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Atomic and Electronic Properties of Neutral and Cationic Metallic Clusters.

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ATOMIC AND ELECTRONIC PROPERTIES OF
NEUTRAL AND CATIONIC METALLIC CLUSTERS

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in
The Department of Physics and Astronomy

by
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DEDICATION

Warmly dedicated to all the good people of the State of Louisiana.
ACKNOWLEDGEMENTS

Heading the long list of those who have helped me in the course of my research here, is of course, my advisor Professor Randall Hall, who agreed to be my advisor for a project that was not directly in his line of research and to which he has since devoted so much time and interest. I can't thank him enough for his unfailing support and optimism throughout our work together. I also wish to thank Professor Neil Kestner for the many talks we've had regarding this project and for the insights he has provided.

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We find optimal atomic and electronic structures for neutral and singly, positively charged clusters of beryllium and beryllium-lithium (of the form $BeLi_k$) using density functional theory in the local spin density approximation. Ions are moved with a steepest descent method, and the electronic wave functions optimized using a fictitious dynamics with simulated annealing, as conceived by Car and Parrinello. Shell-like orbitals, filling angular momentum states in the order: 1s 2p 2s 1d, are obtained for the beryllium clusters. The same ordering is found for the $BeLi_k$ clusters which indicates a departure from the ordering found in pure alkali clusters by the lowering of the 2s level to below the 1d level due to the larger electron affinity of the $Be$ impurity.

We similarly calculate an atomic basis to which we relate these shell-like orbitals, and employ a Mulliken population analysis to visualize how the atomic orbitals might hybridize to create them. This analysis also allows us to observe an increasingly metallic behavior with cluster size, by associating the electron density distribution, and in the case of a charged cluster, the distribution of the hole, with atomic sites, and with regions of overlap between atom pairs. We quantitatively show the increase in density associated with bonding as cluster size increases, and the tendency of the hole to distribute itself near the most exterior atomic sites in clusters of high symmetry.

Our results are compared with the predictions of the shell/jellium model in the context of our calculated binding energies and ionization potentials.
CHAPTER 1

INTRODUCTION

Cluster Physics, the study of small aggregates of atoms, is a field of some attraction as it holds the key to how such aggregates change from entities exhibiting atomic behavior to those exhibiting bulk properties during the growth process. In the course of such growth, clusters display characteristics of both forms of matter to varying degrees depending on their size and atomic and electronic structures [1]. Experimental interest has been heating up since the 1980's with the advent of new techniques for the production of clusters such as high energy ion bombardment of surfaces [2] and laser vaporization[3-5]. First principles theoretical studies, once confined to investigating very small clusters subject to many geometric constraints using configuration interaction with inferior basis sets or semiempirical methods, are now performed using recently developed optimization schemes applied to density functional theory (DFT)[6-8]. With the appearance of supercomputers larger clusters, on the order of hundreds of atoms, are being studied and the recent affordability of personal computers now allows the harnessing of many such units into inexpensive clusters that can rival the supercomputers.

Issues that scientists address include ion and electron solvation by clusters to form cationic and anionic species, fragmentation processes by which larger clusters split to form smaller ones, chemical reactivity, and photoexcitation and ionization. The evolution of binding energies and changes in the nature of bond formation with increasing cluster size along with the determination of the most stable geometries in homogeneous clusters can allow one to predict
the growth mechanisms by which small clusters coalesce to form structures approaching the bulk material [8].

Earlier models for studying clusters attacked the problem from the points of view of sphere packing [9] and pair interactions such as the Lennard-Jones potentials. Experimental work on neutral [10] and charged [11] clusters appeared to justify these approaches showing peaks in the abundance spectra of xenon and argon for icosahedral and cubooctahedral structures, implying their relative stabilities.

The work of Knight et. al. [12] investigating the abundance spectra of sodium clusters led to the idea that the alkali metals, and perhaps metals in general, have a shell-type structure as found in atoms and nuclei.

In atoms, the shell structure arises from considering each electron to be under the influence of a central potential representing its interaction with the nucleus and the other electrons. Discrete energy levels result containing shells of orbital angular momentum $\ell$, each capable of holding $2(2\ell + 1)$ electrons according to Pauli's exclusion principle for fermions. When a shell is filled and the next level is particularly high such that the addition of another electron would greatly lower the ionization energy, a "closed shell" is indicated.

When nuclei containing "magic numbers" of nucleons were observed to be particularly stable indicating a shell structure, workers proposed a Fermi gas model for the nucleus in which each nucleon moves in a central potential represented by a square well, a harmonic oscillator, or some interpolation between the two [13], and modified by a strong inverted spin-orbit coupling.

Early calculations of electronic structure of metallic crystals have replaced the lattice with a uniform positively charged background referred to as a "jellium". The idea was that there was little spatial variation of the ionic
potential over the unit cell except in the vicinity of ion cores where there would be little concentration of the valence electron density due to repulsion from the core electrons [14]. Knight's work led Chou et. al. [15] to apply the spherical jellium model to clusters of the alkali metals lithium, sodium, and potassium. This model assumes a uniform positive charge density

\[ \rho_{\text{ion}} = \frac{1}{\frac{4}{3}\pi r_s^3} \]

where \( r_s \) is the radius of a sphere containing one electron in the free electron model of the bulk material. This charge density extends over a sphere of radius \( R = Z^{1/3} r_s \) where \( Z \) is the number of valence electrons in the cluster. The resulting potential

\[ V_{\text{ion}} = -\frac{Z}{2R} \left( 3 - \frac{r^2}{R} \right); \quad r \leq R \]

\[ = -\frac{Z}{r}; \quad r > R \]

can then be used as the external potential acting on the valence electrons in the framework of density functional theory, which is described in some detail in the next chapter. Shell closings were found in this computational work and identified to appear in the order: 1s 1p 1d 2s 1f 2p ..., corresponding to the abundances found by Knight. Subsequent work by Chou and Cohen [16] applying the spherical jellium model to magnesium and aluminum showed the high stability clusters to be keyed to the number of valence electrons rather than to the number of ions in the cluster, causing them to conclude that delocalization of these electrons rather than ion packing was responsible for the phenomenon. Kappes, Radi, Schar, and Schumacher [17] (KRSS) take some exception to the shell/jellium model reporting that while it may account
for some abundance spectra, it can fail to predict the trends of ionization potentials. We will return to these issues later in the course of this work.

Here, we’ll present density functional calculations applied to small clusters of pure Beryllium and mixed Beryllium-Lithium; both neutral and charged. Beryllium clusters are interesting as their binding energies increase from the weakly bound dimer to a strongly bonded metal in the bulk. The drawback to beryllium is its toxicity, so that experimental data for their clusters do not exist, to our knowledge, with the exception of the dimer [18]. Beryllium clusters have been studied extensively with configuration interaction (CI) methods [19-30]. The results vary greatly depending on the basis sets used and beyond the five atom cluster, the use of smaller basis sets have led to some uncertainty in the nature of the lowest lying energy states. Some studies have been done using the DFT approach. Studies of the Group IIa dimers have been made by Jones [31], Painter and Averill [32], and by Ortiz and Ballone [33]. Khanna, Reuse, and Buttet (KRB) [34] performed all electron calculations for neutral, singly, and doubly charged clusters of up to five atoms. Blaisten-Barojas and Khanna [35] fitted a classical many-body potential to the results, predicted the structural and binding properties for much larger clusters, and investigated the approach to the bulk material. Kawai and Weare (KW) [8] used a pseudopotential, optimized the atomic and electronic properties simultaneously, and predicted the growth and evolution of neutral Be clusters of up to 20 atoms. All of this work has been in the framework of the local spin density (LSD) approximation [36, 37] with the exception of that of Ortiz and Ballone [33], who used gradient corrections of the density to the exchange-correlation potentials.

In the case of the mixed clusters, we compare our work with CI calculations performed by Pewestorf, Bonacic-Koutecky, and Koutecky [38] on
these systems and with experimental work done by (KRSS) who studied the isovalent systems of mixed Magnesium-Potassium clusters.

We explore the metallic behavior and qualities of these clusters pertaining to the shell model in terms of a shell-like electronic structure and increased stability of clusters having magic numbers of electrons. How atomic orbitals might hybridize to create shell-like molecular orbitals is also discussed even though the molecular orbitals are not optimized directly over an atomic basis. In the case of the charged species, we look at how the excess charge is distributed over the clusters in view of their sizes and geometries. In the case of the multiply charged Beryllium dimer, we demonstrate the phenomenon of Coulomb explosion [39], in which the repulsion between holes in multiply charged clusters below a critical size render the cluster unstable, in this case the dissociation leading to two singly charged ions.

We begin in the next chapter by describing the nature of the electronic structure problem and the application of density functional theory to solve it. The succeeding chapter discusses the Car-Parrinello method of simultaneously optimizing ion geometry and electronic wave functions to minimize the total energy of the system, and the application of a plane wave basis to the problem. Chapter 4 discusses computational details of the codes developed for this project and methods of analysis developed to study the results. In chapter 5, we present our results and analysis for the systems we considered, and conclude in the final chapter with a review of the salient features of our work along with a critique of the methods used. The mathematical descriptions of the methods used in our calculations are kept fairly brief with more detailed analyses relegated to the three appendices for those who wish to be more circumspect.
2.1 Description of a Material

A material system of $M$ nuclei and $N$ electrons can be described nonrelativistically by the many-body Schrödinger equation

$$\mathcal{H}\Psi = \left[ -\sum_{i=1}^{N} \nabla_i^2 - \sum_{l=1}^{M} \frac{1}{M_l} \nabla_l^2 - \sum_{i=1}^{N} \sum_{l=1}^{M} \frac{2Z_l}{|r_i - R_l|} \right. \nonumber$$

$$\left. + 2 \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|r_i - r_j|} + 2 \sum_{l=1}^{M} \sum_{j>l}^{M} \frac{Z_l Z_j}{|R_l - R_j|} \right] \Psi = E_{\text{tot}} \Psi, \quad (2.1)$$

where $r_i$ and $R_l$ are the positions of the $i^{th}$ electron and $l^{th}$ nucleus respectively and $Z_l$, $M_l$; the charge and mass of the $l^{th}$ nucleus. Its solution is a many-body wavefunction

$$\Psi = \Psi(r_1, s_1, r_2, s_2, \cdots, r_N, s_N), \quad (2.2)$$

where $s_i$ is the spin state of the $i^{th}$ electron. Atomic units are used in which the electronic mass, $m$, is $1/2$, the square of its charge, $e^2$ is $2$, and $\hbar$ is $1$ so that energies are given in Rydbergs. The nuclear masses are expressed in units of the electronic mass.

Using the Born-Oppenheimer Approximation in which the much heavier nuclei are considered fixed, that is, having no kinetic energy and a constant mutual repulsion, we can cast the electronic problem as
\[ \mathcal{H}_{\text{elect}} \Psi = \sum_{i=1}^{N} (-\nabla_i^2 - \sum_{l=1}^{M_1} \frac{2Z_l}{|r_i - R_l|} + \sum_{j \neq i}^{N} \frac{1}{|r_i - r_j|})\Psi \]

\[ = E_{\text{elect}} \Psi. \quad (2.3) \]

The Born-Oppenheimer Approximation, from the perspective view of the nuclei, views the electronic motion as being fast enough to be regarded as an average field. The Hamiltonian for the nuclei is then

\[ \mathcal{H}_{\text{nuc}} = -\sum_{i=1}^{M_1} \frac{\nabla_i^2}{M_1} + \langle \mathcal{H}_{\text{elect}} \rangle + 2 \sum_{l=1}^{M_1} \sum_{j > l}^{M_1} \frac{Z_lZ_j}{|R_l - R_j|}. \quad (2.4) \]

Since the expectation value of \( \mathcal{H}_{\text{elect}} \) calculates to a function of the nuclear coordinates, this nuclear Hamiltonian can be regarded as a kinetic term plus an effective potential term

\[ \mathcal{H}_{\text{nuc}} = -\sum_{i=1}^{M_1} \frac{\nabla_i^2}{M_1} + V_{\text{BO}}(\{R_l\}). \quad (2.5) \]

Plotted as a function of the \( \{R_l\} \), \( V_{\text{BO}} \) is known as the Born-Oppenheimer surface.

### 2.2 One-Electron Treatments

Since the electronic problem described above is often too computationally unwieldy, many approaches strive towards a one-electron treatment with the solution being in the form of occupied electron orbitals, rather than the many-body wavefunction. This can be done via variational methods. For example, in the Hartree-Fock (HF) Approximation, the many-body wavefunction is approximated by an antisymmetrized product (Slater determinant) of single particle orbitals: \( \{\psi_i\} \). The expectation value

\[ \langle \mathcal{H}_{\text{elect}} \rangle = \frac{\langle \Psi | \mathcal{H}_{\text{elect}} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]
is then minimized with respect to say, the $i^{th}$ orbital, resulting in a set of eigenvalue equations

$$\mathcal{H}\psi_i(r) = \varepsilon_i\psi_i(r).$$

The HF approximation, while accounting for the exchange nature of the electrons, leaves out other correlative effects between them since each electron is treated as seeing the averaged field of the others. This neglected energy is called the correlation energy. Methods of configuration interaction are usually used to supplement HF calculations. After the HF equations are solved self consistently, the resulting Hamiltonian is diagonalized to obtain excited states. A new many-body wavefunction is then constructed as a linear combination of the ground state and some of the excited states and their coefficients optimized. In some cases, the HF equations are solved using more than one Slater determinant so that several spin states are represented in the original wavefunction. This approach, then followed by CI is known as multireference configuration interaction (MRCI). The correlation and exchange energy are nonlocal in nature. Slater [40] proposed averaging them over the electronic states to arrive at a local exchange-correlation potential, and to then cast this potential as a functional of the electron density.

2.3 Density Functional Theory

The aim of density functional theory (DFT) is to allow us to approach the many-body problem via the much simpler electron density rather than the many-body wavefunction and its associated Hamiltonian. Its foundation rests on the Hohenberg-Kohn theorem[36] which states that the external potential, $V_{\text{ext}}(r)$, exerted on an electron gas is determined uniquely by the electron density $n(r)$. Since $V_{\text{ext}}(r)$ fixes the many-body Hamiltonian, the
many-body wavefunction $\Psi$ is also a unique functional of $n(r)$, along with the total energy, $E$ of the system. This energy, as a functional of $n(r)$ can be expressed as

$$E[n(r)] = \int V_{ext}(r)n(r)dr + \int \frac{n(r)n(r')}{|r-r'|}drdr' + T[n(r)] + E_{xc}[n(r)], \quad (2.6)$$

where $T[n(r)]$ is the kinetic energy of a system of non-interacting electrons of density $n(r)$ and $E_{xc}[n(r)]$; the exchange and correlation energy. If $n(r)$ is slowly varying enough, we can cast $E_{xc}[n(r)]$ as

$$E_{xc}[n(r)] = \int n(r)\varepsilon_{xc}(n(r))dr. \quad (2.7)$$

Here, $\varepsilon_{xc}(n(r))$, a function of the electron density, is the exchange-correlation energy per electron of a uniform electron gas of density $n(r)$. We are estimating the exchange-correlation density at a point $r$ to be what it would be if the electron gas was of a uniform density equal to the value of the actual density at that point $r$. This simplification is known as the local density approximation (LDA). The exact form of the exchange-correlation energy is not known, and better approximations for it are arrived at using a spin polarized density. This formulation, called the local spin density (LSD) approximation, is essential in cases where magnetic fields or unpaired electrons are present. The exchange-correlation energies, $E_{xc}[n_\uparrow(r), n_\downarrow(r)]$ and $\varepsilon_{xc}[n_\uparrow(r), n_\downarrow(r)]$ are then functionals of "up spin" and "down spin" densities with

$$n(r) = n_\uparrow(r) + n_\downarrow(r)$$
and \( N \), the number of electrons is

\[
N = \int n(r) \, dr.
\]

In this work, we use an LSD functional arrived at by Perdew and Zunger [41] through parametrization of Monte Carlo calculations of Ceperley and Alder [42] on homogeneous electron gases of various densities.

