6 \sim 8 \), showing that the molecular bond length of \( \text{AlI} \) is maintained. This similarity in bond lengths between molecular \( \text{AlI} \) and the Al-I bonds present for the \( \text{Al}_{13}\Gamma \) and \( \text{Al}_{14}\Gamma \) families of clusters further shows the preference for the formation of Al-I bonds in the ground state clusters of this size regime as well.

A complete comparison must be made between the iodized aluminum clusters and the pure aluminum clusters. To this effort, an analysis of the \( \text{Al}_x \) clusters was also conducted for \( x = 6 \) to 8 Al atoms. Results were consistent with previous efforts [47, 57] in regards to geometries and spin multiplicities. Upon iodizing these clusters, it is found that the geometrical shapes remain relatively unperturbed, but various Al-Al bond distances do change some to accommodate the addition of an I atom. The mild changes in the Al-Al bond distances upon adding a single I atom are expected on such small clusters due to the induced charge transfer that takes place directed from the pure aluminum cluster towards the I atom. All of the electron affinities of such pure aluminum clusters are presented in table 6.1.1 and are much lower than that of the iodine.
atom, allowing for the extra charge to more readily accumulate about the iodine atom bound to the cluster.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Adiabatic Electron Affinity (AEA) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{6}</td>
<td>2.47</td>
</tr>
<tr>
<td>Al\textsubscript{7}</td>
<td>2.10</td>
</tr>
<tr>
<td>Al\textsubscript{8}</td>
<td>2.13</td>
</tr>
</tbody>
</table>

**Table 6.1.1:** Electron affinities of pure Al\textsubscript{x} clusters for x = 6-8.

Of primary interest is information that can be gathered in regards to the electronic stability of the clusters. Hence, the change in energies $\Delta_{n}^{X}$ upon removing different units were considered for Al\textsubscript{x}I$^{-}$ clusters where 5 ≤ n ≤ 8 and where X = Al, I, AlI, and I$^{-}$ are the units that are removed from these clusters. The following equations show how the gain in energy in adding various units to the preceding cluster were calculated from the total energies of the respective clusters involved for all of the anionic clusters:

\[
\Delta_{n}^{\text{Al}} = E(\text{Al}_{x-1}I^-) + E(\text{Al}) - E(\text{Al}_{n}I^-)
\]

\[
\Delta_{n}^{I} = E(\text{Al}_{x}^-) + E(I) - E(\text{Al}_{n}I^-)
\]

\[
\Delta_{n}^{\text{AlI}} = E(\text{Al}_{x-1}I^-) + E(\text{AlI}) - E(\text{Al}_{n}I^-)
\]

\[
\Delta_{n}^{I^-} = E(\text{Al}_{x}) + E(I^-) - E(\text{Al}_{n}I^-).
\]

The $\Delta_{n}^{X}$ energies characterize the significance of the energies involved in the various fragmentation pathways involving X as the fragment. Both neutral and anionic cluster fragmentation channels were carried out and are conveniently shown in figure 6.1.2E and 6.1.2D, respectively. The fragmentation pathways for the neutral clusters are:

\[
\Delta_{n}^{\text{Al}} = E(\text{Al}_{x-1}I) + E(\text{Al}) - E(\text{Al}_{n}I)
\]
\[ \Delta_n^1 = E(Al_x) + E(I) - E(Al_nI) \]
\[ \Delta_n^{All} = E(Al_{x-1}I) + E(AlII) - E(Al_nI) \]
\[ \Delta_n^{1-} = E(Al_x^+) + E(I^-) - E(Al_nI). \]

It is clear that an analysis of the cationic Al\(_x^+\) clusters was needed for a complete comparison between the neutral and anion variety and thus these clusters were also considered in the calculations.

There is a wealth of information that can be provided by looking at the energetics present within the various fragmentation channels considered in figure 6.1.2. A peak in the fragmentation channels is a result of there being a requirement of additional energy needed relative to its neighbors in order to fragment a certain molecule from the cluster about which the peak is located in forming the final fragmented product. Hence, the cluster about which the peak occurs is more stable than its neighbors with regards to fragmentation of the molecule of that channel. Thus it requires more energy added to the system to allow for fragmentation. Hence, peaks for multiple fragmentation channels present around a single cluster are an indication of a highly stable cluster.

Al\(_7\)I\(^-\) and Al\(_7\)I demonstrate exceptional stability based on the fragmentation channels. The fragmentation channel pertaining to Al\(_7\)I + \(\Delta_n^{1-} \rightarrow Al_7^+ + I^-\) requires over 6eV of energy and indicates that the I\(^-\) is indeed strongly bound to the neutral Al\(_7\)I cluster, as a result of the very high electron affinity of I and the bonding that takes place in allowing its 5p orbital to become filled, creating a very stable entity. What is remarkable though, is that upon the addition of an extra charge to the neutral species in forming Al\(_7\)I\(^-\) is that there is still bonding present between Al\(_7\) and I\(^-\) atom. The I\(^-\) atom
does not find it favorable to readily dissociate from the cluster once a final electron is provided and that there still exists bonding between it and the pure aluminum portion of the cluster.

A primary trend shown in the fragmentation channels depicted in the figure show that for all fragmentation pathways, there are more pronounced peaks present for the Al$_7$I neutral cluster as opposed to the less pronounced peaks found in the anionic variety. The values of the peaks pertaining to the energy required to fragment the cluster under observation are more intense for the neutral Al$_7$I as well. Also, the lowest energy fragmentation channel of the neutral Al$_7$I is higher than that of the anion and pertains to the fragmentation of AlI. These three observations again demonstrate the pronounced stability found in the neutral Al$_7$I cluster that is still present to a slightly reduced degree upon the addition of an extra charge.

It is also of interest to consider the effects present in the fragmentation channels in relating them with an analysis of the stability of such clusters that can be found in an experiment. The Al channel of fragmentation for the clusters under investigation is of higher energy for Al$_6$I$^-$ and Al$_7$I$^-$. Thus these clusters can be considered much less susceptible towards oxygen etching in forming AlO$_2$. This gives further reason towards the possibility that these clusters be present in molecular beams of mass spectrometry experiments after oxygen etching such as that in figure 5.3.2.

The energetic observations in the fragmentation pathways show strong support towards enhanced stability in the Al$_7$I and Al$_7$I$^-$. Now lets consider the development of a model to further explain the marked stability present in these clusters.
First, let’s consider the implications of using the jellium model to describe the stability of the clusters. Neutral Al$_7$I has an aluminum core where each Al atom can contribute three valence electrons for a total of 21 electrons that can interact with the potential created due to the positive background charge produced by considering the effects of the nuclei and innermost electrons of the cluster. Upon this interaction, the electronic configuration revealed is 1s$^2$ 1p$^6$ 1d$^{10}$ 2s$^2$ 2p$^1$. This is not a shell closure in the jellium model, but it has one more electron than the 20 electrons that makeup the closest nearby electron count that has a filled shell. The iodine atom has an electronic configuration of 1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 3d$^{10}$ 4s$^2$ 4p$^6$ 4d$^{10}$ 5s$^2$ 5p$^5$, with an unfilled 5p orbital. The electronic configurations are given to facilitate the consideration of the single electron energy levels shown in figure 6.1.3 for Al$_7$, Al$_7$I, Al$_7^+$, Al$_7$I$^-$, and I. On the surface, it may appear that there is no novelty to the Al$_7$I cluster, but it may be interesting to consider its properties in developing a mechanism that allows for pronounced stability in this cluster as well as its anionic counterpart.