Having cast the energy of the many-body system as a functional of the electron density, we now express this density as a sum of one-electron orbitals

\[
n(r) = \sum_{i=1}^{N} f_i \psi_i^*(r) \psi_i(r). \tag{2.8}
\]

Here, \( f_i \) is the occupation number of the \( i^{th} \) orbital, which is further decomposed into spin up and spin down occupation numbers

\[
f_i = f_{i\uparrow} + f_{i\downarrow}.
\]

Applying the variational principle to the energy functional, we can arrive at a set of Schrödinger equations which can be solved self-consistently for the ground state energy of the system. The equations

\[
\mathcal{H}_{KS} \psi_i(r) = \left[ -\nabla^2 + V_{ext}(r) + \int \frac{n(r')}{|r-r'|} \, dr' + \left( \frac{f_{i\uparrow}}{f_i} \mu_{xc\uparrow} + \frac{f_{i\downarrow}}{f_i} \mu_{xc\downarrow} \right) \right] \psi_i(r)
\]

\[
= \epsilon_i \psi_i(r) \tag{2.9}
\]

are called the Kohn-Sham (KS) equations [37], where

\[
\mu_{xc\uparrow,\downarrow} = \frac{\partial (\epsilon_{xc}[n_{\uparrow}, n_{\downarrow}] n(r))}{\partial n_{\uparrow,\downarrow}} \tag{2.10}
\]

are the LSD exchange-correlation potentials. The traditional approach to solving these equations is to start with an initial guess for \( n(r) \), calculate the
resulting KS-Hamiltonian, diagonalize it, and use the resulting eigenfunctions to calculate a new density. A new Hamiltonian is calculated usually using some mix of the new and old densities (for reasons of numerical stability), and this process is iterated until self-consistency is obtained.

The KS-orbitals are usually expressed over some set of basis functions such as Gaussians or plane waves with the number of basis states being far greater than the number of orbitals. With \( N_b \) being the number of basis states, the diagonalization of the KS-Hamiltonian is an \( \mathcal{O}(N_b^3) \) operation. The need to use high mixture ratios of old to new densities in the guesses further slows the convergence process. Also, if the form of the external potential changes, as is the case when atomic positions are simultaneously optimized, diagonalization methods often lead to numerical instabilities. In light of these drawbacks, alternative methods to solving the KS-equations have been developed over the past decade and a half involving the direct minimization of the energy functional. Greedy algorithms such as steepest descent (SD) and conjugate gradients (CG) [7] will minimize the energy progressively downhill to the nearest local minimum in the configuration space of the energy versus the set of parameters defining the KS-orbitals. Other methods are of global optimization striving to escape entrapment into local minima by employing some mechanism for sampling the configuration space with an increasingly tightening restriction in the sampling method as more optimal solutions are encountered. Sampling strategies include Monte Carlo (MC) and molecular dynamics (MD), often used in conjunction with simulated annealing [43] to gradually restrict the sampling range.
2.4 The Energy Functional

In our present application of DFT in which the external potential $V_{\text{ext}}(r)$ is due to the nuclei or ions composed of nuclei and core electrons, the total energy functional is

$$E[\{\psi_i\}, \{R_i\}] = \sum_i \int f_i \psi_i^*(r)(-\nabla^2)\psi_i(r) \, dr$$

$$+ \int \int \frac{n(r)n(r')}{|r - r'|} \, dr \, dr' + E_{xc}[n_n(r), n_s(r)]$$

$$+ \int V_{\text{ion}}^L(r)n(r) \, dr + \sum_i <\psi_i|\hat{V}_{\text{ion}}^N|\psi_i>$$

$$+ \sum_i \sum_{j,l}^{'} \frac{Z_i Z_j}{|R_i - R_j|^l}$$  \hspace{1cm} (2.11)

where the first term is the independent orbital quantum kinetic energy, followed by the Hartree and exchange-correlation energies.

The next two terms in equation (2.11) contain the electron-nuclear or electron-ion interaction. In an all-electron calculation, it would be the Coulomb interaction between the electrons and the nuclei. When one is concerned mainly with the bonding nature within a system, it is often possible to deal with the valence electrons only, and to find some way to model the effect of the ion cores on these outer electrons. This gives rise to the pseudopotential technique, in which the components of the model potential for the ion are such that the resulting pseudoatomic wavefunctions will match those obtained for the all electron calculation beyond some radius from the core. In this way, the wavefunctions are smoothed out near and within the core. This normally allows us to use a smaller basis set since we avoid having to describe the rapidly varying regions of all-electron wavefunctions. The disadvantage
to using pseudopotentials lies in their transferability properties. Those derived from crystalline environments may not work well in atomic or chemical environments and vice versa. A pseudopotential can be either wholly local and angular momentum independent or have angular momentum dependent components that render it nonlocal in the angular coordinates. Here, the nonlocal term is represented with the operator

$$\hat{V}_{\text{ion}, \mu}^{NL} = \sum_{\mu_f} \sum_{l} \sum_{m} |lm > V_{i,\mu}(r - R_{\mu_f}) < lm|$$  \hspace{1cm} (2.12)

where $\mu_f$ runs over the ions of species $\mu$ located at positions $\{R_{\mu_f}\}$, and the function $V_{i,\mu}(r - R_{\mu_f})$ is spherically symmetric about $R_{\mu_f}$. The projection operator $|lm > < lm|$ matches the $l$-dependent potentials to the $l$-dependent components in the $\{\psi_l\}$. Further details related to the pseudopotential method and to the one used in this work can be found in appendix C.

The final term in equation (2.11) are from interactions between nuclei or ions where the prime on the summations indicate exclusion of terms in which $I = J$. Our use in this work of a plane wave basis discussed in the next chapter, introduces periodic boundary conditions to our problem. The system is therefore modelled as being in a box, or supercell, that is periodically replicated over all space and the summation must extend over ions in all the replicated cells. Such summations converge slowly when computed in the above form and are best calculated either wholly or in part in Fourier space. Application of this technique (known as the Ewald method [44]) to our problem along with related issues of supercell size, charge neutrality, and cancellation of diverging contributions from the origin of the Fourier space are discussed in Appendix A.
CHAPTER 3

THE METHOD OF CAR AND PARRINELLO

3.1 The Car-Parrinello Lagrangian

The Car-Parrinello method of molecular dynamics (MD) provides a way to optimize atomic positions concurrently with the KS-orbitals. The parameters defining the KS-orbitals are treated as generalized coordinates in a fictitious Lagrangian whose potential energy is the total energy functional of DFT. These parameters are given fictitious masses and velocities and the resulting Euler-Lagrange equations integrated. The assigned velocities allow us to sample the configuration space, while the equations of motion propel the system to regions of lower potential, hence directly minimizing the energy functional. The velocities are periodically damped (simulated annealing [43]) to gradually restrict the sampling range. The nuclei or ions are then allowed to move either through MD or SD or CG techniques. Alternating between atomic and electronic motions leads to an optimal solution for the ground state of the system with respect to both geometry and electronic structure.

The Lagrangian is formed as

$$\mathcal{L} = \mu \sum_i \int f_i \psi_i^* \psi_i \, dr + \frac{1}{2} \sum_i M_i \dot{R}_i^2 - E[\{\psi_i\}, \{R_i\}] + \sum_i \sum_j f_i \lambda_{ij} \left[ \int \psi_i^* \psi_j \, dr - \delta_{ij} \right].$$

(3.1)

Here, the first two terms are respectively, the fictitious kinetic energies of the electronic degrees of freedom and the physical kinetic energy of the ions. The next term is the energy functional of equation (2.11) and the final term...
contains constraints of orthonormality (ON) imposed on the KS-orbitals through the introduction of Lagrange multipliers \( \{\lambda_{ij}\} \).

For a fixed ion configuration, the electronic equations of motion can be formed by taking the Euler-Lagrange equations

\[
\frac{d}{dt} \left( \frac{\delta \mathcal{L}}{\delta \psi_i^*} \right) = \frac{\delta \mathcal{L}}{\delta \psi_i},
\]

while

\[
\frac{d}{dt} \left( \frac{\delta \mathcal{L}}{\delta R_i} \right) = \frac{\delta \mathcal{L}}{\delta R_i}
\]

provides the ion dynamics. The electronic equations of motion then become (see appendix B)

\[
\mu \ddot{\psi}_i(r) = -\mathcal{H}_{KS}(r) + \sum_j \lambda_{ij} \psi_j.
\]

where \( \mathcal{H}_{KS} \) is the KS-Hamiltonian of equation (2.9) with the external potential replaced by the local ion potential and the nonlocal operator of equation (2.12). Discretizing these equations in time using the Verlet Algorithm [45], we can express them as

\[
\psi_i(t + \Delta t) = -\psi_i(t - \Delta t) + 2\psi_i(t)
\]

\[
+ \frac{(\Delta t)^2}{\mu} \left( \mathcal{H}_{KS}(t) + \sum_j \lambda_{ij} \psi_j(t) \right)
\]

where the \( r \)-dependence has been suppressed. Letting the system evolve for a time step without imposing the ON constraint gives us an unconstrained wavefunction, \( \tilde{\psi}_i(t + \Delta t) \) with the relationship

\[
\psi_i(t + \Delta t) = \tilde{\psi}_i(t + \Delta t) + \frac{(\Delta t)^2}{\mu} \sum_j \lambda_{ij} \psi_j(t).
\]
Substituting this into the condition for orthonormality

\[ \delta_{ij} = \int \psi_i^*(t + \Delta t) \psi_j(t + \Delta t) \, dr \]

allows us to construct an equation which can be solved iteratively to obtain the elements of the constraint matrix, \( \lambda \), which we use to correct the unconstrained wave functions. The details of this method can be found in appendix B.

After the KS-orbitals have been optimized for a given ion configuration the ions can be moved according to their equations of motion. The combination of a set of ion coordinates with optimized wave functions defines a point on the Born-Oppenheimer (BO) surface. Alternating between ion movements and electronic wave function optimizations while always staying on the BO surface allows one to simulate the molecular dynamics from a first-principles approach. Alternatively, if one is interested only in the final optimal state of the system, the ions can be moved using steepest descents or conjugate gradients.

**3.2 Expansion over Plane Waves**

When the KS-orbitals are expanded over a plane wave basis, the generalized coordinates in the Car-Parrinello Lagrangian are the Fourier coefficients of the expansion. The KS-orbitals, constrained to be periodic over some volume, \( \Omega \), can be expanded as

\[ \psi_i(r) = \frac{1}{\sqrt{\Omega}} \sum_G C_{i,G} e^{iG \cdot r} \]  

(3.4)

with the corresponding reverse transforms

\[ C_{i,G} = \frac{1}{\sqrt{\Omega}} \int_{\Omega} \psi_i(r) e^{-iG \cdot r} \, dr. \]  

(3.5)
Similar expansions, chosen for the charge distributions and potentials are of the form

\[ V(r) = \sum_G \tilde{V}_G e^{iG \cdot r} \quad (3.6) \]

and

\[ \tilde{V}_G = \frac{1}{\Omega} \int \Omega V(r) e^{-iG \cdot r} dr. \quad (3.7) \]

Substitution of the plane wave expansions into the unconstrained equations of motion (3.2), (see appendix B), results in

\[ \mu \ddot{C}_{i,G} + G^2 C_{i,G} - \sum_j \lambda_{ij} C_{j,G} + \sum_{G'} \tilde{V}_{L_{\sigma-\sigma'}} C_{i,G'} + \frac{1}{\Omega} \sum_{G'} C_{i,G'} \tilde{V}^{NL}_{cal}(G, G') = 0, \quad (3.8) \]

where \( \tilde{V}_{L_{\sigma-\sigma'}} \) contains the Hartree, exchange-correlation, and local part of the pseudopotential contributions. The term \( \tilde{V}^{NL}_{cal}(G, G') \) contains the non-local pseudopotential contribution calculated in appendix C and defined by equations C.13, C.11, and C.9.

Advantages of a plane wave basis include the ability to use the fast Fourier transform to switch from real space representations and the periodicity introduced lends itself well to the description of periodic crystals. Drawbacks include the need for many plane waves to describe rapidly varying regions of wave functions and potentials, and to create cancellation in regions of vacuum. Also, the periodicity introduced is nonphysical when dealing with aperiodic systems such as clusters, so spurious intercluster interactions are present. This situation, exacerbated in the case of charged clusters, requires the use of a large box as the periodic volume in order to decouple the clusters as much as possible. This in turn requires the use of many plane waves since the spacing of frequencies between contributing plane waves is inversely proportional to the dimensions of the box.
There are divergent contributions at the $G = 0$ point from the Hartree, ion-ion, and local electron-ion interactions. All of these cancel in the case of a charge neutral system. In the case of a charged system, a neutralizing uniform background density (jellium) is introduced to maintain these cancellations. In the limit of a large box, this jellium background approaches zero. Recently, Makov and Payne [46] proposed corrections to mitigate the effects of a finite sized box and to correct for the addition of the jellium background through third order in the boxlength. Details related to the cancellation of singularities and the Makov-Payne corrections can be found in appendix A. The change in energies due to these corrections and the increased quality of convergence with boxlength are dramatic as will be seen in the results of this work.
CHAPTER 4

COMPUTATIONAL DETAILS AND METHODS OF ANALYSIS

The code developed for this work uses the conjugate gradient method to move the ions. While the user can specify the number of iterations to be applied to the ionic degrees of freedom, one iteration (amounting to an optimized steepest descent) was found to result consistently in more optimal geometries. The size of the step in each conjugate direction was calculated by minimizing the energy in that direction with a golden section search, as opposed to calculation of the Hessian of the energy with respect to the ion coordinates.

Since the optimal geometry of a cluster often has some specific symmetry, investigation of a cluster typically entails runs constraining the geometry to that symmetry and runs without such a constraint. To apply the symmetry constraints we first allow the ions to move unconstrained under the CG technique and then average the bondlengths characterizing the symmetry. The ions are then set in the symmetry with this average separation and with the center of geometry set at the origin.

The Fourier coefficients of the electronic wavefunctions were optimized using the fictitious dynamics described in the last chapter. Equation (3.8) was obtained by a substitution of the Fourier expansions of the KS-orbitals and potentials into equation (3.2). This requires a lengthy calculation of the resultant local potential under a loop over the basis for each coefficient, amounting to a double loop over all the plane waves for each time step. An alternative method\(^1\) is to multiply the sum of the local potentials by the

\(^1\)I am indebted to Professor Fuyuki Shimojo for pointing out this optimization.
KS-orbital, all in real space, and to FFT the product into the Fourier space. Since the diverging Coulomb contributions at the \( \mathbf{G} = 0 \) point need to be excluded, we calculate the local potentials in \( \mathbf{G} \)-space; zero these contributions and FFT the result into real space in preparation for the multiplication by the real space KS-orbital. This optimization typically sped up our code by 40% with the basis sets used, with a negligible loss in accuracy.

A preliminary code is run for the purpose of setting array lengths in which the user specifies a minimum energy cutoff and the boxlengths of the supercell to be used. In the case of the clusters, a simple cubic cell has been used. This code returns the grid spacings, the number of gridpoints, and the number of plane waves. These form inputs to the main code. The FFT algorithm used requires the number of gridpoints in each dimension to be a power of two. Also, equation (3.8) requires that the grid accommodate Fourier components up to twice the energy cutoff. The FFT algorithm is of order \( O(N_c \log_2 N_c) \) with \( N_c \) being the number of gridpoints. An upgrade in grid density therefore represents a 16-fold increase in grid related computational work and an 8-fold increase in memory requirements.

With these restrictions, and the computational resources available, simultaneous optimization of atomic positions and Fourier coefficients is untenable for grids involving more than \( (32)^3 \) gridpoints. This also limits the size of the boxlength and energy cutoff combination to below about 2500 plane waves. Calculations for this project have shown, however, that binding energies (involving energy differences between clusters) converge much faster than the energy values themselves. Also, convergence testing in this work has shown that the optimal geometries obtained were very insensitive to energy cutoff and boxlength variations so that one can optimize the geometry with a smaller basis set and then optimize the wavefunctions with a larger basis
keeping the optimal geometry fixed. This is a common practice among those using configuration interaction wherein the geometry is optimized using only Hartree-Fock or using an inferior basis set in CI and a better basis set for the final energy calculation.

Initial conditions were normally set with the ions set in some symmetric arrangement and a random set of coefficients generated with no center of mass motion. For larger clusters, we have obtained lower energies by first optimizing ionic positions under a Lennard-Jones potential, using Monte Carlo and simulated annealing. An initial set of coefficients were then generated by placing optimized orbitals obtained from a one-atom run at the atomic sites and diagonalizing their overlap matrix.

For optimization of the electronic wavefunctions we typically used a fictitious mass and initial temperature of 500K, annealing 20 times between ion moves. Occasionally a trapping of the system at an obviously less than optimal energy would require the run to be repeated starting from a higher temperature. The temperature was reduced by 10% at each anneal and we used the Verlet algorithm with a variable time step ranging from $5.0 \times 10^{-3}$ to $2.5 \times 10^{-4}$ fs, depending on stability criteria tested for periodically in the code. After each ion move, the fictitious temperature was reset to 80% of the value it had at the start of the previous optimization cycle. Convergence of the total energy was taken beyond $10^{-7}$ Rydbergs, and the average distances between ions, beyond $10^{-4}$ a.u. A high order of convergence of the energy is desirable in order to achieve well converged wavefunctions.

The output of the main code are the ground state energy of the system and the Fourier coefficients of the orbitals obtained for this state. Expanding the KS orbitals over a plane wave basis and optimizing the coefficients introduces an arbitrariness into the spatial form of these orbitals, since any linear
combination of them will yield the same energy. We therefore diagonalize the final ground state Hamiltonian over the basis of the orbitals giving its final eigenfunctions and eigenvalues. These new orbitals, \{\psi_i\}, are projected onto spherical harmonics located at the center of geometry of the cluster and the resulting radial distributions, \{C^i_{lm}(r)\}, numerically integrated for each \ell-value to arrive at weights \(w^i_{\ell}\) for each orbital. That is,

\[
C^i_{lm}(r) = \int_\Omega \psi_i(r) Y^*_{lm}(\Omega) \, d\Omega \tag{4.1}
\]
and

\[
w^i_{\ell} = \sum_m \int C^i_{lm}(r) r^2 \, dr. \tag{4.2}
\]

Most orbitals analyzed in this way turned out to be surprisingly pure in their dominant \(\ell\)-components as will be seen in the next chapter.

Another aspect of interest is to investigate how these KS-eigenfunctions may arise from atomic orbitals. By diagonalizing the Hamiltonian after optimization for one atom in Fourier space we obtained the four lowest lying (one occupied s and three virtual p) atomic orbitals. These were used to form an atomic basis, \{|\phi_i\rangle\}, for each cluster, composed of copies of these orbitals translated to the atomic sites. Each KS orbital (KSO), \(|\psi_i\rangle\) was then expanded over this basis as \(|\psi_i\rangle = \sum_j c_j^{(i)}|\phi_j\rangle\) and the coefficients \(c_j^{(i)}\) solved for, in order to see how such orbitals might arise as linear combinations of atomic orbitals (AO's). This also allows us to perform a Mulliken population analysis [47], by constructing a matrix from the terms that sum to form the inner product of each KSO as

\[
<\psi_i|\psi_i> = 1 \approx \sum_j q_j^{(i)} + \sum_j \sum_{k>j} P_{jk}^{(i)}
\]
where

\[ q_j^{(i)} = |c_j^{(i)}|^2 \]

and

\[ p_{jk}^{(i)} = 2 \text{Re}(c_j^{(i)}*c_k^{(i)} < \phi_j | \phi_k >) \]

where the lower diagonal elements have been incorporated into those of the upper diagonal.

The diagonal elements \( \{q_j^{(i)}\} \) give a measure of each KS orbital's contribution to density populations associated with atomic sites, while the off diagonal elements \( \{p_{jk}^{(i)}\} \) reflect contributions to density populations associated with regions of overlap (OV) between pairs of atoms. Positive, negative, and small OV populations typically indicate bonding, anti-bonding, and non-bonding regions, respectively. The elements of the matrix sum very nearly to unity for each orbital, showing that only sp hybridization occurs.

We can sum the p-type contributions at each atomic site to determine the s-type and p-type populations at these sites. Further, we can sum all contributions at each atomic site and in each overlap region to give the overall contribution to the electron density at each site due to a KSO. Summing such contributions over all KSO's then gives us the total electron density for each atomic site and overlap region due to all electrons in the cluster.
CHAPTER 5
APPLICATIONS TO CLUSTERS

We applied our methods to pure clusters of Beryllium and to mixed clusters of Beryllium-Lithium, the latter being of the form $B_eL_k$ for $k$ equal to 1 through 8.

5.1 Beryllium Clusters

Our studies include neutral and singly charged clusters having from one to six atoms. Only the singlet or doublet states were looked at with the exception of the six atom clusters for which we investigated spin multiplicities through the quintet.

5.1.1 Neutral Clusters

The excitation energy of the $Be$ atom from the singlet to the triplet state was calculated to be 2.67 eV, in close agreement with the experimental value of 2.73 eV [48]. This same calculated value was obtained whether by taking the difference of the energies of the two states or by taking the difference of their highest lying KS eigenvalues. The latter calculation suggests that while the KS eigenvalue of the highest occupied state, calculated using LSD, may fall short of its theoretical correspondence to the first ionization (Koopman's theorem) potential [49, 50] (our 5.41 eV compared to the experimental 9.32 eV [48]), differences in eigenvalues may be more useful. This is consistent with recent work done by Stowasser and Hoffmann [51], who propose a linear scaling be applied to eigenvalues for quantitative interpretation.

Our convergence data for the $Be_5$ cluster related to boxlength and basis set are shown in Table 5.1. While total energies may vary appreciably with changes in the energy cutoff, the binding energies obtained differ much less.
Table 5.1: Convergence of binding energy per atom ($E_b$) with changes in boxlength $L$ and energy cutoff $E_{\text{cut}}$ for the neutral Be$_5$ cluster.

<table>
<thead>
<tr>
<th>$E_{\text{cut}} = 6.0$ Ryd</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$ (a.u.)</td>
<td>18</td>
</tr>
<tr>
<td>$E_b$ (eV/atom)</td>
<td>1.27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$L = 20.0$ (a.u.)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{cut}}$ (Ryd)</td>
<td>5.5</td>
</tr>
<tr>
<td>$E_b$ (eV/atom)</td>
<td>1.24</td>
</tr>
</tbody>
</table>

$^a$Ions fixed in the geometry obtained from the case of $L = 20$ a.u.

The geometries corresponding to the lowest energies obtained proved to be nearly identical.

The geometries and binding energies of our lowest energy configurations are shown in Table 5.2 for clusters containing up to 6 atoms, along with the results of earlier calculations. The binding energies are slightly higher than those obtained by KRB, whose all electron LSD calculations used a Gaussian Type Orbital (GTO) (9s,3p) basis set, and lower than those of KW, whose calculations, while similar to ours, used larger energy cutoffs with the Kleinman-Bylander transformation [52].

The dimer is the only cluster, to our knowledge, for which experimental data exist. Bondybey [18], using laser induced fluorescence, measured a binding energy of 0.10 eV and a separation of 4.63 a.u. for the $X^1\Sigma_g^+$ ground state. Specific results of CI calculations for the dimer are reviewed extensively by Harrison and Handy [24]. Their own values of 0.098 eV and
Table 5.2: Binding energies and geometries for neutral beryllium clusters $n=1-6$.

<table>
<thead>
<tr>
<th>cluster size</th>
<th>equilibrium geometry</th>
<th>binding energies/atom (eV)</th>
<th>(bond lengths) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>this work</td>
<td>$a$</td>
</tr>
<tr>
<td>2 (singlet)</td>
<td></td>
<td>.18 (4.84)</td>
<td>.18 (4.87)</td>
</tr>
<tr>
<td>3 (singlet)</td>
<td>equilateral triangle</td>
<td>.57 (4.21)</td>
<td>.53 (4.33)</td>
</tr>
<tr>
<td>4 (singlet)</td>
<td>regular tetrahedron</td>
<td>1.18 (3.93)</td>
<td>1.09 (4.04)</td>
</tr>
<tr>
<td>5 (singlet)</td>
<td>trigonal bipyramid</td>
<td>1.26 (3.91)</td>
<td>1.22 (3.88)</td>
</tr>
<tr>
<td></td>
<td>(base)</td>
<td>3.91 (3.90)</td>
<td>3.88 (4.01)</td>
</tr>
<tr>
<td></td>
<td>(apical)</td>
<td>3.90 (3.94)</td>
<td>3.88 (3.97)</td>
</tr>
<tr>
<td>6 (singlet)</td>
<td>regular octahedron</td>
<td>1.21 (3.94)</td>
<td>1.59$^f$ (3.95)</td>
</tr>
<tr>
<td>6 (triplet)</td>
<td>regular octahedron</td>
<td>1.22 (3.95)</td>
<td></td>
</tr>
<tr>
<td>6 (quintet)</td>
<td>regular octahedron$^g$</td>
<td>1.22 (3.96)</td>
<td>.44, .82</td>
</tr>
</tbody>
</table>

$^a$ref. [34]; LSD calculations, all electron with GTO (9s,3p) basis set.
$^b$ref. [28]; MP4/6-31G
$^c$ref. [28]; MP4/6-31G*
$^d$ref. [30]; MP4/6-311+G* for energies of n=3-5, MP4/6-311G* for energy of n=6, MP2/6-311+G* for bond lengths of n=3-5 MP2/6-31G* for bond lengths of n=6
$^e$ref. [24]
$^f$ref. [35]; interatomic potential fit to ref. [34]
$^g$slightly distorted; bond lengths ranging from 3.94 to 3.95 a.u.
4.65 a.u. are very close to the experimental result. Our values of .36 eV with a separation of 4.84 a.u. are typical of LSD calculations. Significantly higher binding energies were calculated by Painter and Averill [32] using LSD with other exchange-correlation functionals than that of Perdew and Zunger [41], including the $X\alpha$ method, but they obtained separations very close to the experimental value.

Despite the high binding energy calculated using the LSD approximation relative to the experimental result, the KS-orbitals found for the dimer were confirmed to be symmetric and antisymmetric combinations of the orbital obtained from one-atom calculations translated to the atomic sites of the dimer. The charge density due to each of these molecular orbitals is shown in Figure 5.1 for the up spins, illustrating their bonding and antibonding natures. Results for the down spins are correspondingly similar. Projection of these KS-orbitals onto spherical harmonics centered at the center of geometry, with the subsequent radial integration of each projection, shows the lower and higher orbitals to be almost purely $s$ and purely $p$ respectively, in nature.

Such shell-like orbitals were obtained for clusters of up to six atoms, filling in the order of $1s\ 1p\ 2s\ 1d$. Representative orbitals are shown in Figure 5.2 for the $Be_6$ quintet.

Diagonalization of this cluster's Hamiltonian in Fourier space allowed us to see the higher unoccupied states and showed $2\ell + 1$ orbitals for each value of $\ell$. In analogy to shell closings in atoms such as the inert gases being due to the relatively large gap between the unoccupied $s$-state and the filled $p$-state below it, a common measure of a cluster's stability is its second difference of the energy [53]. This is the difference between the energy gaps to the
Figure 5.1: Contours in the plane through the origin, perpendicular to the Z axis, of the squares of singly occupied bonding and antibonding orbitals for Be$_2$. Filled circles indicate projected positions of the ions. Units are electrons/(a.u.).

The symmetries of our lowest energy clusters agree with those of KRB for beryllium, and to similar work done by Reuse, Khanna, deCoulon, and Buttet (RKCB) [54] on magnesium for clusters containing up to 5 atoms. For the 6 atom cluster, our binding energies and geometries came out very nearly...
Figure 5.2: Contours in the plane containing the base of the octahedral $Be_8$ quintet. Filled circles indicate projected positions of ions. Units are in $10^{-3}/$(a.u.).
Figure 5.3: Second difference of the energy: $\Delta_2(N) = E(N+1) + E(N-1) - 2E(N)$ plotted against cluster size ($N$). The point at $N = 6$ is calculated from our current estimate of the lowest energy for the seven atom cluster.
Table 5.3: Fragmentation channels for neutral Beₙ clusters. Energies are in eV.

<table>
<thead>
<tr>
<th>Beₙ₊ₘ</th>
<th>→ Beₙ + Beₘ</th>
<th>Eₙ + Eₘ − Eₙ₊ₘ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be₆</td>
<td>→ Be₅+Be₁</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>→ Be₄+Be₂</td>
<td>2.24</td>
</tr>
<tr>
<td></td>
<td>→ Be₃+Be₃</td>
<td>3.93</td>
</tr>
<tr>
<td>Be₅</td>
<td>→ Be₄+Be₁</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>→ Be₃+Be₂</td>
<td>4.22</td>
</tr>
<tr>
<td>Be₄</td>
<td>→ Be₃+Be₁</td>
<td>3.03</td>
</tr>
<tr>
<td></td>
<td>→ Be₂+Be₂</td>
<td>4.00</td>
</tr>
<tr>
<td>Be₃</td>
<td>→ Be₂+Be₁</td>
<td>1.34</td>
</tr>
<tr>
<td>Be₂</td>
<td>→ Be₁+Be₁</td>
<td>0.36</td>
</tr>
</tbody>
</table>

the same for all the spin multiplicities investigated. While our result agrees well geometrically with the CI calculations of Marino and Ermler [28] for the Be₆ quintet (their ground state), they obtain trigonal antiprisms for the less stable singlet and triplet states. A distorted singlet structure of Cᵥ symmetry (a trapezoidal bipyramid) has been reported by Sudhakar and Lammersma (SL). They attribute the distortion to the Jahn-Teller effect [55], that is, ions will move in order to break degeneracies arising from the incomplete occupation of degenerate spatial orbitals if the atomic configuration is nonlinear. The orbitals obtained by us for the Be₆ quintet (an undistorted octahedron) form a spatially nondegenerate system with complete fillings of the 1s, 1p shells (two electrons per orbital) and the 2s and 1d shells (one electron per orbital), the latter being triply degenerate (t₂g) leaving the doubly degenerate (e₉) d-shell completely unoccupied. We obtained a slightly
distorted octahedron for the triplet state with two nondegenerate d-orbitals; a mostly $d_{z^2-y^2}$ orbital lying .16 eV below an orbital containing nearly equal mixtures of the $xy$, $xz$, and $yz$ bases, the octahedral symmetry being sufficiently violated to break the $t_{2g}/e_g$ degeneracies. The distortion was obtained by relaxing a constraint to octahedral symmetry with a reheat of the electronic degrees of freedom, resulting in a lowering of the energy by .10 eV. Our lowest energy singlet state turned out to be an undistorted octahedron despite our expectations of obtaining a Jahn-Teller distorted structure. Two singly occupied d-orbitals of opposite spin were obtained; a $d_{xz}$ and a $d_{yz}$. The Mulliken population analysis for this cluster shows each of these two orbitals to correspond to a diagonally placed pair of atoms on the base of the octahedron. Approximately .18 electrons are contributed to each of the basal atomic sites in its pair, .11 electrons to each of its basal atoms' overlap with each of the capping atoms and .15 electrons to each of the capping atomic sites. Small negative overlap populations also exist amounting to about -.1 electrons. Reheating of this cluster with a subsequent relaxing of the octahedral constraint, and investigation using constraints to the lower symmetries of rectangular and rhombus based bipyramids, SL’s $C_{2v}$ structure, and the trigonal antiprism did not yield lower energies. For the analogous $Mg_6$ cluster RKCB report a singlet rectangular bipyramid as their ground state. Our inability to obtain the expected distortion is probably due to the breaking of octahedral symmetry for the overall system of the cluster and its periodic images by using the supercell method along with our use of singly occupied orbitals. The latter leads to a breaking of symmetry with even small differences in distributions between the up/down orbital pairs. Our main focus here however, is on how atomic orbitals may hybridize to form shell-like
Table 5.4: Fractional S, P, and OV populations for each cluster.

<table>
<thead>
<tr>
<th>cluster size</th>
<th>spin state</th>
<th>S</th>
<th>P</th>
<th>OV</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>singlet</td>
<td>.83</td>
<td>.06</td>
<td>.11</td>
</tr>
<tr>
<td>3</td>
<td>singlet</td>
<td>.69</td>
<td>.11</td>
<td>.20</td>
</tr>
<tr>
<td>4</td>
<td>singlet</td>
<td>.72</td>
<td>.16</td>
<td>.12</td>
</tr>
<tr>
<td>5</td>
<td>singlet</td>
<td>.75</td>
<td>.27</td>
<td>-.03</td>
</tr>
<tr>
<td>6</td>
<td>singlet</td>
<td>.51</td>
<td>.36</td>
<td>.14</td>
</tr>
<tr>
<td>6</td>
<td>triplet</td>
<td>.49</td>
<td>.35</td>
<td>.16</td>
</tr>
<tr>
<td>6</td>
<td>quintet</td>
<td>.45</td>
<td>.36</td>
<td>.20</td>
</tr>
</tbody>
</table>

KS-orbitals and we do not expect the trends in our results to be significantly changed by an analysis of the correct Jahn-Teller distorted structures.