Figure 6.1.3 shows a solid line that indicates a filled level and a dotted line that indicates an unfilled level. 1, 2, or 3 indicate the degeneracy type for the levels to facilitate reading the picture and the arrows are indicative of the spin up or spin down states. The iodine atom shows the 5p filled electron levels and the figure caption shows a zoom-box that shows the 5p unfilled level is degenerate with the two outermost filled levels, as expected. Let’s begin with the discussion of the one-electron levels of Al$_7$. The two filled states at −12.40eV that are outside of the scale and are not shown in addition to the nineteen filled electron levels that are shown form the 21 electrons that
are considered in this system for comparison with the jellium model. A large HOMO-LUMO gap is an indicative marker for highly stable clusters. We can see that the HOMO-LUMO gap of the Al$_7$ cluster is only 0.79eV, which is considered a small gap.

Now consider the reaction that takes place between the iodine atom and Al$_7$ shown in the figure and how the electron levels will restructure to form the Al$_7$I. The 5p states of the iodine atom interact with the 1$f^1$ electron (by the jellium model interpretation) in the highest occupied molecular orbital of the Al$_7$ cluster and form a bonding and anti-bonding pair located at approximately $-6$eV in a filled level and $-2$eV in an unoccupied level, respectively. The figure also shows that the interaction that takes place reduces the energy of all of the bonding levels found in the separate units of Al$_7$ and I to form the more stable structure found in Al$_7$I. The bonding states remain stably occupied in a low energy configuration of the neutral Al$_7$I cluster. The anti-bonding states remain unfilled for the Al$_7$I cluster and help emphasize its stability. Also, upon formation of the stable neutral cluster with seven aluminum atoms and one iodine atom, the HOMO-LUMO gap increases to 1.74eV, which is considered a gap expected of a highly stable cluster. The Al$_7^+$ cluster is also shown to aid in comparison with the neutral Al$_7$I cluster. There are ten of the twenty valence electrons that form a shell closing by the jellium model that are shown as filled electron levels that are shown in the figure for Al$_7^+$. The remainder of the electron levels is not in the scale of the figure shown. Interestingly enough, the HOMO-LUMO gap of the Al$_7^+$ cluster is found to be similar to that found in the neutral Al$_7$I cluster. This provides a clue as to the possibility of the pure aluminum portion of the neutral Al$_7$I cluster behaving in a manner reminiscent of the cationic Al$_7^+$. 
Mulliken charge analysis is a means of calculating partial charges on atomic sites via a mathematical method [58]. Figure 6.1.4F and 6.4G show the Mulliken charge populations for the anionic Al$_7$I$^-$ and neutral Al$_7$I clusters, respectively. Shown in the figure is a Mulliken charge of $-0.25\, e^-$ on the I site and a Mulliken charge of $+0.19e^-$ on the Al site. Hence, a complex is created that describes the cluster as Al$_7^{+0.25}$I$^{-0.25}$ and this is representative as jellium compound that is created upon forming a complex from Al$_7$ and I as ingredients. Such a complex is mediated by a change in oxidation state of a central metal atom as a result of the interaction with the surrounding ligands that are bound to the metal atom. This in turn shows an effect in the filling of the orbitals like that shown in figure 6.1.3. The resulting complex that is created is of the Al$^{+6}$I$^{-8}$ type, whose parts form a jellium compound and upon interaction there is an induced change of those parts that can be seen in the electronic structure reordering. The Al$_7$I cluster is only one example of this, and it would be most interesting to find other clusters that behave in a similar manner and can be classified in the same way.

There is clearly a charge transfer to I in the Al$_7$I cluster as shown by the Mulliken charge analysis, and the resulting calculated electric dipole moment is 1.10au (2.79D). In comparison, the dipole moment of NaCl gas is 3.54au (9.0D) by experiment and the calculation of this is 3.37au. Various clusters of the neutral, cationic, and anionic Al$_n$I series have their dipole moments listed in table 6.1.2. Upon adding an electron to the neutral Al$_7$I cluster, the dipole moment increases to 6.24D. Adding an electron to the neutral Al$_6$I cluster increases the dipole moment from 2.08D to 9.78D, indicating that this cluster experiences a much larger charge separation than Al$_7$I upon additional charge
introduced to the system. Since Al₆I is not found to be particularly stable, this in combination with the increase in the dipole moment suggests that this particular cluster would not be stable with respect to introducing an electron due to interactions that would ensue based on its more active nature as well as the increased moment that would also increase the probability of it reacting with some external species. But neutral Al₇I does not exhibit such behavior, suggesting that the extra electron can indeed be added to it without perturbing its dipole moment, suggesting that the interaction of the extra charge and the neutral cluster’s dipole moment does indeed play a role in stabilization of this cluster.

Now let’s turn to further describe the behavior of the Al₇I⁻ cluster. Upon adding the extra electron to the Al₇I cluster, figure 6.1.3 shows that there is a reconstruction that takes place in the orbital layout due to the extra electron occupying the 1f orbital of the Al₇ cluster. The result is shown in the Al₇I⁻ figure at the filled electron level located at −1.50eV. This reconfiguration effectively reduces the HOMO-LUMO gap that was found in the neutral cluster. Figure 6.1.4F shows that the extra electron accumulates an additional Mulliken charge of −0.16e⁻ on the iodine site and the remaining 0.84e⁻ charge is distributed on the seven aluminum sites. Also, the addition of the extra charge reduces the positive charge buildup on the closest Al site neighboring the I atom by 0.04e⁻. The final product is best described as an Al₇⁻⁶.₅₉I⁻⁰.₄₁ cluster. Typically, the addition of an extra charge to a stable closed-shell cluster would decimate its stability and leave a highly reactive cluster. Certain symptoms of this are found in the reduced HOMO-LUMO gap of the Al₇I⁻ cluster, but the lack of extensive structural reorganization
between the neutral and anionic clusters in addition to the results found in the fragmentation patterns of figure 6.1.2D indicate that this cluster is remaining stable upon adding the extra charge. The extra charge becomes bound to the dipole created by the neutral cluster upon its implementation and this is the characteristic that stabilizes the extra charge and results in a stable anionic form of the Al$_7$I$^-$ cluster. The electron affinity of the Al$_7$I cluster is calculated to be 2.09eV, which is an appreciable amount, and further alludes to the result that the dipole moment present in the Al$_7$I cluster allows for the stabilization of the extra charge and further calculation. Hence, both the neutral and the anion can be stable. This is especially appealing since the neutral cluster cannot be detected in experiments but the anion can. Now we shall move on to a brief discussion regarding the experiments that show the existence of Al$_7$I$^-$ as a truly stable cluster.
<table>
<thead>
<tr>
<th>Cluster</th>
<th>Electric Dipole Moment (Debye)</th>
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</thead>
<tbody>
<tr>
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</tr>
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</tr>
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</tr>
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<td>Al₈I</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>1.55</td>
</tr>
<tr>
<td>Al₈I⁻</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 6.1.2: The electric dipole moments of various neutral, anionic, and cationic AlₙI clusters are listed.
Figure 6.1.1: Geometrical structure of the (A) Al₆I, (B) Al₇I, and (C) Al₈I clusters.