Table 5.4 shows the total s and p fractional populations associated with atomic sites (S and P) and the total overlap (OV) fractional population in each cluster. From this, we can see an overall decrease in s and increase in p populations with increasing cluster size. A dramatic decrease in the OV population occurs at the five atom cluster due to the advent of a 2s orbital, whose contribution to the OV population is -.41 electrons per orbital. In general, the higher lying KSO's are more localized on atomic sites. Increases in the OV population with the addition of atoms to a cluster appear to arise mainly from further delocalization of the lowest lying state. This situation is clearly shown in Table 5.5 which shows the breakdown of these contributions by the KSO's along with their KS eigenvalues for each cluster. The six atom cluster is particularly interesting as it shows shell-like p-orbitals to be composed mainly of localized, atomic s-orbitals and shell-like d-orbitals to be composed mainly of localized, atomic p-orbitals. As noted above, the 1s-orbital arises from atom-pair overlaps, while the 2s-orbital, in stark contrast, arises from sp hybridization localized at the atomic sites.
Table 5.5: Fractional S, P, and OV populations by KS-orbital for neutral Be clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Orbital</th>
<th>$\psi_i$</th>
<th>$\Gamma$</th>
<th>$\epsilon_i$ (eV)</th>
<th>$w_i$</th>
<th>S</th>
<th>P</th>
<th>OV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be$_2$</td>
<td>$\psi_1$</td>
<td>$\sigma^+_g$</td>
<td>-6.76</td>
<td>.97s</td>
<td>.58</td>
<td>.04</td>
<td>.38</td>
<td></td>
</tr>
<tr>
<td>(D$_{\infty h}$)</td>
<td>$\psi_2$</td>
<td>$\sigma^+_u$</td>
<td>-4.29</td>
<td>.96p</td>
<td>1.08</td>
<td>.07</td>
<td>-.15</td>
<td></td>
</tr>
<tr>
<td>Be$_3$</td>
<td>$\psi_1$</td>
<td>$a'_1$</td>
<td>-8.53</td>
<td>.99s</td>
<td>.28</td>
<td>.10</td>
<td>.62</td>
<td></td>
</tr>
<tr>
<td>(D$_{3h}$)</td>
<td>$\psi_2$</td>
<td>$e'$</td>
<td>-4.56</td>
<td>.96p</td>
<td>.89</td>
<td>.12</td>
<td>-.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\psi_3$</td>
<td>$e'$</td>
<td>-4.55</td>
<td>.96p</td>
<td>.89</td>
<td>.12</td>
<td>-.01</td>
<td></td>
</tr>
<tr>
<td>Be$_4$</td>
<td>$\psi_1$</td>
<td>$a_1$</td>
<td>-9.79</td>
<td>.99s</td>
<td>.13</td>
<td>.16</td>
<td>.71</td>
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</tr>
<tr>
<td>(T$_d$)</td>
<td>$\psi_2$</td>
<td>$t_2$</td>
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<td>.97p</td>
<td>.92</td>
<td>.16</td>
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<tr>
<td></td>
<td>$\psi_3$</td>
<td>$t_2$</td>
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<td>.97p</td>
<td>.91</td>
<td>.16</td>
<td>-.07</td>
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<tr>
<td></td>
<td>$\psi_4$</td>
<td>$t_2$</td>
<td>-4.95</td>
<td>.97p</td>
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<tr>
<td>Be$_5$</td>
<td>$\psi_1$</td>
<td>$a'_1$</td>
<td>-10.91</td>
<td>.98s</td>
<td>.10</td>
<td>.15</td>
<td>.74</td>
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<tr>
<td>(D$_{3h}$)</td>
<td>$\psi_2$</td>
<td>$a''_2$</td>
<td>-7.20</td>
<td>.98p$_x$</td>
<td>.72</td>
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<tr>
<td></td>
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<td>$e'$</td>
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<tr>
<td></td>
<td>$\psi_5$</td>
<td>$a'_1$</td>
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<td>.82s .12d</td>
<td>.79</td>
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<td>.99s</td>
<td>.08</td>
<td>.13</td>
<td>.79</td>
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</tr>
<tr>
<td>(O$_h$)</td>
<td>$\psi_2$</td>
<td>$t_{1u}$</td>
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<td>.97p</td>
<td>.80</td>
<td>.19</td>
<td>.01</td>
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</tr>
<tr>
<td></td>
<td>$\psi_3$</td>
<td>$t_{1u}$</td>
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<td>.97p</td>
<td>.78</td>
<td>.18</td>
<td>.05</td>
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<tr>
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<td>$\psi_4$</td>
<td>$t_{1u}$</td>
<td>-6.73</td>
<td>.97p</td>
<td>.78</td>
<td>.18</td>
<td>.05</td>
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</tr>
<tr>
<td></td>
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<td>$a_{1g}$</td>
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<td>.96s</td>
<td>.54</td>
<td>.66</td>
<td>-.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\psi_6$</td>
<td>$t_{2g}$</td>
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<td>.98d</td>
<td>.00</td>
<td>.74</td>
<td>.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\psi_7$</td>
<td>$t_{2g}$</td>
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<td>.98d</td>
<td>.00</td>
<td>.78</td>
<td>.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\psi_8$</td>
<td>$t_{2g}$</td>
<td>-3.48</td>
<td>.98d</td>
<td>.00</td>
<td>.78</td>
<td>.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\psi_{11}$</td>
<td>$a_{1g}$</td>
<td>-10.42</td>
<td>.99s</td>
<td>.07</td>
<td>.14</td>
<td>.79</td>
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<tr>
<td></td>
<td>$\psi_{24}$</td>
<td>$t_{1u}$</td>
<td>-5.82</td>
<td>.97p</td>
<td>.77</td>
<td>.18</td>
<td>.05</td>
<td></td>
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<tr>
<td></td>
<td>$\psi_{34}$</td>
<td>$t_{1u}$</td>
<td>-5.80</td>
<td>.97p</td>
<td>.75</td>
<td>.17</td>
<td>.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\psi_{44}$</td>
<td>$t_{1u}$</td>
<td>-5.80</td>
<td>.97p</td>
<td>.75</td>
<td>.17</td>
<td>.09</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Orbitals are spin up unless otherwise noted. For singlet states of two through five atoms, spin down figures are very nearly the same. All orbitals are shown for the Be$_6$ quintet.

$^b$Irreducible representations

$^c$Components amounting to less than 5% are omitted.
Table 5.6: Convergence of binding energy \( (E_b) \) with changes in boxlength \( L \) for the charged \( \text{Be}_3^+ \) cluster.

\[
\begin{array}{lcccc}
E_{\text{cut}} = 6.0 \text{ Ryd} \\
\hline
L (\text{a.u.}) & 18 & 20 & 22 & 23^a \\
\hline
E_b^{b} (\text{eV}) & 8.94 & 8.81 & 8.74 & 8.73 \\
E_b^{c} (\text{eV}) & 8.60 & 8.57 & 8.56 & 8.57 \\
\hline
\end{array}
\]

^a ions fixed in the geometry obtained from the case of \( L=20 \) a.u.
^b uncorrected
^c corrected according to ref. [46]

5.1.2 Charged Clusters

Our estimate of the ionization energy for the \( \text{Be} \) atom, calculated as the difference in energies between the charged and the neutral species, rose from 6.87 eV to 8.85 eV by using the Makov-Payne correction as compared with the experimental value of 9.32 eV [48]. The major portion of this rise (> 97.5%) is due to the interaction of the jellium with the monopole moment (net charge) of the cluster. The rest is proportional to the quadrupole moment of the calculated charge distribution with the embedded point charge. The first term, being independent of cluster size, subtracts out in the calculation of binding energies. The latter term was found to have a dramatic effect in lowering the binding energies obtained and in converging our energies with boxlength. This is evident from Table 5.6, which compares corrected and uncorrected binding energies obtained for the \( \text{Be}_3^+ \) cluster at various boxlengths. As with the neutral clusters, the geometries corresponding to the lowest energies were nearly independent of boxlength.
Table 5.7 shows the most stable geometries of the charged clusters along with their binding energies. The binding energy of a cluster of $n$ atoms was calculated as

$$E_b(n) = E_{Be^+_2} - ((n - 1)E_{Be^+_1} + E_{Be^+_1}). \quad (5.1)$$

The removal of an electron from the 3 atom cluster resulted in a symmetric linear arrangement lower in energy from the undistorted $C_{3v}$ symmetry by .36 eV, consistent with the work of KRB on beryllium and with that of RKCB, Eriksson [56], Davidson and Frey (DF) [57], and Knight, Cleveland, Frey, and Davidson [58] on magnesium; the latter using SCF with correlation effects taken into account. We obtained a highly distorted tetrahedron for the four atom cluster, consistent with the work of KRB, and in contrast to their (RKCB), Eriksson's and DF's similar work on magnesium in which slightly lower lying linear arrangements were found. The large extent of the linear cluster renders its investigation impractical in the present work due to the surface effects inherent in the supercell method. For the 5 atom cluster we obtained an undistorted trigonal biprism as did KRB for beryllium and RKCB, Eriksson, and DF for magnesium. For the case of $Be^+_2$ we investigated starting configurations of the octahedron and the rectangular bipyramid with runs constrained to these symmetries (with a subsequent reheat and relaxation of the constraints) along with unconstrained runs. The clusters of $O_h$ symmetry yielded the lowest energies in contrast to the work of RKCB on magnesium who arrived at the rectangular bipyramid as their lowest energy configuration. Eriksson reported a triangular biprism as lying .35 eV below the rectangular bipyramid for $Mg^+_2$ while DF found a trapezoidal bipyramid to lie .25 eV below rhomboidal and rectangular bipyramids. The latter two configurations were found to be nearly degenerate with the rectangular
Table 5.7: Binding energies and geometries for charged beryllium clusters n=1-6.

<table>
<thead>
<tr>
<th>cluster size</th>
<th>spin state</th>
<th>equilibrium geometry</th>
<th>binding energy (eV) (bond lengths) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a, b</td>
</tr>
<tr>
<td>2</td>
<td>doublet</td>
<td>2.18, 2.22 (4.24)</td>
<td>2.19</td>
</tr>
<tr>
<td>3</td>
<td>doublet</td>
<td>3.85, 3.91 (4.17)</td>
<td>3.91</td>
</tr>
<tr>
<td>4</td>
<td>doublet</td>
<td>5.79, 5.96 (4.12 average)</td>
<td>5.61</td>
</tr>
<tr>
<td></td>
<td>distorted tetrahedron</td>
<td>8.57, 8.80 (4.08 base) (3.99 apical)</td>
<td>8.45 (4.02 base) (4.08 apical)</td>
</tr>
<tr>
<td>6</td>
<td>doublet</td>
<td>9.58, 9.90 (4.00)</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>quartet</td>
<td>9.69, 9.99 (4.02)</td>
<td>-</td>
</tr>
</tbody>
</table>

*corrected using ref. [46]

uncorrected

ref. [34] LSD calculations

bipyramid lying about 3 meV higher than the rhomboidal bipyramid. We found the geometries of the doublet and quartet states of Be$_6^-$ to be similar with the former having a bondlength shorter by .02 a.u. and an energy greater by about .11 eV. Again, our more symmetric structures are probably due to symmetry-breaking issues discussed above for the neutral clusters; the problem of periodic boundary conditions being much more pronounced for charged clusters.

Our interest centers on the distribution of the hole density. One spin down electron was removed to create the hole. In our use of singly occupied orbitals, those of the same spin are constrained to be spatially orthogonal, but no constraints relate orbitals of opposite spin. In the course of our calculations,
we have found for every "spin up" orbital in the doublet clusters (excepting the odd one), a corresponding "spin down" orbital whose projection on the former is within .01 of unity with the exception of the $Be_4^+$ cluster which has one pair projecting of .98 and another of .90. The spin density, defined as the spin down density minus the spin up density, that is, $n_\downarrow(r) - n_\uparrow(r)$, is therefore an excellent measure of the hole density, for the doublet clusters $n=2$ through $n=5$. Following the example of KRB, we also calculated the difference in electron density between charged clusters and neutral clusters having the charged geometry. For convenience, we denote this as the vertical density difference. Figures 5.4 and 5.5 show contours of the hole density and the vertical density difference respectively, along with their radial distributions. The position of the outermost atom from the origin is marked on each curve. Since negative values correspond to regions of higher hole density, we can see from the contour plots that the hole is mostly distributed outside the cluster in all cases. An interesting trapping of a small portion of the hole within the base of the trigonal bipyramid is found in $Be_5^+$. 

To get some quantitative measure of the distribution of the hole density, we summed the Mulliken population matrices for the down spins and the up spins and took the difference between these two matrices. Where negative numbers refer to regions of abundant hole density, Table 5.8 shows the distribution of the hole relative to atomic positions and to overlap regions between atoms. Refer to Figure 5.6 for the geometry and numbering of the atoms used in Table 5.8. Inspection of the distributions shows the tendency of the hole to distribute itself at the extreme ends of the cluster, accompanied by a smaller tendency to lie in the vicinity of atomic sites. This is especially noticeable for the three and five atom clusters.
Figure 5.4: Figures (a)-(d): Contours through the origin, perpendicular to the Z axis, of the hole density: $n_4(r) - n_7(r)$. Filled circles indicate projected positions of ions. Figure (e): same for Be$_2^+$ in a plane perpendicular to the trigonal base. Figure (f): Radial distributions of the hole density for clusters of 2 through 5 atoms. Filled circles indicate positions of atoms furthest from the origin. Units are electrons/(a.u.).

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Figure 5.5: Figures (a)-(e): Contours through the origin, perpendicular to the Z axis, of the vertical density difference. Circles indicate projected positions of the ions. Figure (f): Radial distributions of the hole density for clusters of 2 through 5 atoms. Filled circles indicate positions of atoms furthest from the origin. Units are electrons/(a.u.).

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Table 5.8: Distribution of the hole density at atomic sites and in overlap regions. Lower off diagonal elements have been incorporated into the upper off diagonal elements. Negative numbers refer to higher concentrations of the hole. Refer to Fig. 5.6 for the geometry and numbering of the atoms.

\[
\begin{array}{ccc}
Be_2^+ & & \\
1 & 2 & \\
1 & -.65 & .31 \\
2 & - & -.64 \\
\end{array}
\]

\[
\begin{array}{ccc}
Be_3^+ & & \\
1 & 2 & 3 \\
1 & -.50 & .13 & -.04 \\
2 & - & -.19 & .14 \\
3 & - & - & -.52 \\
\end{array}
\]

\[
\begin{array}{cccc}
Be_4^+ & & & \\
1 & 2 & 3 & 4 \\
1 & -.60 & .76 & -.34 & .11 \\
2 & - & -.71 & .21 & -.30 \\
3 & - & - & -.09 & .07 \\
4 & - & - & - & -.07 \\
\end{array}
\]

\[
\begin{array}{ccccc}
Be_5^+ & & & & \\
1 & 2 & 3 & 4 & 5 \\
1 & -.09 & -.03 & -.03 & .09 & .09 \\
2 & - & -.09 & -.03 & .09 & .09 \\
3 & - & - & -.10 & .10 & .10 \\
4 & - & - & - & -.57 & -.03 \\
5 & - & - & - & - & -.57 \\
\end{array}
\]

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Figure 5.6: Geometries and numbering of atoms in charged clusters. Distances are in a.u.
The asymmetric four atom cluster has two atoms, labelled 1 and 2 in Figure 5.6, that are particularly close to each other. These atoms trap a large percentage of the hole in a way that is very similar to the case of the charged dimer. Each of the two other atoms attracts some of the hole density from one of the first two atoms, causing an appreciable delocalization into the overlap regions between two pairs of atoms (atoms 1 and 3, atoms 2 and 4 in Figure 5.6).

5.1.3 Coulomb Explosion

The phenomenon of Coulomb explosion [39], in which holes present in a multiply charged cluster repel each other causing dissociation of the cluster has been investigated by KRB for doubly charged clusters of Beryllium. Our calculation of the dissociation energy for the doubly charged dimer to break into two singly charged ions illustrates how the necessity for the Makov-Payne correction escalates when dealing with multiply charged clusters in a periodic calculation such as is presented here. Our bondlength for $Be_2^{++}$ was calculated to be 4.12 a.u. in reasonable agreement with KRB’s value of 4.20 a.u. Without the Makov-Payne correction, we found this dimer to be slightly stable with a binding energy of 1.14 eV. Once corrected, however, Coulomb explosion was demonstrated with a negative (unstable) binding energy of -2.48 eV, within .1 eV of KRB’s value of -2.57 eV, demonstrating the increasing necessity of using the Makov-Payne correction with increasing magnitude of charge on the periodic cell.

5.2 Mixed Clusters: Beryllium-Lithium

Here we study clusters of lithium each having one beryllium atom as an impurity to see how the electronic structure is affected. While no experimental work has been done on such clusters, Kappes, Radi, Schar, and
Schumacher [17] (KRSS) have carried out photoionization experiments on neutral clusters of $MgK_k$ and we might expect the trends in stability to be similar. Pewestorf, Bonacic-Koutecky, and Koutecky [38] (PKK) have studied $BeLi_k$ and $BeLi_k^+$ clusters for values of $k$ ranging from 2 up to 8 and 9 respectively using Hartree-Fock to optimize geometries and a multireference configuration interaction (MRCI) procedure to further optimize the energies, while Rao and Jena [59] (RJ) performed similar calculations on $MgLi_k$. Zhang, Cohen, and Chou [60] (ZCC), in an attempt to identify shell structure, calculated the electronic structure of $MgNa_6$ and $MgNa_8$ with constrained symmetries of a centered octahedron and centered cube respectively. Their work, similar in nature to ours, used a simple cubic supercell of boxlength 21.8 a.u. and an energy cutoff of 4 Rydbergs.