Bond lengths are written in angstroms.
Figure 6.1.2: (D) The fragmentation energy $\Delta_n^X$ defined in the text to remove various fragments from $\text{Al}_n\Gamma$ clusters. (E) The fragmentation energy $\Delta_n^X$ defined in the text to remove various fragments from neutral $\text{Al}_n\Gamma$ clusters.
Figure 6.1.3: Electron energy levels for I, Al$_7$, Al$_7$I, Al$_7^+$, and Al$_7$I$^-$. Filled electron levels are indicated by a solid line and a dotted line refers to unfilled levels. The numbers 1, 2, and 3 indicate the degeneracy type for the filled electron levels.
Figure 6.1.4: The Mulliken population analysis for (F) Al₇I⁻ and (G) Al₇I. (H) The charge density of the HOMO in Al₇I⁻.
6.2 Mass Spectra and Reactivity Experiments: Al$_7$I$^-$. 

The work completed in regards to Al$_7$I$^-$ is a joint experimental and theoretical effort [56]. The experimental evidence supporting the truly stable nature of this cluster will thus be presented to suppress any doubt about the feasibility of creating such a cluster that is discussed. Details regarding the experimental setup are described previously within this document and details are provided in the corresponding references [47, 57].

Figure 6.2.1A shows the resulting mass spectra after Al$_n$- clusters react with molecular iodine that is introduced into the first reactant gas inlet. Major peaks corresponding to the Al$_{13}$I$_x$- and Al$_{14}$I$_x$- family of clusters appear, expectedly. Upon allowing methyl iodide vapor to react with the clusters produced in figure 6.2.1A, the mass spectra are recorded in figure 6.2.1B. The ensuing reaction results in diminished intensity for Al$_{13}$I$_x$- clusters of odd $x$, providing additional experimental protection for the theory explaining the marked stability in the clusters of even $x$ for this series. Note that the experimental results are indicative of solely the presence of these clusters and cannot determine if the clusters in this family are resistant towards attack of the methyl iodide or formed via fragmentation occurring during the reaction. All of the Al$_{14}$I$^-$ peaks experience reduced intensities upon interacting with the methyl iodide, showing a reactive tendency towards the molecular vapor. This is also not a surprise, considering the theoretical investigations found small active centers to be present even for the more stable Al$_{14}$I$_x$- clusters of odd $x$. Now let's consider the new highly intense features in the
spectra. \( \Gamma \) and \( I_3^- \) both are found to have intense peaks after the methyl iodide vapor is introduced.

The most intense feature depicted in the spectra belongs to \( Al_7I^- \). This cluster is also of notable abundance in previous spectra shown in figure 5.3.2 found through oxygen etching of \( Al_xI_y^- \) clusters. The presence of this cluster in the spectra shows that there exists a method of creating this cluster in abundance and provides evidence that claims this cluster is of a highly stable nature. The experimental observations coupled with the theoretical results show that this cluster is indeed special.

To further probe the characterization of the aluminum iodide clusters, an additional experiment was considered where the apparatus holding the \( I_2 \) vapor was exposed to increased heating and reacted with aluminum clusters to form the spectra of \( Al_xI_y^- \) clusters shown in figure 6.2.2A. The resulting clusters have a higher ratio of iodine present; notably \( AlI^- \) forms as a stable species.

These clusters are then exposed to methyl iodide and the reaction that takes place forms the features seen in the spectra of figure 6.2.2B. Of significant abundance is again \( \Gamma \), \( I_3^- \), and \( Al_7I^- \) in the lower mass region. Also note that the peaks corresponding to clusters of the even \( x \) \( Al_{13}I_x^- \) are present as well. The presence of these peaks shows that the \( Al_{13}I_x^- \) clusters in this experiment are the result of the etching process that takes place upon reaction of the clusters in figure 6.2.2A with methyl iodide, where no peaks of that variety are present. This is also the case for \( Al_7I^- \), which is evidenced for the second experiment as being the product of reactants including those of the larger mass region that were etched by methyl iodide and formed the resulting peak seen in figure 6.2.2B.
Experiments further demonstrate the truly unique nature of some of the families of clusters consisting of aluminum and iodine atoms in varying amounts. The noted presence of Al\textsubscript{13}I\textsubscript{x}\textsuperscript{−} clusters upon reaction with methyl iodide further supports the presence of active sites that make clusters of odd x in this family more susceptible to attack by reagents. The quenching of the active sites by an additional iodine atom in forming the even x Al\textsubscript{13}I\textsubscript{x}\textsuperscript{−} clusters become protected from the attack and are subsequently found in high quantities in the mass spectra after attack by methyl iodide or molecular oxygen. Furthermore, there is a resounding affirmation that Al\textsubscript{7}I\textsuperscript{−} can be formed by experiments and is indeed a very intense feature of the spectra further supports the notion that this cluster is highly stable. Theoretical insight shows us that this cluster can be considered a "jellium compound" that stems from the highly stable nature of the neutral Al\textsubscript{7}I cluster, an entity that cannot be conclusively examined by experiments due to the limitations considering the mass to charge ratio. The results here show how a synergistic effort between experiment and theory can provide a formidable sea of insight and ideas that lead to a conclusive result.
Figure 6.2.1: (A) $\text{Al}_n\text{I}_\kappa^-$ clusters generated via reaction of $\text{Al}_n^-$ with $\text{I}_2$ and (B) reacted with methyl iodide. Both spectra are shown on identical scales without normalization. Unlabeled peaks correspond to clusters with atomic oxygen or CH$_3$ present [56].
Figure 6.2.2: (A) Mass spectrum of I-rich Al\(_n\)I\(_x\) clusters generated by increased heating of the I\(_2\) vessel and then (B) reacted with methyl iodide. Both spectra are shown on identical scales without normalization [56].
Chapter 7. Aluminum Clusters on Organic Templates

7.1 The Association of Propene to \( \text{Al}_{12}^- \).

Thus far we have discussed three different types of clusters that have a remarkable degree of stability inherent in their geometries and electronic structures. The clusters observed to be stable are of \( \text{Al}_{13}^- \), \( \text{Al}_{14}^- \) for even \( x \), \( \text{Al}_{14}^x^- \) for odd \( x \) and neutral and anionic species of seven Al and one I atoms. Stability was shown to exist in these clusters through theoretical analysis of fragmentation patterns, HOMO-LUMO gaps, electronic configurations, geometrical comparisons, charge distributions, dipole moment and electron affinity considerations, and various spatial distribution plots describing the behavior of valence electrons and unfilled orbitals centered on the importance of the active sites present in the HOMO charge density. A simple model can be described that attributes the stability to a consideration of the jellium model and counting the number of confined valence electrons that interact with the background charge distribution of these clusters forming stable closed shell closures for the forty electron systems of \( \text{Al}_{13}^- \) and \( \text{Al}_{14}^{2+} \) such that these clusters act as a stable core upon which larger clusters can be built. The extra charge accumulation in forming the \( \text{Al}_{17}^+ \) cluster from the very stable neutral species allows it to behave in a manner that introduces the concept of a jellium compound to describe the coupling of the extra charge in the anion to the dipole moment of the highly stable neutral cluster. The core of this system is the twenty-electron \( \text{Al}_{17}^+ \) cluster. The introduction of three stable cores upon which larger clusters can be built that are also stable entities reveals that the nature of the cores including their valence suggests
a comparison to similar elements on the periodic table. The Al$_{13}^-$ cluster behaves as an electronegative halogen atom that has accumulated an extra electron, thus filling its shell. The Al$_{14}^{2+}$ cluster has similarities with the alkaline earth atom of the group II elements that have been doubly ionized and subsequently form a closed shell species. The characteristics of the Al$_7^+$ cluster is reminiscent to the highly electropositive atoms present in the alkaline group I column of the periodic table of elements upon the removal of a single charge, forming a closed shell species. The behavior of the cores aptly calls for the naming convention that demonstrates their respective properties and hence the Al$_{13}$ cluster can be considered a superhalogen, Al$_{14}$ a superalkaline-earth, and Al$_7$ a superalkaline. The characteristics of these superatoms entail use of unique properties in these clusters that can be enhanced upon construction of a lattice whose main constituents are of superatom character.

This now brings us to a consideration regarding the impact of aluminum clusters on organic templates [59]. Initiating this investigation are the calculations that can be done towards revealing the resulting nature of inclusion of a superhalogen in a reaction with alkenes that would be of great importance to the organic chemistry community. In consideration of a model alkene that would be useful in a study, the ethene (C$_2$H$_4$) class of hydrocarbons is the simplest and propene (C$_3$H$_6$) substitutes one H from the ethane group for a CH$_3$. Ethene also has biological and industrial importance, but the usefulness of propene currently as a fuel makes it of interest towards interactions that may ensue between it and clusters of the Al$_n^-$ form. Both propene and ethane have one C=C double bond, but the substitution for one H atom of ethane with CH$_3$ to yield the structure of
propene that subsequently introduces a C-C bond in addition to the C=C double bond that may reveal some interesting chemistry upon a reaction between propene and a cluster of the Al\textsubscript{n}⁻ spectrum.

Now one must consider the Al\textsubscript{n}⁻ cluster upon which the hydrocarbon may induce interesting behavior when it is adsorbed. Reactivity of the cluster is under prime scrutiny here. Aluminum clusters are modeled well by the jellium model where the background charge of the core and ionic constituents of the cluster can be found to allow interaction with the valence electrons of the metal clusters. Therefore a consideration of the number of electrons necessary in forming a closed shell is of importance since these clusters would be found to be less reactive to such species as propene. The Al\textsubscript{13}⁻ cluster forms a forty-electron complex and the result would most likely not allow for a reaction with any of the hydrocarbons. The addition of an atom to Al\textsubscript{13} to form the resulting fourteen aluminum atom complex would also not be of interest in forming reactive sites of adequate strength upon which to adsorb a hydrocarbon. This is due to the stable Al\textsubscript{14}²⁺ entity that governs highly stable clusters around this region and shows a lack of perturbation found in the icosahedral geometry of the Al\textsubscript{13} cluster found upon the addition of an Al atom to a triangular face.

Next under consideration would be the removal of a single Al atom from the Al\textsubscript{13}⁻ cluster. This indeed alters the compact icosahedral structure of the stable superhalogen and breaks the symmetry enough to actively provide the possibility for further reactions with organic species. Additionally, considering each Al atom to contribute three valence
electrons, the $\text{Al}_{12}^-$ cluster would be a 37-electron system. Hence it is not a closed geometric [46] or electronic shell and reactions can indeed be likely between it and propene.

Before beginning such a calculation of $(\text{C}_3\text{H}_6)\cdot\text{Al}_{12}^-$, one can imagine how such a reaction may occur. The reactive $\text{Al}_{12}^-$ species is three electrons short of a shell closure, which begs for a consideration of a reorganization of the bonding in propene such that three electrons are donated, one from each carbon site, may be possible. The two carbon atoms that share a double bond may be able to donate an electron a piece, breaking the double bond. But one carbon atom experiences a single bond association to another carbon and three polar bonds towards three hydrogen atoms. Even the migration of one of the three hydrogen atoms in the CH$_3$ portion to some other region in this cluster would allow for extensive bonding to occur between the third carbon atom that was previously bonded by a single bond to another carbon, but may reduce the ability of a previously double bonded carbon atom to donate charge due to the association of a migrated H atom. This will result in a 39-electron complex and provides a most interesting entry point into calculations that can provide more details about the characteristics of the $(\text{C}_3\text{H}_6)\cdot\text{Al}_{12}^-$ product that can form. It is of interest to find if the incomplete geometric and electronic shell of the $\text{Al}_{12}^-$ cluster that leads to its stability can be altered through a reaction between it and propene, forming a resulting more stable cluster.

The instability of $\text{Al}_{12}^-$ can be seen in a smaller HOMO-LUMO gap. Recent investigations published in the literature by Chrétien and et al. [60-62] have provided
interesting explanations pertaining to the reactivity of propene with metal clusters of silver and also of gold by use of density functional theory towards explaining experimental observations. Both gold and silver are metals and can be considered similar in regards to being free electron systems [63, 64], similar to aluminum. The rules that they proposed insist that the propene donates charge to the metal species from its highest occupied molecular orbital. The charge transfer then occurs between the propene and metal cluster by a donation of charge from the HOMO level of the propene to the LUMO level of the metal cluster. Metal clusters that have a lower LUMO level allow for a greater binding between them and the propene providing charge due to the charge transfer that ensues [60-62]. In addition to a metal cluster's LUMO level orientation playing a role in binding to the propene cluster, the spatial distribution of the LUMO level into the geometrical space around the cluster also plays a role in the binding taking place at the site where the LUMO is oriented most outward from the cluster. In a sense, the orientation of the LUMO level acts as an active site upon which the propene can bind and charge transfer can take place between the HOMO of the propene to the LUMO of the metal cluster.