We've optimized our geometries and energies subject to the constraints of symmetry in most cases used by PKK with a final heat up of the electronic degrees of freedom and relaxing of the constraints to allow for some distortion. No runs were performed completely unconstrained since in our experience only one previous case had actually yielded a minimum energy unconstrained ($Be_i^+$). In our treatments of the neutral and charged clusters, only singlet and doublet states were investigated.

### 5.2.1 Neutral Clusters

Our convergence testing for these clusters was performed only with regard to looking at changes in binding energy with increasing boxlength. Optimizing the geometry for the $BeLi_6$ cluster with our production parameters of a cubic supercell of sidelength 20 a.u. and an energy cutoff of 6.0 Rydbergs, we then optimized the electronic wavefunctions for boxlengths of 18, 22, and 23 a.u. keeping the ions fixed in the geometry obtained for the
Table 5.9: Convergence of Atomization energy per atom with changes in boxlength $L$ for the neutral $BeLi_6$ cluster. Ions were kept fixed in the geometry optimized for the case of $L=20$ a.u. Energy cutoff was 6.0 Rydbergs.

\begin{tabular}{lcccc}
\hline
$E_{\text{cut}}$ & 6.0 Ryd & \\
$L$ (a.u.) & 18 & 20 & 22 & 23 \\
\hline
$E_b$ (eV/atom) & 1.25 & 1.29 & 1.31 & 1.31 \\
\hline
\end{tabular}

production run. Table 5.9 shows the convergence of this binding energy with boxlength.

Our binding energies for the neutral $BeLi_k$ clusters are shown in Table 5.10 along with those of PKK; our geometries are shown in Figure 5.7. For structures in which our symmetries coincide with those of PKK, our bondlengths tend to be smaller than theirs by about .3 to .5 a.u. A DFT all-electron calculation carried out on $BeLi$ however\(^1\), yielded a binding energy of .47 eV and a bondlength of 4.84 a.u., with which our own values of .50 eV and 4.86 a.u. agree reasonably well. For the $BeLi_3$ clusters, we show two structures of very different geometries, both originally of $C_{2v}$ symmetry except that the second became distorted. We found the first to be only very slightly lower in energy (.02 eV) whereas PKK found it to be lower than the second type (undistorted) by .11 eV. Also, for the $BeLi_5$ cluster PKK found a $C_{2v}$ structure lower in energy by .29 eV than the centered pentagon

\(^1\)performed by Chris Harwell using Gaussian92
Table 5.10: Atomization Energies per atom for neutral $BeLi_k$ clusters defined as $E_b/(k+1) \equiv [E_{Be} + kE_{Li} - E_{BeLi_k}]/(k+1)$ for $k = 1 - 8$. See Figure 5.7 for geometries. Negative values indicate unstable clusters.

<table>
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<tr>
<th>$k$</th>
<th>Number of electrons</th>
<th>atomization energy per atom (eV)</th>
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</thead>
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</tr>
<tr>
<td>1</td>
<td>3</td>
<td>.26</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
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<tr>
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</tr>
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<td>8</td>
<td>1.29</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>1.18</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>1.33</td>
</tr>
</tbody>
</table>

$^a$basis set 3-21G, geometries optimized at Hartree-Fock level; energies with MRD-CI procedure.

$^b$same as above with 6-31G* basis set.

featured in Figure 5.7 and a centered trigonal bipyramid nearly degenerate (7 meV lower) with the pentagon. RJ, on the other hand, reported a centered pentagon as the lowest energy geometry for their work on $MgLi_5$. We tried the centered trigonal bipyramid symmetry and found its energy to be .09 eV higher than that of the centered pentagon, but the supercell method used in this work may favor planar symmetries due to their larger spatial extent and resulting larger interactions with their periodic images.

While our binding energies are much larger than those obtained using MRCI, as is symptomatic of the LSD approximation, the trends of stability are similar. Both calculations show an enhanced stability enjoyed by the 8-electron $BeLi_6$ cluster relative to its neighbors of less and more atoms. The second differences of our energies are shown in Figure 5.8 where a peak can be plainly seen for that cluster.
Figure 5.7: Lowest energy configurations obtained for Be\_L\_i\_h clusters for \( k = 1 \) through 8. The Be atom is either in the center of the cluster or is the smallest of the circles. For BeLi\_3, the first geometry shown was found to be of lowest energy. Dimensions are in a.u.
Figure 5.8: Second difference of the energy for neutral $BeLi_k$ clusters:
$\Delta_2(N) = E(N + 1) + E(N - 1) - 2E(N)$ plotted against number of electrons in the cluster $(N_e)$. Solid line is this work, dashed line is that of PKK [38].
A significant difference between our work and that of PPK exists for the larger clusters having 7 and 8 lithium atoms. We show $BeLi_7$ to be relatively unstable compared to its neighbors with $BeLi_8$ having a much higher binding energy while PPK show a rather flat distribution of binding energies over the range of $k$ equal to 6 through 8. Our trend is consistent with the experimental work of KRSS whose mass spectra found a small abundance of $MgK_6$ and a much larger peak for $MgK_8$ while finding no occurrences of other clusters containing less than five lithium atoms. That peak, and our high binding energy for the ten electron $BeLi_8$ cluster could imply that the observed shell fillings of 1s 1p 1d 2s ... for clusters of alkali atoms changes to 1s 1p 2s 1d ... by the addition of a member from the alkaline-earth group. This turns out to be the case as is shown in Table 5.12 where we find a shell-like filling in the same order as was found for the pure beryllium clusters. For clusters of lower symmetry, we projected $Y_{lm}$'s centered at the center of the electronic charge density onto the KSO's in order to illustrate their $\ell$-characters. This ordering was found by ZCC and PKK as well. Diagonalizing of the final Hamiltonian for $BeLi_8$ and the subsequent projection of $Y_{lm}$’s onto its excited states revealed 5 $d$-type orbitals, a lower lying doubly degenerate set ($e_g$) and a higher lying triply degenerate set ($t_{2g}$) consistent with the $O_h$ symmetry obeyed by a cubic geometry. The falling of the 2s level below the 1d can be explained by the deepening of the potential well at the center of the cluster due to the presence of a more attractive alkaline-earth atom (refer to Figure C.1 where the BHS pseudopotentials of lithium and beryllium are compared). The $s$-orbitals have maxima near the origin where the $p$ and $d$ orbitals have nodes, so one would expect a lowering of the $s$ level. ZCC, ever trying to justify a jellium model, also did a calculation of $MgNa_{58}$ in which the magnesium atom was modelled as a central sphere of jellium and the
sodium atoms a surrounding spherical distribution of jellium, the dimensions determined by the bulk \( r_s \) values as described in the introduction. In this manner, they also arrived at a general lowering of the \( s \)-states, in particular, a \( 3s \)-state falling below a \( 2d \)-state; a reversal of the result they obtained for a straight \( Na_{58} \) cluster performed with the jellium model.

The jellium model, however, appears to have its limitations in the context of these much smaller clusters. The lack of symmetry in the lower energy \( BeLi_3 \) cluster which has the \( Be \) atom off to one side has a marked lack of purity in its orbitals even though they have been projected onto \( Y_{im} \)'s centered at the center of the electronic charge distribution. Also, we see in the centered pentagonal \( BeLi_5 \) cluster, a lowering of the \( 2s \) orbital so as to appear after the second \( 1p \) orbital. Diagonalizing of its Hamiltonian in \( G \)-space shows it to be followed by a third \( p \)-orbital lying .33 eV higher at -2.14 eV and then a \( d \)-orbital at -2.04 eV. These latter excited states have small \( f \)-components of 11% and 6% respectively. The higher energy centered trigonal bipyramid, on the other hand, has the orbitals appearing in the conventional order of \( 1s \) followed by \( 3p \)-orbitals.

Another failing of the jellium model, appears to be its inability, to predict ionization potentials (IP's). KRSS found their more abundant (i.e. more stable) \( MgK_8 \) cluster to have a lower IP than the less stable \( MgK_6 \). They point out that this would be inconsistent with a theory that ignores ion positions. Our IP's, calculated, using runs done on singly charged clusters presented below, are tabulated in Table 5.11 along with those of PKK and KRSS. Our results are consistent with KRSS in that our \( BeLi_8 \) cluster has an appreciably higher binding energy yet a much lower IP than \( BeLi_8 \). In Figure 5.9, we plot the IP's for easier comparison, and next to it, we plot the IP's we obtain through Koopman's theorem which interprets the
Figure 5.9: (a): Adiabatic ionization potentials from this work (solid line), from PPK (reference [38], dashed line), and vertical IP's for MgKk from KRSS (reference [17] plotted circles). (b): Negative of Kohn-Sham eigenvalues for the highest occupied orbitals of each cluster (this work) corresponding to IP's via Koopman's theorem.

KS-eigenvalue of the highest occupied state to be the negative of the ionization potential. Koopman's theorem neglects the effects due to relaxing of the electron density. Considering this limitation, the trend the last three points follow ($N_e = 8$ through 10) is strikingly similar to the vertical IP's measured by KRSS.

In the case of the pure Be clusters we saw a slight increasing in the overlap population with increasing cluster size due mainly to increasing delocalization of the lowest lying KS-orbital (see Tables 5.4 and 5.5). The mixed clusters on the other hand, show a rapid increase in the OV population, leveling off around $k=6$ as can be seen in Table 5.13. While Table 5.12 shows a slightly increasing delocalization of the lowest lying orbital, we can see plainly that the preponderance of the OV population increase is due to the higher lying orbitals. All of the orbitals play an appreciable role in the bonding; none show an antibonding behavior as was seen in the pure Be clusters. Here again, the Be atom's relatively deep potential well compared to those of the surrounding
Table 5.11: Calculated adiabatic ionization potentials for BeLi<sub>k</sub> clusters and experimental vertical IP's for some MgK<sub>k</sub> clusters.

| \( \kappa \) | Ionization Potentials (eV) |
|---|---|---|
| | this work | Ref. \[38\]<sup>a</sup> | Ref. \[17\]<sup>b</sup> |
| 1 | 5.11 | 4.08 | |
| 2 | 4.53 | 4.36 | |
| 3 | 4.00 | 4.00 | |
| 4 | 4.05 | 4.16 | |
| 5 | 3.55 | 3.82 | |
| 6 | 3.96 | 4.12 | 3.95(10) |
| 7 | 3.13 | 3.31 | 3.85(20) |
| 8 | 2.99 | 3.74 | 3.38(10) |

<sup>a</sup>basis set 3-21G, geometries optimized at Hartree-Fock level; energies with MRD-CI procedure.
<sup>b</sup>vertical IP's for MgK<sub>k</sub> clusters; uncertainties in last two digits are in parentheses.

Lithium atoms is probably at cause. Relative to its neighbors, and usually at the center of the cluster, it keeps the low lying 1s state more localized while electrons from the lithium atoms contribute to the higher states. Table 5.14 shows for each of the three representative orbitals (1s 1p 2s), the orbital’s degree of localization on the Be site, the combined Li sites, and their degree of participation in Be-Li and Li-Li bonding. Figure 5.10 compares the highly bonding 2s orbital of the cubic BeLi<sub>3</sub> cluster with the anti-bonding 2s orbital of the octahedral Be<sub>6</sub> quintet. Note the much higher concentration of the latter localized in the center of the octahedron where an ion is not even located compared to the much more spread out orbital of the BeLi<sub>3</sub> cluster.
Table 5.12: Fractional S, P, and OV populations by KS-orbital for neutral BeLi\textsubscript{k} clusters. (Table is continued on next page.)

<table>
<thead>
<tr>
<th>cluster</th>
<th>$\psi_i$</th>
<th>$\epsilon_i$(eV)</th>
<th>$w_i$</th>
<th>S</th>
<th>P</th>
<th>OV</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeLi\textsubscript{1}</td>
<td>$\psi_1$</td>
<td>-5.50</td>
<td>.97s</td>
<td>.63</td>
<td>.04</td>
<td>.33</td>
</tr>
<tr>
<td></td>
<td>$\psi_2$</td>
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<td>.05s.90p</td>
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<td>.35</td>
<td>.03</td>
</tr>
<tr>
<td></td>
<td>$\psi_{1\downarrow}$</td>
<td>-5.11</td>
<td>.98s</td>
<td>.61</td>
<td>.05</td>
<td>.35</td>
</tr>
<tr>
<td>BeLi\textsubscript{2}</td>
<td>$\psi_1$</td>
<td>-4.87</td>
<td>.98s</td>
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<td>.03</td>
<td>.47</td>
</tr>
<tr>
<td></td>
<td>$\psi_2$</td>
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<td>.99p</td>
<td>.70</td>
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<td>.09</td>
</tr>
<tr>
<td>BeLi\textsubscript{3}</td>
<td>$\psi_1$</td>
<td>-5.74</td>
<td>.75s.21p</td>
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<td>.04</td>
<td>.48</td>
</tr>
<tr>
<td>(C\textsubscript{2v})</td>
<td>$\psi_2$</td>
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<td>.20s.75p</td>
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<td>.17</td>
<td>.54</td>
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<td></td>
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<td>.78s.17p</td>
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<td>.52</td>
</tr>
<tr>
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<td>.03</td>
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<tr>
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<td></td>
<td>$\psi_2$</td>
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<td>.97p</td>
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<td>-2.41</td>
<td>.97p</td>
<td>.34</td>
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<td>.42</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Orbitals are spin up unless otherwise noted. For singlet states of clusters having an even number of electrons, spin down values are very nearly the same. All orbitals are shown for the doublet states of clusters with an odd number of electrons.

\textsuperscript{b}Components amounting to less than 5% are omitted. For BeLi\textsubscript{1} and BeLi\textsubscript{3} orbitals are projected on $Y_m$'s centered at the center of the electronic charge density; all others are centered at the center of geometry.
Table 5.12 (continued)

<table>
<thead>
<tr>
<th>cluster</th>
<th>$\psi_i^a$</th>
<th>$\varepsilon_i$(eV)</th>
<th>$w_i^b$</th>
<th>S</th>
<th>P</th>
<th>OV</th>
</tr>
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<td>.03</td>
<td>.64</td>
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<tr>
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<td>.23</td>
<td>.50</td>
<td></td>
</tr>
<tr>
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<td>.49</td>
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<td>.22</td>
<td>.25</td>
<td>.54</td>
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<tr>
<td></td>
<td>$\psi_3$</td>
<td>-2.58 .96p</td>
<td>.18</td>
<td>.25</td>
<td>.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\psi_4$</td>
<td>-2.58 .96p</td>
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<td>.25</td>
<td>.57</td>
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<td>.17</td>
<td>.58</td>
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<td></td>
<td>$\psi_3$</td>
<td>-3.03 .98p</td>
<td>.23</td>
<td>.18</td>
<td>.59</td>
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<td>.23</td>
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<tr>
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<td>.23</td>
<td>.48</td>
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<td>.04</td>
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<td>.19</td>
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<td></td>
<td>$\psi_{34}$</td>
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<td>.58</td>
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<td>.18</td>
<td>.23</td>
<td>.60</td>
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<td>$\psi_4$</td>
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<td>.23</td>
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<td>-2.34 .97s</td>
<td>.45</td>
<td>.16</td>
<td>.39</td>
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*Orbitals are spin up unless otherwise noted. For singlet states of clusters having an even number of electrons, spin down values are very nearly the same. All orbitals are shown for the doublet states of clusters with an odd number of electrons.

*bcomponents amounting to less than 5% are omitted.
Table 5.13: Fractional S, P, and OV populations for each mixed cluster $BeLi_k$.