Chrétien considered binding between propene and gold clusters of various net charges as well as the Au (111) surface, small silver clusters of neutral and cationic charge, and mixed clusters also [60-62]. The site where the LUMO protrudes the most in free cluster calculations tends to be the site upon which propene binding would take place [60-62]. Figure 7.1.1 shows the HOMO and LUMO charge densities for the Al_{12}^- cluster that is under consideration here. The structure of the Al_{12}^- cluster can be
described as an Al capped pentagonal face that is bound by another capped pentagonal face in the staggered orientation to it. Analysis of the spatial distribution of the LUMO in the figure shows that the Al atom at the vertex has the greatest portion of the LUMO spatial distribution extending furthest outward from the confined region of the cluster. This site would then be most favorable for propene association by Chrétien's rules [60-62] since it protrudes outmost from the geometrical configuration of the cluster. Now an analysis of the characteristic features of this cluster shall follow.

Pure aluminum clusters containing 7-14 atoms were examined. Considerations of many initial geometrical configurations were done and subsequent optimization through moving the atoms in the direction of forces until the final geometrical configurations were found, dictated by the notable presence of the forces dropping below the threshold value of 0.001 Hartree/bohr. Only ground state results in regards to the electronic characteristics are useful and subsequently reported here. In addition to geometrical relaxation from a host of possible initial geometries, various spin configurations were also considered as well. The results show the tendency towards the lowest spin multiplicity for the ground state structures.

The final results show some interesting features. Figure 7.1.2 shows the HOMO-LUMO gap of the converged ground state Alₙ⁺ (n=7-14) clusters under scrutiny and their respective LUMO orientations relative to one another. Quite prominent is the expected presence of a large gap for the Al₁₃⁺ cluster as expected. All other clusters exhibit a much smaller HOMO-LUMO gap than this very stable cluster. Al₇ is an exception, of course, for its gap is the second largest of the sampled clusters. Interestingly, the gap of Al₁₂⁺ is
the smallest featured in the examined clusters. This is expected due to the lack of closure in its electronic structure or geometrical shell and in agreement with previous results [46, 47]. Thus, the prediction that Al$_{12}^-$ is reactive seems justified thus far.

Now consider the orientation of the LUMO level of the clusters relative to one another in figure 7.1.2B. There is a peak for the LUMO level placement in the electronic configuration for the Al$_{13}^-$ cluster as one would expect as well. Even higher relative to the Al$_{12}^-$ cluster LUMO is that of the Al$_7^-$ cluster. This indicates that neither of these clusters (Al$_{13}^-$ or Al$_7^-$) would be favorable in producing a reaction with propene by considering the rules proposed by Chrétien. The decreased preference of binding propene to these clusters was also predicted above when considering the stable geometrical and electronic nature of Al$_7^-$ and Al$_{13}^-$. Additionally, we note that there is a valley in the absolute LUMO energies for the Al$_{12}^-$ cluster. Of the entire series considered, Al$_{12}^-$ is also the lowest energy LUMO level.

Calculations on the Al$_{12}^-$ cluster reveal several satisfying results. Energetics show that considering the neighboring clusters of a similar size, the Al$_{12}^-$ cluster has the lowest HOMO-LUMO gap and the lowest energy LUMO. Additionally, the LUMO charge density plotted in figure 7.1.1 shows that there is a localization of the spatial distribution that protrudes most from the cluster located on the Al site that is the apex of the cluster. According to Chrétien’s rules, Al$_{12}^-$ does seem to be a prime candidate for adsorption of C$_3$H$_6$ onto it and the result would be a very stable species.

Now we consider the placement of the hydrocarbon propene onto the Al$_{12}^-$ metal cluster. Results of the calculation show the affinity of propene towards the protruding
site depicted on the apical atom shown in the LUMO spatial distribution of figure 7.1.1 is indeed found to be the ground state orientation and is subsequently shown in figure 7.1.3. Additional orientations initiating the approach of C\textsubscript{3}H\textsubscript{6} to the Al\textsubscript{12}\textsuperscript{-} geometry were considered and a variety of spin configurations were tried, revealing one additional state that serves as an isomer with regard to the ground state structure shown in the figure. The isomeric structure represents propene binding to the pentagonal face of the uncapped region of the metal Al\textsubscript{12}\textsuperscript{-} cluster. Binding in this structure behaves in such a manner that the C\textsubscript{3}H\textsubscript{6} hydrocarbon donates charge from its HOMO level to the LUMO of the metal cluster where in this case the spatial distribution of the LUMO level of the isolated Al\textsubscript{12}\textsuperscript{-} cluster reveals that there is a large portion of accumulated LUMO density on the uncapped pentagonal ring where it can bind and is shown in the resulting geometry. The energy difference between the two isomers for the two binding sites is 0.01eV. This shows that either the apical Al atomic site or the bridge site of the uncapped pentagonal ring of the Al\textsubscript{12}\textsuperscript{-} cluster can provide regions where charge can be readily accepted as the propene adsorbs to the cluster. Nonetheless, this shows that a reaction can occur when considering the association of aluminum clusters to organic templates.

In an extension to the results, let’s now consider the possibility of adsorption of hydrocarbons to clusters of the Al\textsubscript{13}I\textsubscript{x}\textsuperscript{-} and Al\textsubscript{14}I\textsubscript{x}\textsuperscript{-} families. Clusters of odd x for the Al\textsubscript{13}I\textsubscript{x}\textsuperscript{-} series and even x for the Al\textsubscript{14}I\textsubscript{x}\textsuperscript{-} moiety exhibit the preponderance of active sites in their HOMO charge distribution plots. The protruding lobes present in the active clusters that were subsequently quenched upon adding another I atom can be looked at being equivalent to that of the LUMO spatial distribution of the Al\textsubscript{12}\textsuperscript{-} cluster that allows for
accurate approximation to the site upon which the associating propene will most likely donate charge. The HOMO charge density of the Al\textsubscript{12}\textsuperscript{-} cluster is shown in figure 7.1.1 and is roughly the equivalent of the LUMO spatial distribution that has been rotated by 90 degrees about the apical Al atom that caps the pentagonal ring. This suggests that such an electronic similarity may also exist in the LUMO levels of the other aluminum iodide species with active sites that can dictate the preferred association of propene or other hydrocarbons to those sites. Further reaction mechanisms can be found in a separate study, but it is interesting to note that any identification in bonding changes and other effects upon propene association would be most exciting to convey and compare between the superhalogen clusters and their halogen atom analogues.

Additionally, let’s consider how the results can be interpreted upon extension into larger clusters. The Al\textsubscript{12}\textsuperscript{-} cluster can be considered the staggered stacking of two capped pentagonal rings. The stacking of clusters to form a stable result has been described in the literature for mixed metallic systems [65-67]. Subsequently adding six more Al atoms in the form of stacking another capped pentagonal ring to this structure in a staggered orientation would not greatly alter the character of the LUMO spatial distribution since according to the resulting stacked geometry, there would still only exist one apical Al atom and a single pentagonal ring upon which adsorption of propene can still occur in the extended cluster of Al\textsubscript{18}\textsuperscript{-}. Further sequencing of the stacked species through addition of a capped pentagon in a staggered manner relative to the previously stacked constituent would reveal clusters of a similar nature and maybe show a propensity of Al\textsubscript{24}\textsuperscript{-} and subsequently stacked structures as being prime candidates for
propene binding. The stacking can also evolve through the association of triangular arrangements of Al atoms to the more active site of the cluster, forming upon a single addition of Al$_3$ to Al$_{12}$ to bind and subsequently still allow association of the propene through its bridge site. If this trend continues and relaxation occurs for when 6n additional aluminum atoms associate and form the stacked structure described above, there is the possibility for a complete series of arrangements that would allow for hydrocarbon binding to the metal clusters of the type Al$_{12+3n}$.

Another possibility of extended structures and their reactivity with hydrocarbons is the inclusion of triangular faces of Al atoms that can be added to the faces of the C$_{3v}$ symmetrized structure of Al$_{13}$ to form additional elements whereby reaction may ensue with propene upon removal of a single Al atom from the resulting cluster. This would form a Al$_{12+3n}$ series of clusters capable of reacting with propene. Now we will turn to the experimental observations in regard to aluminum clusters on organic templates.
Figure 7.1.1: Lowest energy structure and maps of the charge density for the HOMO (top) and LUMO (bottom) of Al_{12}$^\cdot$. 
Figure 7.1.2: (A) Plot of the HOMO-LUMO gap as a function of cluster size in the series Al$_n^+$. (B) Plot of the energy of the LUMO as a function of cluster size in the series Al$_n^-$. The energy is set relative to the LUMO energy for Al$_{12}^-$, which is shown here as zero.
Figure 7.1.3: (A) Ground state geometry of C₃H₆ associated with Al₁₂⁻ and (B) a low lying isomer. Bond lengths are in Å and ΔE, in eV, is the difference in total energy relative to the ground state.
7.2 Mass Spectra Experiments: Association of Propene to Al_{12+3n}⁻.

The work completed in regards to C₃H₆ association to Alₙ⁻ clusters is a joint experimental and theoretical effort [59]. The experimental evidence supporting the characteristics of using the propene and Alₙ⁻ reactants to form the resulting stable products will thus be presented to suppress any doubt about the feasibility of creating such a broad range of clusters that are discussed. Details regarding the experimental setup are described previously within this document and details are provided in the corresponding references [47, 57].

Figure 7.2.1 shows the experimental results upon a reaction between the Alₙ⁻ clusters that were created and shown in figure 7.2.1A with 200sccm of C₃H₆ (Figure 7.2.1B). The result of the reactions shows that solely Al₁₂⁻ reacts with the propene and is shown by an asterisk in the figure. Figure 7.2.1C shows the branching ratio as a function of increasing flow rates of propene from 0 to 200sccm. Here, we see that the (C₃H₆)Al₁₂⁻ contribution increases as the Al₁₂⁻ contribution decreases upon increasing the flow rate of propene. This is further evidence that a reaction occurs between the propene and Al₁₂⁻, leaving a stable combined species that is found as a peak in the mass spectra.

Additionally, a higher concentration of propene is shown to be introduced to the previously formed Alₙ⁻ clusters in figure 7.2.2A to form the resulting products’ intensities in the spectra of figure 7.2.2B. The result is shown by the asterisks that point out the most intense peaks of the spectra that are of the series corresponding to (C₃H₆)Al₁₂+3n⁻ for
n=0-3. The arrows indicate the decreased intensities of the $\text{Al}_{12+3n}^-$ peaks to allow formation of the propene associated aluminum cluster anions.

The experimental evidence points out that a resulting cluster of $(\text{C}_3\text{H}_6)\text{Al}_{12}^-$ is indeed formed and found to be stable even under smaller concentrations of propene. Upon increasing the concentration of propene into the system, stable peaks corresponding to $(\text{C}_3\text{H}_6)\text{Al}_{12+3n}^-$ (n=0-3) are formed at the expense of decreasing intensities in the pure $\text{Al}_{12+3n}^-$ cluster peaks indicating that the reaction does indeed take place and is not the result of any type of fragmentation of larger clusters. This all suggests that there is indeed validity in considering the HOMO-LUMO gap, relative energy of the LUMO level, and closed geometric and electronic shells in aluminum cluster anions to predict which clusters would indeed be most favorable in providing the environment upon which electron donation may occur as the hydrocarbon group transfers an electron from its highest occupied molecular orbital to fill the lowest unoccupied molecular orbital of the aluminum cluster. Hence the experimental results are in complete agreement with the theoretical model.
Figure 7.2.1: Mass spectra of (A) Al$_n^-$ clusters (B) reacted with 200 sccm of C$_3$H$_6$. The asterisk indicates the C$_3$H$_6$Al$_{12}^-$ peak. The branching ratio (C) shows the contribution of Al$_{12}^-$ (outlined squares) and C$_3$H$_6$Al$_{12}^-$ (filled diamonds) to the sum total of both species’ ion signal as a function of increasing C$_3$H$_6$ concentration. The y axes indicate peak intensity [59].
Figure 7.2.2: Mass spectra of (A) $\text{Al}_n^-$ clusters (B) introduced to a large concentration of propene, arrows point to the peaks of reduced intensity that correspond to the $\text{Al}_{12+3n}^-$ ($n = 0 – 3$); asterisks indicate the $\text{C}_3\text{H}_6\text{Al}_{12+3n}^-$ species. The y axes indicate peak intensity [59].
Chapter 8. Conclusions

8.1 Summary

Herein, we have discussed three different classes of very stable clusters that were analyzed through state of the art density functional theory calculations. All clusters considered were geometrically and electronically optimized under the premise of including many initial geometrical configurations and spin moments. Characteristics of the clusters were studied through a detailed analysis that included energetic observations in the HOMO-LUMO gap, disassociation energies and pathways of various fragments of the parent clusters, distribution of the electronic structure and its change in subsequent binding of additional elements, electron affinity considerations, spatial distributions of various electronic orbitals, and binding energies. Geometrical configurations, closures, and behaviorism in various structures were also considered as well as Mulliken charges, dipole moment trends, and ionization potentials. The consideration of all of these features exhibit a complete picture that encompasses the full nature of the clusters and allows for the presentation of a simple model that can be used in explanation of the trends that are found in the highly stable clusters of Al$_{13}$I$_x^-$ for $x$=even, Al$_{14}$I$_x^-$ for $x$=odd, and neutral and anionic Al$_{17}$. 