<table>
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<th>S</th>
<th>P</th>
<th>OV</th>
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<td>.14</td>
<td>.24</td>
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<tr>
<td>2</td>
<td>.60</td>
<td>.12</td>
<td>.28</td>
</tr>
<tr>
<td>3(distorted)</td>
<td>.45</td>
<td>.16</td>
<td>.39</td>
</tr>
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<td>3($C_{2v}$)</td>
<td>.38</td>
<td>.17</td>
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<tr>
<td>4</td>
<td>.34</td>
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<td>.49</td>
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<td>5</td>
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<td>7</td>
<td>.28</td>
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<tr>
<td>8</td>
<td>.24</td>
<td>.17</td>
<td>.58</td>
</tr>
</tbody>
</table>

Table 5.14: Degree of localization on atomic sites and participation in $BeLi$ and Li-Li bonding by three representative orbitals of the $BeLi_8$ cluster. Units are electrons.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Be</th>
<th>Be-Li</th>
<th>Li</th>
<th>Li-Li</th>
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<td>.06</td>
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<td>1p</td>
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<td>.26</td>
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<td>2s</td>
<td>.08</td>
<td>-.06</td>
<td>.52</td>
<td>.46</td>
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</table>

Figure 5.10: Contours of the 2s orbital in the plane containing (a): the centered Be atom of cubic $BeLi_8$ perpendicular to a face of the cube and (b): the base of the octahedral $Be_8$ quintet. Filled circles indicate ions or their projected positions. Units are in $10^{-3}$/a.u. Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
5.2.2 Charged Clusters

In Table 5.15 we show our binding energies for the singly charged $BeLi^+_k$ clusters calculated using the Makov-Payne correction with those obtained by PKK. Geometries are shown in Figure 5.11 with about the same disparity in bondlengths from PKK found in the neutral cases for clusters of comparable symmetry. We differ from PKK's work in that our $BeLi^+_5$ cluster is distorted from the $C_{2v}$ resulting in a decrease of .15 eV from the undistorted structure. Also, for the $BeLi^+_6$ cluster PKK found a $D_{3d}$ structure (centered trigonal antiprism) to be lower in energy than a very nearly octahedral centered square bipyramid by .06 eV (at the SCF level) while we found a centered octahedron to be lower than the $D_{3d}$ structure by an appreciable .23 eV. Both of our structures are shown in Figure 5.11. Our disagreement with the predictions of the shell model is severe and at odds with PKK as can be seen from our values for the second differences of the energy for the clusters having 7 and 8 electrons (see Figure 5.12) but our energies did give us a trend for the ionization energies of the neutral clusters that were more akin to the measurements of KRSS. Still, it must be conceded that surface effects may well be at work here in view of the decent agreement we have with PKK for the clusters containing up to 6 electrons.
Figure 5.11: Lowest energy configurations obtained for \( \text{BeLi}^+_k \) clusters for \( k = 1 \) through 8. The Be atom is either in the center of the cluster or is the smallest of the circles. For \( \text{BeLi}^+_6 \), the first geometry shown was found to be of lowest energy. Dimensions are in a.u.
Figure 5.12: Second difference of the energy for charged $BeLi^+_k$ clusters: 
$\Delta_2(N) = E(N + 1) + E(N - 1) - 2E(N)$ plotted against number of electrons in the cluster ($N_e$). Solid line is this work, dashed line is that of PKK [38].

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Table 5.15: Atomization Energies per atom for charged $\text{BeLi}_k^+$ clusters defined as $E_b^+/ (k + 1) \equiv \left[ E_{\text{Be}} + E_{\text{Li}^+} + (k - 1)E_{\text{Li}} - E_{\text{BeLi}_k^+} \right] / (k + 1)$ for $k = 1 - 8$. The energy of the $\text{Li}^+$ has been taken as zero in our pseudopotential calculation. See Figure 5.11 for geometries.

<table>
<thead>
<tr>
<th>$k$</th>
<th>Number of electrons</th>
<th>Atomization energy per atom (eV)</th>
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</thead>
<tbody>
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<tr>
<td>8</td>
<td>9</td>
<td>1.60</td>
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</table>

°basis set 3-21G, geometries optimized at Hartree-Fock level; energies with MRD-CI procedure.

°same as above with 6-31G* basis set.
In this work, we have shown how small beryllium clusters have characteristics typical of a shell model from the points of view of stability and electronic structure. We found a higher relative stability for the four atom cluster with the magic number of eight valence electrons and obtained orbitals of mostly pure $\ell$-states centered about each cluster's center of geometry. These orbitals were expanded over a similarly calculated atomic basis to see how they might arise from hybridization of atomic orbitals and to examine how they contribute to the overall binding in the cluster. An atomic basis consisting solely of $s$ and $p$ orbitals was found to be very nearly complete in describing the shell-like orbitals. We identified the order of filling for the $\ell$-states, namely, $1s\ 1p\ 2s\ 1d$. Further, using a Mulliken population analysis, we found the $1s$ state to be highly delocalized, the $2s$ state to be highly localized and hybridized, and the $1p$ and $1d$ states to be localized and composed mainly of pure $s$ and pure $p$ atomic orbitals respectively.

In a similar fashion, we decomposed the hole densities for the singly positively charged clusters into contributions to the population density in regions of atomic sites and in regions of overlap between pairs of atoms. We showed the hole's tendency to be concentrated at the extreme extents of the cluster and, in clusters of high symmetry, to favor atomic sites rather than overlap regions.

In the case of the neutral BeLi$_k$ clusters we found the addition of a Be atom to lower the $2s$ state below the $1d$ state, reversing the order of shell
filling found of 1s 1p 1d 2s ..., and bringing the order to match that which we have found for the pure Be clusters. While our binding energies for the neutral clusters imply the workability of a shell/jellium model, other results we've presented suggest it has its limitations. The higher binding energy but lower ionization potential of the \( \text{BeLi}_8 \) cluster relative to \( \text{BeLi}_6 \), supported experimentally for the presumably similar \( \text{MgK}_k \) systems by KRSS appear to contradict the model. Also, our lowest energy \( \text{BeLi}_3 \) structure, the one of \( C_{2v} \) symmetry (also reported by PKK as their lowest energy configuration) was found to have orbitals of relatively impure \( l \)-states, implying that some semblance of symmetry in the atomic positions is needed to achieve a symmetric enough charge density to obtain shell-like orbitals. In the limit of large clusters, however, for which the application of jellium models are intended, this should not be a problem. We were unable in terms of binding energy to find a shell structure for the charged clusters but their orbitals had about the same degree of purity in \( l \)-states as was found for the neutral clusters. As mentioned above, surface effects may be at cause here and further work with larger boxlengths will be needed to resolve this issue. The \( \text{BeLi}_k \) clusters showed a much more rapid increase in delocalization of the electronic density with increasing cluster size than the pure Be clusters which was to be expected from the higher reactivity of the Li atoms.

Limitations in the quality of the work presented here include the use of the LSD approximation, the use of the pseudopotential, and the use of the supercell method. We have tried to estimate errors in the latter through the presentation of our convergence data. The errors in our binding energies due to the pseudopotential at least for the \( \text{Be} \) dimer appear small since we arrived

\[1\text{Ref. [15] and confirmed by us for a fixed geometry of Na}_{20} \text{ optimized under a Lennard-Jones potential.}\]
at the same value (.36 eV) as the LSD all-electron real space calculation of KRB. The dimer, being of small extent would filter out errors due to the supercell method, however, the BHS pseudopotential was constructed at the atomic level and its transferability could be expected to decrease with increasing cluster size. The LSD approximation is well known to overestimate binding energies especially in the case of weakly bound systems. Illustrative of this is the value of the binding energy of the \textit{Be} dimer whose LSD value is almost four times the experimental and CI values of .10 eV. Also, our \textit{BeLi}_1 cluster is bound whereas the CI calculation of PKK finds it unbound. The LSD approximation, nevertheless has been found useful in predicting trends of binding energies and stability as has been demonstrated here at least for the neutral clusters. Future work planned includes the incorporation of gradient-corrected exchange-correlation functionals into the code. These will of course be more computationally expensive being no longer local in nature.

Also related to the quality of work here are the optimization parameters of initial fictitious kinetic energy ($E_{f\text{kin}}$) and the rate at which the simulated annealing is carried out, how the ions are moved, and the initial ion configuration. In cases in which some symmetry constraint on the ions has been used as a roadmap, we have found little or no change going to higher initial values of $E_{f\text{kin}}$ or to slower annealing rates than those mentioned in Chapter 4 of this work. However, runs performed on one-atom cases in which the basis set was much larger (needed for convergence testing) have occasionally required us to increase $E_{f\text{kin}}$ and/or slow down the annealing rate to avoid a local minimum. It would be reasonable to assume that the larger configuration spaces require more sampling to find the optimal regions.

I'll conclude this work by mentioning that its attraction to me has been two-fold. First the idea of being able to predict the properties of systems
from first principles with a minimum of periodic table information (pseudopotential aside for the moment), and second, the allure of the general field of optimization. That is, to find an optimal solution to a problem whether it be minimizing energy, costs, or maximizing profits when a direct solution can't be solved in polynomial time and when greedy algorithms won't provide solutions that are optimal enough. The field abounds with exciting algorithms beyond the Monte Carlo and molecular dynamics schemes mentioned here, encompassing genetic algorithms in which sampling schemes mimic the processes thought to be responsible for the evolution of life here, and genetic programming in which the actual algorithms themselves are evolved in the course of running, to optimize the search for a globally optimal solution.
REFERENCES


In this appendix, we discuss the construction of the energy functional for a periodic system, along with some of the issues that arise when such a system is being used to model an aperiodic one by considering the limit of a large period. We begin by calculating the electrostatic energy of a system of periodically repeating charge neutral cells which follows Makov and Payne’s generalization [46] of a similar treatment applied to point charges done by DeLeeuw et. al. [61]. Next we apply the result to the specific case of ions immersed in an electron gas. Finally, we extend the treatment to the case of a system in which the periodically repeating cells each have a net charge.

### A.1 Electrostatic Energy of a Periodic System of Charge Neutral Cells

Suppose we have a periodic charge density \( \rho(r) \) such that \( \rho(r) = \rho(r + L_n) \) where \( L_n \) is a lattice vector specifying any \( n^{th} \) cell. With each cell being charge neutral we have

\[
\int_{\Omega} \rho(r) \, dr = 0 \quad (A.1)
\]

where \( \Omega \) is the volume of the cell. The electrostatic energy per cell is

\[
E = \frac{1}{2} \int_{\Omega} \rho(r) \phi(r) \, dr \quad (A.2)
\]

where \( \phi(r) \) is the Coulomb potential

\[
\phi(r) = \sum_n \int_{\Omega} \frac{\rho(r')}{|x + L_n|} \, dr' \quad (A.3)
\]
arising from \( \rho(r) \). Here, \( x = r - r' \) and the contributions are summed over the \( N_c \) cells of some sample. The lattice sum in Eq. A.3 converges very slowly when calculated purely in real space. The Ewald formulation \([44]\) is a method by which the summation is recast partly in Fourier space enabling faster convergence, allowing us to sum over fewer cells surrounding the central cell. The real space long range effects of the potential are captured in the \( G \)-space portion. Before splitting the sum, we multiply each of its terms by a convergence factor \( e^{-s|L_n|^2} \) with the limit of \( s \) taken to zero so as to give it the property of absolute convergence. Defining a new lattice sum then, as

\[
\tilde{\psi}(x, s) = \sum_n e^{-s|L_n|^2} \frac{1}{|x + L_n|} \tag{A.4}
\]

so that

\[
\phi(r) = \lim_{s \to 0} \sum_n \int_\Omega \rho(r') \tilde{\psi}(x, s) \, dr' \tag{A.5}
\]

and substituting the identity

\[
\frac{1}{r} = \frac{2}{\sqrt{\pi}} \int_0^\infty dt \, e^{-t^2}
\]

into equation A.4, we split the integral into intervals from zero to some parameter \( \alpha \) and from \( \alpha \) to infinity, giving us

\[
\tilde{\psi}(x, s) = \frac{2}{\sqrt{\pi}} \sum_n \int_0^\alpha e^{-t^2(x+L_n)^2} e^{-s|L_n|^2} \, dt
\]

\[
+ \sum_n \frac{\Phi_c(\alpha|x + L_n|)}{|x + L_n|} e^{-s|L_n|^2}
\]

\[
\equiv I_1 + I_2 \tag{A.6}
\]
where $\Phi_c(x)$ is the complementary error function. Looking at the first term

$$I_1 = \int_0^\infty g(x, t)e^{-x^2} dt$$

where

$$g(x, t) \equiv \frac{2}{\sqrt{\pi}} \sum_n e^{-i^2(x+L_n)^2},$$

the property of absolute convergence allowing us to reverse the integral and summation. Since $g(x, t)$ is periodic with the lattice, we can expand it over $G$-space as

$$g(x, t) = \sum_G \tilde{g}(G, t)e^{iG\cdot x} dx$$

with

$$\tilde{g}(G, t) = \frac{1}{\Omega} \int_\Omega g(x, t)e^{-iG\cdot x} dx$$

Calculating $\tilde{g}(G, t)$:

$$\tilde{g}(G, t) = \frac{1}{\Omega} \frac{2}{\sqrt{\pi}} \int_\Omega \sum_n e^{-i^2(x+L_n)^2} e^{-iG\cdot x} dx$$

$$= \frac{1}{N_c\Omega} \frac{2}{\sqrt{\pi}} \sum_n e^{iG\cdot L_n} \int_{N_c\Omega} e^{-x^2t^2} e^{-iG\cdot x'} dx'$$

where the substitution $x' \equiv x + L_n$ has been made and the periodicity of $g(x, t)$ has been used so as to extend the integral over the entire sample. Considering the sample large enough to extend limits on the integral to infinity, and factoring the integral:
\[ \tilde{g}(G, t) = \frac{1}{\Omega \sqrt{\pi}} \frac{1}{2} \sum_n \sum_{L_n} e^{iG \cdot L_n} \prod_{k=1}^3 \left[ \int_{-\infty}^{\infty} e^{-\frac{\alpha^2}{4}t^2} e^{iG_k x_k} \right] \]

\[ = \frac{1}{\Omega \sqrt{\pi}} \frac{\pi^{3/2}}{t^3} e^{-G^2/4t^2} \quad (A.9) \]

where we've used

\[ \frac{1}{N_c} \sum_n e^{iG \cdot L_n} = 1 \]

Substituting Eq. A.9 into the definition of \( g(x, t) \) (Eq. A.8), we have

\[ g(x, t) = \frac{1}{\Omega \sqrt{\pi}} \frac{\pi^{3/2}}{t^3} \sum_G e^{-G^2/4t^2} e^{iG \cdot x}. \]

Making the variable change \( v \equiv t^2 \), the definition and equation become

\[ g(x, v) = \frac{2}{\sqrt{\pi}} \sum_n e^{-v(x+L_n)^2} \]

\[ = \frac{1}{\Omega \sqrt{\pi}} \left( \frac{\pi}{v} \right)^{3/2} \sum_G e^{-G^2/4v} e^{iG \cdot x}. \quad (A.10) \]

The same variable change applied to Eq. A.7 gives (with a little massaging)

\[ I_1 = \int_0^{\alpha^2} g(x, v) e^{-s|L_n|^2} \left( \frac{1}{2} v^{-1/2} \right) dv \]

\[ = \frac{1}{\sqrt{\pi}} \int_0^{\alpha^2} \sum_n e^{-v(x+L_n)^2} v^{-1/2} e^{-s|L_n|^2} dv \]

\[ = \frac{1}{\sqrt{\pi}} \int_0^{\alpha^2} v^{-1/2} \left[ \sum_n e^{-v(s+u)(L_n+xv/(s+u))^2} \right] e^{-x^2u(s+u)/(s-v)} dv. \quad (A.11) \]
Applying the Fourier expansion of Eq. A.10 to the above expression in brackets, with arguments: \((\frac{xv}{s+v}, s + v)\) instead of \((x, v)\) gives

\[
I_1 = \frac{1}{\sqrt{\pi}} \int_0^{\alpha^2} u^{-1/2} dv \left( \frac{\pi^{3/2}}{(s + v)^{3/2}} \right) \times \sum_G e^{-G^2/4(s+v)} e^{iG \cdot xv/(s+v)} e^{-x^2us/(s+v)}.
\]  

(A.12)

If we isolate the singular \(G = 0\) term and for the rest of the expression, take the limit of \(s\) to zero and integrate, we have

\[
(I_1)_{G \neq 0, s \to 0} = \sum_G' \frac{4\pi}{\Omega G^2} e^{-G^2/4\alpha^2} e^{iG \cdot x}
\]  

(A.13)

and the singular term, making the variable change: \(u \equiv v(s + v)^{-1}\), is

\[
(I_1)_{G = 0} = \frac{\pi}{\Omega} \int_0^{\alpha^2} dv \frac{e^{-x^2us/(s+v)}}{u^{-1/2}(s + v)^{3/2}}
\]

\[
= \frac{\pi}{\Omega s} \int_0^{\alpha^2/(s+\alpha^2)} u^{-1/2} e^{-x^2u} du.
\]  

(A.14)

Expanding the exponential about Eq. A.14, integrating, and expanding the denominators gives

\[
(I_1)_{G = 0} = \frac{\pi}{\Omega s} \left[ \frac{2\alpha}{\sqrt{\alpha^2 + s}} - \frac{2}{3} x^2 s \frac{\alpha^3}{(\alpha^3 + s)} \right]^{3/2} + \mathcal{O}(s^2)
\]

\[
= \frac{2\pi}{\Omega s} \left[ 1 - \frac{1}{2} \frac{s}{2\alpha^2} + \ldots \right] - \frac{2\pi}{3\Omega} x^2 \left[ 1 - \frac{13}{22} \frac{s}{\alpha^2} + \ldots \right]
\]

\[
= \frac{2\pi}{\Omega s} - \frac{\pi}{\Omega \alpha^2} - \frac{2\pi}{3\Omega} x^2 + \mathcal{O}(s).
\]
Substituting in for $x$ we arrive at

$$\langle I_1 \rangle_{G=0} = \frac{2\pi}{\Omega s} - \frac{\pi}{\Omega \alpha^2} - \frac{2\pi}{3\Omega} \left( r^2 + r'^2 - 2r \cdot r' \right) + O(s). \quad (A.15)$$

When $\langle I_1 \rangle_{G=0}$ is multiplied by the charge density $\rho(r')$ and integrated over the cell volume to calculate the potential as in Eq. A.5, the first three terms, independent of $r'$, are zeroed for a charge neutral cell.