Theoretical treatment of Al$_{13}$I$_x^-$ clusters discloses several novel characteristics that are not found to occur in conventional polyiodides. The iodine atoms in these clusters do not
bind as molecular iodine of the form $I_2$ but instead as I atoms that preferentially bind to a single Al atom on the surface of the metal cluster. There are even and odd stability patterns that are found and describe the physical nature of the formation of active centers for odd $x$ and their subsequent quenching upon occupation by an additional iodine atom. The presence of even-odd alternations of stability is also seen in the HOMO-LUMO gap variations upon increasing iodine content of the clusters and alternations in the iodine dissociation energy pattern. For $x \leq 8$, there is a geometrically unperturbed $Al_{13}^-$ upon which the cluster is built, forming a superhalogene core upon which larger extended structures are built. The superatom core type is deduced based on the similarity in the electronic structure and electronegativity of the $Al_{13}$ cluster and the halogen elements in the periodic table. A simple model is proposed to explain the stability present in this series of clusters. The electronic and geometric shell closings of the metal cluster core allow use of the jellium model to provide a model picture of the behavior of these clusters. Within such a model, the forty valence electrons in the $Al_{13}^-$ cluster interact with the uniform charge created by the nuclei and core electrons of the spherical cluster and hence form a stable electronic shell closure by use of the jellium model that remains intact upon increasing the amount of iodine atoms adsorbing onto the surface.

Qualities of the $Al_{14}I_x$ family of clusters are also unique and provide novel concepts that arise. Theoretical studies that have analyzed this series of clusters reveal some similarities in their nature with the $Al_{13}I_x$ family of clusters such as the tendency towards breaking the molecular iodine $I_2$ bonds in favor of situation of atomic iodine binding to the on top sites of the aluminum atoms on the cluster surface. Differences arise in the
trends for stability of these clusters. The odd-even alterations in stability are different from the superhalogen core aluminum iodide series as well as the noted identification of Al$_{14}$I$_3^-$ as the first stable entity in the series. Investigations into the HOMO-LUMO gap and dissociation energy of removing subsequent iodine atoms from the clusters in this family show this trend. The marked geometrical feature upon which this novel character hinges is the inclusion of one additional aluminum atom to the Al$_{13}$ core and its relaxation at a site on the triangular face. The result is a decrease in the electron affinity of the Al$_{14}$ cluster below that of the iodine atoms. Additionally, it was found that the stable core upon which larger clusters are built is geometrically reminiscent to Al$_{14}^{2+}$. Thus the simple model picture of Al$_{14}$I$_3^-$ is that of the Al$_{14}$ portion of the cluster donating two electrons to the I sites and the addition of the extra charge to stabilize the cluster resulting in the formation of a forty-electron superalkaline-earth atom core. The similarity between Al$_{14}$ and the atoms of group II of the periodic table of elements in stability and propensity to donate charge is remarkable. Upon further adding more iodine atoms to the stable core, larger clusters are formed with the same compact core structure for x≤8. Beyond this, the central atom of the icosahedral-like core cluster finds it favorable to migrate to the surface towards forming maximal Al bonding. Also, the presence of active sites plays a role in the even-odd alternations in stability for clusters of this type.

There is considerable experimental evidence supporting the presence of a unique trend of aluminum iodide clusters present in the mass spectra. Clusters of Al$_{13}$I$_x^-$ and Al$_{14}$I$_x^-$ are enhanced in peak intensity upon I$_2$ vapor exposure to a laser ablated aluminum
mist. Experiments show that oxygen etching these clusters reveal intense features in even x for Al$_{13}$I$_x$ and odd x for Al$_{14}$I$_x$. This allows for further evidence towards the ease of generation of these clusters and their marked stability.

One additional cluster of remarkable stability has been considered, that of Al$_7$I$. The stability in this cluster hinges on the marked stable nature found in the neutral-charged variety of this species. Comparative studies of fragmentation pathways of these two clusters and geometrical considerations arrive at a remarkable stability present in the neutral Al$_7$I that can be described as a compound jellium model, behaving similarly to molecules found in inorganic chemistry that change the oxidation state of the central metal atom depending on the type and quantity of ligands that bind to it to allow for the most stable shell filling possible. Al$_7$ thus combines with I to create a complex that is stable and the core of such a complex can be considered reminiscent of an Al$_7^+$ cation, which is stable and is an electronically closed-shell twenty electron system. The characterization of this cluster allows for a comparison between it and alkali metals on the periodic table and henceforth the similarities suggest the naming convention of superalkali to describe the Al$_7^+$ type of cluster. Furthermore, it is found that the stability of the neutral Al$_7$I$^-$ cluster arises due to the interaction that ensues between the dipole moment of the neutral cluster and the extra charge and details are shown in studies of the electronic orbital configurations. Identifying a stable anion allows for a comparison with experiment and the result is that an intense peak in the mass spectra is found for Al$_7$I$^-$ is also found upon allowing an interaction between aluminum cluster anions and methyl iodide, and again experiment and theory are shown to agree.
This brings us to the final study, that of association of propene to \( \text{Al}_{12}^- \). An analysis of the energy of the HOMO-LUMO gap and LUMO levels of the \( \text{Al}_n^- \) clusters reveals the significance of this as a prediction tool that can be used to find possibilities of clusters that can be found to most readily react with hydrocarbons. Additional observations of the spatial distribution of the LUMO of the pure \( \text{Al}_{12}^- \) with the rules proposed by Chretien et al. in mind allow for accurate simulation of the most stable geometrical binding site of propene added to the pure aluminum clusters. Both the experiment and theory showed that the \( \text{Al}_{12}^- \) cluster offers the most preferred binding opportunity for \( \text{C}_3\text{H}_6 \) and subsequently forms the product \( (\text{C}_3\text{H}_6)\text{Al}_{12}^- \) in the reaction that follows. The research of aluminum clusters on organic templates not only provides interest towards basic chemistry, but it also suggests that the active sites generated by the aluminum iodide clusters may provide ample strength to allow an ensuing reaction with propene or other hydrocarbons.

The electronic and geometric structure of \( \text{Al}_{13}^- \) remains unchanged upon association with I ligands. Additionally, the \( \text{Al}_{14}\text{I}_3^- \) cluster was found to have a core of \( \text{Al}_{14}^{2+} \) and a spherical shape. The jellium model is used to help interpret the results and provide a sound reasoning towards electronic structure closure of the stable clusters. The reasoning thus far points to the \( \text{Al}_{13}^- \) core acting as a halide ion for the \( \text{Al}_{13}\text{I}_x^- \) series and the \( \text{Al}_{14}^{2+} \) core acting as a doubly ionized group II element of the periodic table for the \( \text{Al}_{14}\text{I}_3^- \) cluster. Also, \( \text{Al}_7^+ \) behaves as a cationic alkaline atom in the \( \text{Al}_7\text{I} \) cluster. Due to analogous electronic structure behavior between these three aluminum cluster cores and atoms on the periodic table we can then condense those similarities and regard the
following clusters of Al$_{13}$, Al$_{14}$, and Al$_7$ as superatoms. Superatom cores provide a reasonable explanation to the stability present for the discussed clusters. Superatoms as cores of larger clusters introduce two important accomplishments in characterization of their unique chemistry. Firstly, there is a description of induced active sites found in varieties of the aluminum iodide clusters that become subsequently quenched with the addition of another iodine atom. Secondly, the bonds of the molecular iodine are broken and associate to the core atomically at the on top orientations.