Finally, the potential of Eq. A.3, becomes

$$\phi(r) = \int_\Omega dr' \left[ \psi(r, r') - \frac{2\pi r'^2}{3\Omega} + \frac{4\pi r \cdot r'}{3\Omega} \right] \quad (A.16)$$

where the real space portion and all but $G = 0$ contribution of the reciprocal space portion have been incorporated into

$$\psi(r, r') = \sum_n \Phi_n \frac{\phi_n(\alpha |r - r' + L_n|)}{|r - r' + L_n|}$$

$$+ \frac{4\pi}{\Omega} \sum_{G \neq 0} \frac{1}{G^2} e^{-G^2/4\alpha^2} e^{iG \cdot x}. \quad (A.17)$$

The energy due to the last two terms of Eq. A.16 is

$$E_d = \frac{1}{2} \int_\Omega \rho(r) \, dr \int_\Omega \rho(r') \left( \frac{-2\pi r'^2}{3\Omega} + \frac{4\pi r \cdot r'}{3\Omega} \right) \, dr'$$

$$= \frac{2\pi}{3\Omega} \left| \int_\Omega \rho(r) \, dr \right|^2 \quad (A.18)$$

where the first term vanishes, again, from charge neutrality.

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A.2 Application to Ions in an Electron Gas

For our situation in which the unit cell consists of point charges immersed in a continuous charge density (valence electron density), we have an overall electron density

\[ \rho(r) = -n(r) + \sum_i Z_i \delta(r - R_i) \]  \hspace{1cm} (A.19)

The Coulomb energy\(^1\) of this distribution, leaving out the \(E_d\) term for the moment is

\[ E_0 = \frac{1}{2} \int_{\Omega} \int_{\Omega} \rho(r) \rho(r') \psi(r, r') \, dr \, dr' \]

\[ = \frac{1}{2} \int_{\Omega} \int_{\Omega} d\mathbf{r} \, d\mathbf{r}' \, n(r) n(r') \psi(r, r') \]

\[ - \sum_i Z_i \int_{\Omega} d\mathbf{r} \, n(r) \psi(r, R_i) \]

\[ + \frac{1}{2} \sum_i \sum_j Z_i Z_j \psi(R_i, R_j) \]  \hspace{1cm} (A.20)

The first term in this expression is the Hartree interaction. The second term is the ion-electron interaction which is modelled by a pseudopotential (appendix C) when the ions are not nuclei since such ions are not point charges. The final term is the ion-ion interaction.

A.2.1 Hartree Energy

Casting the Hartree energy completely in Fourier space (\(\alpha \to \infty\)), we have from Eqs. A.17 and A.20,

\(^1\)Units used in this section are Hartrees
\[ E_{H} = \frac{1}{2} 4\pi \Omega \sum_{G \neq 0} \tilde{n}_G \tilde{n}_G^* G^2 \]  

where we have substituted the expansions

\[ n(r) = \sum_{G} \tilde{n}_G e^{iG \cdot r} \]

and used the relations

\[ \int_{\Omega} e^{i(G-G') \cdot r} \, dr = \Omega \delta_{G,G'} \]

and \( \tilde{n}_G = \tilde{n}_{-G} \) since \( n(r) \) is real.

### A.2.2 Ion-Electron Energy

For all-electron calculations, in which the ions are the nuclei and resemble point charges, taking the lattice sum in Fourier space and substituting the Fourier expansion of the electron density we have

\[ E_{\text{nuc-elec}} = -\sum_{I} Z_I \int_{\Omega} dr n(r) \psi(r, R_I) \]

\[ = -4\pi \sum_{G \neq 0} \frac{1}{G^2} \tilde{n}_G S_G \]  

where \( S_G \) is the structure factor

\[ S_G = \sum_{I} Z_I e^{-iG \cdot R_I} . \]  

A pseudopotential, modelling the effect of ions (nuclei + core electrons) on valence electrons contains both Coulomb and screening parts. The \( G = 0 \)

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portion of the Coulomb part must be subtracted out in order to be consistent with its omission inherent in Eq. A.17. The use of pseudopotentials is discussed in Appendix C and illustrated for the particular pseudopotential used in this work.

A.2.3 Ion-Ion Energy

The ion-ion interaction, from Eq. A.20, with $\mathbf{R}_{IJ} = \mathbf{R}_I - \mathbf{R}_J$ is

$$E_{I-J} = \frac{1}{2} \sum_i \sum_j Z_i Z_j \left[ \sum_n \frac{\Phi_c(\alpha |\mathbf{R}_{IJ} + \mathbf{L}_n|)}{|\mathbf{R}_{IJ} + \mathbf{L}_n|} ight]$$

$$+ \frac{4\pi}{\Omega} \sum_{G \neq 0} \frac{1}{G^2} e^{-G^2/4\alpha^2} e^{i\mathbf{G} \cdot \mathbf{R}_{IJ}}$$

$$= \frac{1}{2} \left[ \frac{4\pi}{\Omega} \sum_{G \neq 0} \frac{1}{G^2} e^{-G^2/4\alpha^2} e^{i\mathbf{G} \cdot \mathbf{R}_{IJ}} ight]$$

$$+ \sum_i \sum_{j \neq I} Z_i Z_j \sum_n \frac{\Phi_c(\alpha |\mathbf{R}_{IJ} + \mathbf{L}_n|)}{|\mathbf{R}_{IJ} + \mathbf{L}_n|}$$

$$+ \sum_i Z_i^2 \sum_n \frac{\Phi_c(\alpha |\mathbf{L}_n|)}{|\mathbf{L}_n|}$$

$$- \lim_{n \to 0} \sum_i Z_i^2 \left( \frac{1}{|\mathbf{L}_n|} \right). \quad (A.24)$$

The last term subtracts out the nonphysical diverging interaction between a point charge and itself, which is inherent in the penultimate term. We can combine these two terms as

$$\sum_i Z_i^2 \sum_{n \neq 0} \frac{\Phi_c(\alpha |\mathbf{L}_n|)}{|\mathbf{L}_n|} + \lim_{n \to 0} \sum_i Z_i^2 \left[ \frac{\Phi_c(\alpha |\mathbf{L}_n|)}{|\mathbf{L}_n|} - \frac{1}{|\mathbf{L}_n|} \right].$$

Substituting the definition of the complementary error function and taking
the limit, gives us

$$\lim_{n \to 0} \left\{ \frac{1}{|L_n|} \left( \Phi_c(\alpha|L_n|) - 1 \right) \right\} = \lim_{n \to 0} \left\{ \frac{1}{|L_n|} \left[ 1 - \frac{2}{\sqrt{\pi}} \int_0^{\alpha|L_n|} e^{-u^2} du - 1 \right] \right\}$$

$$= \lim_{n \to 0} \left\{ -\frac{2}{\sqrt{\pi}} \int_0^{\alpha|L_n|^2} e^{-u^2} du \right\}$$

$$= -\frac{2\alpha}{\sqrt{\pi}}. \quad (A.25)$$

So for the ion-ion interaction, we have

$$E_{i-I} = \frac{1}{2} \left\{ \frac{4\pi}{\Omega} \sum_l \sum_j Z_l Z_j \sum_{G \neq 0} \frac{1}{G^2} e^{-G^2/4\alpha^2} e^{iG \cdot R_{IJ}} \right.$$

$$+ \sum_l \sum_{j \neq l} Z_l Z_j \sum_n \frac{\Phi_c(\alpha|R_{IJ} + L_n|)}{|R_{IJ} + L_n|}$$

$$+ \sum_l Z_l^2 \left[ \sum_{n \neq 0} \frac{\Phi_c(\alpha|L_n|)}{|L_n|} - \frac{2\alpha}{\sqrt{\pi}} \right] \right\}. \quad (A.26)$$

Finally, the dipole dependent term from Eq. A.18 is

$$E_d = \frac{2\pi}{3\Omega} \left| - \int_\Omega n(\mathbf{r}) \mathbf{r} d\mathbf{r} + \sum_l Z_l \mathbf{R}_l \right|^2. \quad (A.27)$$

This dipole term is not obtained if the convergence factor of Eq. A.4 is omitted. Since it goes as $O(1/L^3)$, it does not affect the final result for a truly aperiodic system in which $L \to \infty$. The term has not been used in the gradient calculations needed to move ions and optimize wave functions, but only to correct final energy values. Not surprisingly, we have found its inclusion to be insignificant for homogeneous clusters of high symmetry.
A.3 Applications to a Charged System

Our treatment of the charged clusters is based on the artificial introduction of a neutralizing uniform charge density into the supercell, as suggested by Leslie and Gillan [62], in order to maintain the cancellation of singularities arising from contributions at the origin of the Fourier space to the potentials. This background jellium tends to zero in the limit of large supercells. Usage of the Makov-Payne correction [46] allows us to subtract out some of the nonphysical effects due to the jellium and due to interactions between clusters arising from our use of periodic boundary conditions. These corrections are taken through the order of $1/L^3$, where $L$ is the boxlength of a simple cubic supercell. In this section, we work out the details of these corrections.

In Makov and Payne's treatment, superimposed positive and negative point charges, equal in magnitude to the cell's net charge are added to the system at an arbitrary point $r_0$ to allow separation of the total charge density into two separate neutral densities: one containing the jellium $\rho_0$, and the other, the density of the actual system of ions and electrons that we wish to study $\rho_c(r)$. Where $\rho_0 = -q/\Omega$ we have

$$\rho(r) = \rho_c(r) + \rho_0$$

$$= [q \delta(r - r_0) + \rho_0] + [-q \delta(r + r_0) + \rho_c(r)]$$

$$\equiv \rho_1 + \rho_2. \quad (A.28)$$

The Coulomb energy for this distribution is the sum of the energies of interaction between $\rho_1$ and itself ($E_{11}$), by $\rho_2$ and itself ($E_{22}$), and that of $\rho_1$ with $\rho_2$ ($E_{12}$).

For $E_{11}$, we have, from Eqs. A.2, A.16, and A.18

$$E_{11} = \frac{1}{2} \int_\Omega \int_\Omega \rho_1(\mathbf{r}) \int_\Omega \int_\Omega \psi(\mathbf{r}, \mathbf{r}') + \frac{2\pi}{3\Omega} \left| \int_\Omega \rho_1(\mathbf{r}) \mathbf{r} d\mathbf{r} \right|^2$$
\[
E_{11} = \frac{1}{2} q^2 \left\{ \psi(r_0, r_0) - \frac{2}{\pi} \int_{\Omega} dr \psi(r, r_0) + \frac{1}{\Omega^2} \int_{\Omega} \int_{\Omega} dr \, dr' \psi(r, r') \right. \\
+ \frac{4\pi}{3\Omega r_0^2} \right\}. \tag{A.29}
\]

Consider the G-space part of \( \psi(r, r') \) when integrated over \( r \) (refer to Eq. A.17)

\[
\frac{4\pi}{\Omega} \sum_{G \neq 0} \frac{1}{G^2} e^{-G \cdot \alpha^2} \int_{\Omega} e^{iG \cdot (r-r')} \, dr = 4\pi \sum_{G \neq 0} \frac{1}{G^2} e^{-G \cdot \alpha^2} \delta(G - 0) = 0.
\]

and similar for \( \psi(r, r_0) \).

So our expression for \( E_{11} \) becomes

\[
E_{11} = \frac{1}{2} q^2 \left[ \psi(r_0, r_0) - \frac{2}{\Omega} \int_{\Omega} dr \sum_n \Phi_c(\alpha |r - r_0 + L_n|) \right. \\
+ \left. \frac{1}{\Omega^2} \int_{\Omega} \int_{\Omega} dr \, dr' \sum_n \Phi_c(\alpha |r - r' + L_n|) + \frac{4\pi}{3\Omega r_0^2} \right]. \tag{A.30}
\]

The lattice sums in the middle two terms can be replaced by integrations over all the cells (or all space) as

\[
\frac{2}{\Omega} \int_{N_e\Omega} dr \frac{\Phi_c(\alpha |r - r_0|)}{|r - r_0|} + \frac{1}{\Omega} \int_{\Omega} dr \int_{N_e\Omega} dr' \frac{\Phi_c(\alpha |r - r'|)}{|r - r'|}.
\]

The integral over all space in the second term is independent of the integral over the cell, the latter yielding \( \int_{\Omega} dr = \Omega \), so the two terms combine easily and can then be integrated by parts, as

\[
-\frac{1}{\Omega} \int_{N_e\Omega} dr \frac{\Phi_c(\alpha |r - r_0|)}{|r - r_0|} = -\frac{4\pi}{\Omega} \int_0^\infty \frac{\Phi_c(\alpha r)}{r} \, dr = -\frac{\pi}{\Omega \alpha^2}.
\]
So for $E_{11}$, we have

$$E_{11} = \frac{q^2}{2} \left[ \psi(r_0, r_0) - \frac{\pi}{\Omega \alpha^2} + \frac{4\pi}{3\Omega r_0^2} \right].$$

By Eq. A.17, we have for $\psi(r_0, r_0)$

$$\psi(r_0, r_0) = \sum_n \frac{\Phi_c(\alpha|L_n|)}{|L_n|} + \frac{4\pi}{\Omega} \sum_{G \neq 0} \frac{1}{G^2} e^{-G^2/4\alpha^2}$$

and after subtracting out the nonphysical $\lim_{n \to 0}(\frac{1}{|L_n|})$ term similar to Eq. A.25, we get, for $E_{11}$,

$$E_{11} = \frac{q^2}{2} \left[ \sum_{n \neq 0} \frac{\Phi_c(\alpha|L_n|)}{|L_n|} + \frac{4\pi}{\Omega} \sum_{G \neq 0} \frac{1}{G^2} e^{-G^2/4\alpha^2} \right.$$

$$\left. - \frac{2\alpha}{\sqrt{\pi}} - \frac{\pi}{\Omega \alpha^2} + \frac{4\pi}{3\Omega r_0^2} \right].$$

(A.31)

Now we'll choose $r_0$ such that the dipole moment of $\rho_2$ of Eq. A.28 is zero, that is,

$$r_0 = \frac{1}{q} \int_{\Omega} r \rho(r) \, dr.$$  

(A.32)

For $E_{12}$, in which the charge density acted upon is different from that giving rise to the potential, we generalize Eqs. A.2, A.16, and A.17 (omitting the dipole term via our choice of $r_0$) as

$$E_{12} = \lim_{r \to 0} \int_{\Omega} dr \rho_1(r) \int_{\Omega} dr' \rho_2(r') \psi(x, s)$$

$$= \lim_{r \to 0} \int_{\Omega} dr q \delta(r - r_0) \int_{\Omega} dr' \rho_2(r') \psi(x, s)$$
\[ + \lim_{r \to 0} \int_\Omega \, dr \rho_0 \int_\Omega \, dr' \rho_2(r') \psi(x,s) \]

\[ \equiv E_{12a} + E_{12b} \tag{A.33} \]

where the energy has been split into interactions between \( \rho_2 \) and a point charge, and \( \rho_2 \) and the jellium.

For \( E_{12a} \), if we take the limit \( \alpha \to 0 \), that is, casting the lattice sum completely in real space we have

\[ E_{12a} = \int_\Omega \, dr \, q \delta(r-r_0) \int_\Omega \, dr' \rho_2(r') \sum_n \frac{1}{|r-r'_n|} \]

where \( r'_n \equiv r' - L_n \). Substituting in a form of the multipole expansion [63]

\[ \frac{1}{|r-r'_n|} = \frac{1}{r} - \frac{r \cdot r'_n}{r^3} + \frac{1}{6} \sum_{i,j} Q^n_{ij} \left( \frac{3x_i x_j - r^2 \delta_{ij}}{r^5} \right) + \ldots \]

where \( Q^n_{ij} \equiv 3x'_i x'_j - r_n^2 \delta_{ij} \) is the quadrupole tensor with \( i \) and \( j \) running over the Cartesian indices, and \( n \) over the cells, gives us

\[ E_{12a} = \int_\Omega \, dr \, q \delta(r-r_0) \left\{ \frac{1}{r} \int_\Omega \, dr' \rho_2(r') \sum_n (1) \right\} \]

\[ - \frac{r}{r^3} \int_\Omega \, dr' \sum_n r'_n \]

\[ + \frac{1}{6} \sum_{i,j} \left( \frac{3x_i x_j - r^2 \delta_{ij}}{r^5} \right) \int_\Omega \, dr' \rho_2(r') \sum_n Q^n_{ij} \right\} + O(1/L^5). \]

The first term is zero because of charge neutrality. The second term is zero because our choice of \( r_0 \) renders \( \rho_2 \)'s dipole moment zero. The quadrupole...
term, in general, contributes, but in our present case of a simple cubic structure, $\sum_n \sum_{ij} Q_{ij}^n$ is zero since the $i \neq j$ terms will cancel in summing over the cubic lattice, while the $i = j$ terms will sum to zero within each cell. So for a simple cubic structure, $E_{12a} = \mathcal{O}(1/L^5)$.