We are now at the initiating step of introducing stable clusters of atoms that behave in a manner reminiscent of atoms found in the periodic table of elements. Just as atoms can be assembled in lattice structures, there is suggestion that the assembly of clusters in such three-dimensional structures that will enhance the novel characteristics found in their cluster constituents. The result is the possible synthesis of many exciting new materials and fundamental concepts of physics and chemistry that govern their behavior. This leads us into possibilities that may arise due to clever extension of the fascinating chemistry of the superatom clusters.
Chapter 9. Future Prospects

There are some very exciting implications that are a direct consequence to the results discovered in the theoretical studies. Studies on clusters of $\text{Al}_{13}\text{I}_x^-$ and $\text{Al}_{14}\text{I}_x^-$ suggest that a new class of polyhalides, different from those characterized by conventional halogens, has been shown through a theoretical model derived by conceptualization of extensive theoretical results used as probes for the characterization of these clusters. The investigation has disclosed that stable superatom cores can govern the stability in the larger, extended aluminum iodide species. The superatom concept is further realized with the introduction of the $\text{Al}_7\text{I}^-$ cluster as also containing a superatom core that enhances its stability.

In addition to the theoretical work, there is a synergistic effort provided through experimental observations in the revelation of the oxygen etching studies in unveiling several key results that agree with the theory. First, it provides a method to generating stable aluminum iodide clusters that are stable relative to air. This method can provide an ideological basis that can be expanded upon towards the possibility for future commercial use if needed. Second, the mass spectra prior to oxygen exposure had a distinct signature of enhanced peaks corresponding to all of the cluster series, $\text{Al}_{13}\text{I}_x^-$ and $\text{Al}_{14}\text{I}_x^-$. Third, upon exposure to oxygen, the thermalized aluminum iodide clusters formed even-odd alterations in the spectra, suggesting novel behavior. In a separate study, $\text{Al}_{17}\text{I}^-$ was found to be a stable entity as well. All of this behavior is explained by
the theoretical results and create confidence in the possibility for a bright future in regards to these systems.

Now let’s consider the possibilities in continuing future studies that would be helpful to the scientific community. The possibilities stem from the novel chemistry found in superatoms. First, let us consider the possibility of exploiting the nature of the active sites that are formed in selected aluminum iodide clusters towards potentially revealing new applications.

One such possible application of the Al$\text{}_{13}$I$_x^-$ and Al$_{14}$I$_x^-$ clusters is in regards to the catalytic significance of active sites. An example of this is to treat selected clusters as a catalyst in reducing carbon monoxide. The clusters that have active sites provide the possibility of initiation of a chemical reaction with O$_2$ during its approach to the active site. Calculations on this thus far show that the approach of molecular oxygen to the active centers in the aluminum iodide clusters provide ample strength to allow for the O$_2$ bond to lengthen to 1.50 angstroms. Energetically, this reduces the barrier that will allow dissociation of one of the oxygens by an approaching CO molecule to result in CO$_2$ formation. The current state of the mechanism is shown in figure 9.1. It shows that such a reaction can occur whereby the strength of the O$_2$ bond is reduced upon adsorption to an Al$_{13}$I$_3^-$ such that CO reduction can occur, providing the possibility of these clusters to become useful as nanocatalysts.
**Figure 9.1:** A diagram showing part of the mechanism for CO reduction by an Al$_{13}$I$_3^-$ cluster. The O$_2$ molecule binds most stably to the active site of the Al$_{13}$I$_3^-$ cluster, weakening the oxygen bond. A CO molecule then most favorably approaches the O$_2$ binding site and through an exothermic reaction, CO$_2$ can form by surpassing a much reduced barrier, and subsequently dissociates from the Al$_{13}$I$_3$O$^-$ molecule.

Novel new organic chemistry is also alluded to with future studies that can be conducted providing the basis of metal clusters on organic templates. Research here can potentially provide a better understanding of hydrocarbons role in the origin of life and as fuels. Perchlorates can be used as an oxidizer in fuels for example; maybe novel methods of utilizing the stable clusters discussed here may be possible in providing new methods for fuel production. Also, the medical implications of aluminum iodide clusters towards the treatment of thyroid disorders can also be considered.
Now one may consider possibly further extending on the novel chemistry found in the behavior of the superatoms whereby I$_2$ bonds are broken in favor of adsorption of single I atoms onto the surface of the clusters. The direction here is towards potentially forming new compounds that are not formed by ordinary polyiodides. The clusters studied indeed continue to be stable for larger iodine content due to the basic superatom core structure, and consequently it would be interesting to see to what extent we may be able to use these molecules as building blocks to forming extended structures. It may be possible to begin with the introduction of a potassium atom to act as a charge donor and stabilize neutral variations of these clusters upon which we can build a solid framework such as the cluster-molecule shown in figure 9.2. Due to the shear size of the clusters, molecular charge donors can also be

![Figure 9.2: The K(Al$_{13}$I$_2$)$_2$ cluster-molecule. The extension of these units may be possible in forming bulk materials with clusters as the stable building blocks.](image)

considered in the extension of these clusters towards forming novel geometrical structures such as a crystal lattice of cluster constituents, linear arrangements of clusters doped with metal atoms to increase the magnetic anisotropy of such small systems, ring,
and tube varieties of these clusters can be considered in an extended study that considers the exploitation of the stable nature of the clusters discussed in providing a framework upon which larger clusters can be built. For the first time in cluster research, the joint theoretical and experimental effort suggests that these clusters do indeed have the stability requirement such that their geometrical orientations potentially can remain intact upon clever construction into a lattice. It is currently difficult to see if this could even be a possibility, but the search does continue to find the most stable forms of clusters that may make cluster assembled materials a possibility.

Thus there is an exciting range of possibilities that can stem from the research conducted in this essay. The truly unique and novel characteristics of these clusters can be utilized towards not only the development of new materials, but also provides a wealth of new ideas in regards to basic science. The unconventional chemistry of these clusters in their construction such as the tendency for selected species to form active sites and geometrically stable ground state structures that prefer breaking the molecular I₂ bonds all provides an exciting picture that reveals a few of the many treasures that nature has kept as secrets in its well hidden vault until now. The future merely opens up new opportunities to extend the current research towards new ideas that can stem from the research presented here.
List of References