For $E_{12a}$, if we take the limit of $\alpha \to \infty$, casting the lattice sum totally in $G$-space, we have only a $G = 0$ contribution because of the factor $e^{-G^2/4\alpha^2}$ (see Eqs. A.16 and A.17) and

$$E_{12a} = -\frac{q}{\Omega} \int_\Omega dr \int_\Omega dr' \rho_2(r') \left[ -\frac{2\pi}{3\Omega} r'^2 + \frac{4\pi}{3\Omega} r \cdot r' \right].$$

The second term is lost since $\rho_2$ has no dipole moment and substitution for $\rho_2$ in the first term gives

$$E_{12a} = -\frac{2\pi}{3\Omega} q^2 r_0^2 + \frac{2\pi}{3\Omega} q \int_\Omega \rho_2(r) r^2 dr. \quad (A.34)$$

The interaction of $\rho_2$ with itself (leaving out the noncontributing dipole term) is

$$E_{22} = \frac{1}{2} \int_\Omega dr \rho_2(r) \int_\Omega dr' \rho_2(r') \psi(r, r').$$

Substituting for $\psi(r, r')$, with the limit of $\alpha \to 0$ and substituting in the multipole expansion leads us to contributions of $\mathcal{O}(1/L^5)$ as in our consideration of $E_{12a}$.

We now subtract out from the total calculated energy (due to the charge distribution of Eq. A.28) the terms we've calculated through $\mathcal{O}(1/L^3)$ leaving us with the energy of the isolated charged system:

$$E_{\text{corrected}} = E_{\text{calculated}} - E_{11} - E_{12a} - \mathcal{O}(1/L^5)$$

where $E_{11}$ is given by Eq. A.31 and $E_{12a}$ by Eq. A.34.
APPENDIX B

OPTIMIZATION SCHEME

In this appendix we discuss the methods used in this work to optimize the electronic structure. The relevant equations are derived and their methods of implementation described.

The Car-Parrinello Lagrangian of Eq. 3.1 is

\[ \mathcal{L} = \mu \sum_i \int f_i \psi_i^* \dot{\psi}_i \, dr + \frac{1}{2} \sum_i M_i \ddot{R}_i - E[\{\psi_i\}, \{R_i\}] + \sum_i \sum_j f_i \lambda_{ij} \left[ \int \psi_i^* \psi_j \, dr - \delta_{ij} \right]. \]  

(B.1)

where the energy functional \( E[\{\psi_i\}] \) is from Eq. 2.11

\[ E[\{\psi_i\}, \{R_i\}] = \sum_i \int f_i \psi_i^*(r) (-\nabla^2) \psi_i(r) \, dr \]

\[ + \int \int \frac{n(r)n(r')}{|r-r'|} \, dr \, dr' + E_{zc}[n_1(r), n_2(r)] \]

\[ + \int V_{ion}^L(r)n(r) \, dr + \sum_i \langle \psi_i | \hat{V}_{ion}^{NL} | \psi_i \rangle \]

\[ + \sum_i \sum_{j \neq i} \frac{Z_i Z_f}{|R_i - R_j|}. \]  

(B.2)

Substituting \( \sum_i f_i \psi_i^*(r) \psi_i(r) \) for \( n(r) \) into the Euler-Lagrange equations of motion

\[ \frac{d}{dt} \left( \frac{\delta\mathcal{L}}{\delta \dot{\psi}_i^*} \right) = \frac{\delta\mathcal{L}}{\delta \psi_i^*} \]

and taking the functional derivatives where

\[ \frac{\delta \psi_i^*(r')}{\delta \psi_i^*(r)} = \Omega \delta_{ij} \delta(r - r') \]
yields the electronic equations of motion. In the case of the exchange-correlation we note
\[
\frac{\delta E_{xc}[n(r')]}{\delta \psi_i^*(r)} = \int \frac{\partial e_{xc}[n(r')]}{\partial n_+(r')} \frac{\partial n_+(r')}{\partial \psi_i^*(r)} \, dr' + \frac{\partial e_{xc}[n(r')]}{\partial n_i(r')} \frac{\partial n_i(r')}{\partial \psi_i^*(r)} \, dr'
\]
\[
= \Omega \left[ f_{i+}^{\mu_{xc}} + f_{i-}^{\mu_{xc}} \right] \psi_i(r)
\]
where \( \mu_{xc} \) and \( \mu_{xc} \) are the exchange-correlation potentials defined by Eq. 2.10.

Putting all the terms together and dividing through by \( \mu \Omega f_i \) gives us
\[
\ddot{\psi}_i(r) = \frac{1}{\mu} \left\{ \nabla^2 - V_{\text{ion}}(r) - 2V_H(r) - \left( \frac{f_{i+}}{f_i} \mu_{xc} + \frac{f_{i-}}{f_i} \mu_{xc} \right) \right. \\
- \sum_{\mu} \sum_{lm} V_{i\mu}(r - \mathbf{R}_\mu) < lm | \psi_i(r) - \frac{1}{f_i} \sum_j \lambda_{ij} \psi_j \right\}
\]
where we've defined the Hartree potential
\[
V_H \equiv \int \frac{n(r')}{|r - r'|} \, dr'.
\]
Noting that \( \delta E/\delta \psi_i^* = -\mathcal{H}_{KS} \psi_i \) where \( \mathcal{H}_{KS} \) is the KS-Hamiltonian defined in Eq. 2.9, with the ion potentials cast in the role of the external potential we can express the equations of motion as
\[
\ddot{\psi}_i(r) = \frac{1}{\mu} \left\{ -\mathcal{H}_{KS} \psi_i(r) - \frac{1}{f_i} \sum_j \lambda_{ij} \psi_j \right\}.
\]
Discretizing in time with the Verlet algorithm, we have
\[
\psi_i(t + \Delta t) = -\psi_i(t - \Delta t) + 2\psi_i(t) + \frac{(\Delta t)^2}{\mu} \left( \mathcal{H}_{KS} \psi_i(t) + \sum_j \lambda_{ij} \psi_j(t) \right)
\]
(Equation B.4)

Evolving the system for a time step without imposing the orthonormalization constraint gives us an unconstrained wave function \( \tilde{\psi}_i \), where
\[
\psi_i(t + \Delta t) = \tilde{\psi}_i(t + \Delta t) + \frac{(\Delta t)^2}{\mu} \sum_j \lambda_{ij} \psi_j(t).
\]
Substituting this into the orthonormality condition:

\[ \delta_{ij} = \langle \psi_i(t + \Delta t) | \psi_j(t + \Delta t) \rangle \]

and invoking the orthonormality at the current time step \( t \) gives us the matrix equation

\[ 1 - A = \Lambda \Lambda^\dagger + AB + B^\dagger \Lambda^\dagger \]

where \( 1 \) is the identity matrix, and the matrix elements of \( \Lambda, B, \) and \( A \) are defined as

\[ \Lambda_{ij} \equiv \frac{(\Delta t)^2}{\mu} \lambda_{ij} \]

\[ B_{ij} \equiv \langle \psi_i(t) | \bar{\psi}_j(t + \Delta t) \rangle \]

\[ A_{ij} \equiv \langle \bar{\psi}_i(t + \Delta t) | \bar{\psi}_j(t + \Delta t) \rangle. \]  \hspace{1cm} (B.5)

Solving this equation for \( \Lambda \) and using it to correct the unconstrained wave functions provides us with a method of symmetric orthonormalization in which all of the wavefunctions are treated the same as opposed to the Gram-Schmidt scheme which imposes an order to the orthogonalization, but is independent of the time step. Noting that \( \Lambda \) is hermitian, we have

\[ \Lambda^2 + AB + B^\dagger \Lambda = 1 - A. \]  \hspace{1cm} (B.6)

Considering an element of \( B \), we can expand \( \bar{\psi}_j(t + \Delta t) \), use the time dependent Schrödinger Equation

\[ \mathcal{H} \psi_i = i \frac{\partial \psi_i}{\partial t}, \]
and the hermiticity of $\mathcal{H}$ to estimate $B$'s order in the time step:

$$B_{ij} \approx \left\langle \psi_i(t) \left[ \psi_j(t) + \frac{\partial \psi_j}{\partial t} \Delta t \right] \right\rangle$$

$$= \delta_{ij} + \left\langle \psi_i(t) \left| \frac{\partial \psi_j}{\partial t} \right\rangle \Delta t \right.$$ 

$$= \delta_{ij} + \frac{1}{i} \left\langle \psi_i(t) | \mathcal{H} \psi_j(t) \right\rangle \Delta t$$

So $B \approx 1 + \mathcal{O}(\Delta t)$. Similarly, for $A$ we have

$$A_{ij} = \left\langle \tilde{\psi}_i^*(t + \Delta t) \left| \tilde{\psi}_j(t + \Delta t) \right\rangle \right.$$ 

$$\approx \left\langle \psi_i(t) + \frac{\partial \psi_i}{\partial t} \Delta t \left| \psi_j(t) + \frac{\partial \psi_j}{\partial t} \Delta t \right\rangle \right.$$ 

$$\approx \delta_{ij} + \left[ \left\langle \frac{\partial \psi_i}{\partial t} \left| \psi_j(t) \right\rangle + \left\langle \psi_i(t) \left| \frac{\partial \psi_j}{\partial t} \right\rangle \right\rangle \right] \Delta t + \left\langle \frac{\partial \psi_i}{\partial t} \left| \frac{\partial \psi_j}{\partial t} \right\rangle \Delta t \right.$$ 

and the two middle terms cancel since

$$\left( \frac{\partial}{\partial t} \right)^\dagger = (-i\mathcal{H})^\dagger = -\frac{\partial}{\partial t}$$

leaving us with $A \approx 1 + \mathcal{O}((\Delta t)^2)$. Since $A \approx \mathcal{O}((\Delta t)^2)$, Eq. B.6, to second order in the time step is

$$2\Lambda = 1 - A$$

giving us a first guess for $\Lambda$:

$$\Lambda_0 = \frac{1}{2} (1 - A). \quad (B.7)$$

To obtain an iterative solution for $\Lambda$, let each guess depend on the previous guess as

$$\Lambda_{n+1} = \Lambda_n + \Delta \Lambda$$
and substituting the right hand side of this for $\Lambda$ in Eq. B.6 we have, to leading order in $\Delta \Lambda$

$$\Lambda_n^2 + \Lambda_n B + B^\dagger \Lambda_n + 2\Delta \Lambda = 1 - A$$

Adding and subtracting $2\Lambda_n$ gives

$$\Lambda_n^2 + \Lambda_n B + B^\dagger \Lambda_n + 2\Lambda_{n+1} - 2\Lambda_n = 1 - A$$

and solving for $\Lambda_{n+1}$

$$\Lambda_{n+1} = \frac{1}{2} \left[ 1 - A + \Lambda_n (1 - B) + (1 - B) \Lambda_n - \Delta \Lambda_n^2 \right]$$

which can further be cast into a form more efficient for computation

$$\Lambda_{n+1} = \frac{1}{2} \left[ 1 - A + (1 - B^\dagger)(1 - B) - (1 - B^\dagger - \Lambda_n)(1 - B - \Lambda_n) \right]. \quad (B.8)$$

In this way, one can calculate successively better approximations to the constraint matrix. Convergence to machine accuracy is typically obtained within eight iterations.

Finally, we present the equations of motion and orthonormality conditions in the Fourier space in which they are calculated. Substituting the Fourier expansions of equations 3.4 through 3.7, into Eq. B.3 (leaving out the constraints) yields

$$\sum_G \left\{ \left[ \mu \bar{C}_{i,G} + G^2 C_{i,G} + \frac{1}{\Omega} \sum_{G'} C_{i,G'} \tilde{V}_{\text{eff}}^{N,G'}(G, G') \right] e^{iG \cdot \tau} \right. $$

$$+ C_{i,G} \sum_{G'} \left[ \frac{8\pi}{G^2} \tilde{r}_{G'} + \mu_{sc,G'} + \sum_{\mu=1}^{N_x} \tilde{V}_{\mu,G'} S_{\mu,G'} \right] e^{i(G' + G \cdot \tau)} \left. \right\} = 0 \quad (B.9)$$
where the nonlocal and local parts of the pseudopotential are obtained from Equations C.6 and C.14. The term $\mu_{xc,G'}$ is the Fourier transform of the weighted sum of the potentials $\mu_{xc}$ and $\mu_{xc}$ seen in Eq. B.3. Also, when $G' = 0$ in the summation, the Hartree part $(8\pi n_G / G'^2)$ is omitted, and the local pseudopotential term is replaced by $V_{\mu,0}^L$ defined by Eq. C.7.

Equating components, we get for a given $G$, Eq. 3.8:

\[
\mu \ddot{C}_{i,G} + G^2 C_{i,G} - \sum_j \lambda_{ij} C_{j,G} + \sum_{G'} \tilde{V}_{L_{a-o'}} C_{i,G'} + \frac{1}{\Omega} \sum_{G'} C_{i,G'} \tilde{V}_{eff}^{NL}(G, G') = 0,
\]

and discretizing in time we have

\[
\ddot{C}_{i,G}(t + \Delta t) = \frac{\Delta t^2}{\mu} \left[ -G^2 C_{i,G}(t) - \sum_{G'} \left( \tilde{V}_{L_{a-o'}} + \frac{1}{\Omega} \tilde{V}_{eff}^{NL}(G, G') \right) C_{i,G'}(t) \right]
\]

\[+ 2C_{i,G}(t) - C_{i,G}(t - \Delta t)\]

where $\ddot{C}_{i,G}(t + \Delta t)$ is the unconstrained coefficient at the next time step. We then constrain it as:

\[C_{i,G}(t + \Delta t) = \ddot{C}_{i,G}(t + \Delta t) + \sum_j \lambda_{ij} C_{j,G}(t).\]

Finally, the velocities of the Fourier coefficients are calculated as

\[\dot{C}_{i,G}(t) = \frac{C_{i,G}(t + \Delta t) - C_{i,G}(t - \Delta t)}{2\Delta t}.\]
APPENDIX C

THE PSEUDOPOTENTIAL

The pseudopotential technique offers a way to avoid dealing directly with the core electrons in the ions and concentrate on the valence electrons which are the main participants in chemical bonding. It also eases our dealings with the valence electrons by effectively replacing their wave functions with pseudoatomic wave functions that are smoothed out in the regions of the core electrons, thereby allowing us to escape having to describe the rapidly varying portions of the actual wave functions which would require very large basis sets. The idea evolved from the orthogonalized plane wave (OPW) method in which a basis is constructed out of plane waves that have been made orthogonal to the core states which have been determined from a single atom all-electron calculation. An OPW is therefore a function acting like a plane wave far from the core but is rapidly varying within it, and much fewer OPW's were needed to describe the valence state. In the pseudopotential method, the valence state is modified by removing the wiggles that make it orthogonal to the core states, resulting in a pseudoatomic wave function. Substitution of this pseudoatomic wave function into the Schroedinger equation results in a pseudo-Hamiltonian, characterized by a pseudopotential.

Pseudopotentials have been constructed in numerous different ways. Some are empirical, being fitted to experimental results, others are ab-initio, based on all-electron calculations as mentioned above. They differ in their transferability properties, that is, a pseudopotential fitted to experimental work in a bulk crystal may not work well in the atomic or cluster environment, while one derived from the atomic case may fail when applied to chemical or
crystalline environments. In general, the shorter the core radius, beyond which the pseudoatomic wave function is the same as the actual wave function, the more transferable the pseudopotential will be.

C.1 The BHS Pseudopotential

In this work we use a pseudopotential constructed by Bachelet, Hamann, and Schluter (BHS) [64]. It is norm-conserving, in that the correct electron density is produced outside the core region and semilocal, being nonlocal in the angular coordinates and local in the radial coordinate. Parameters governing it have been worked out for elements from H to Pu. While construction of pseudopotentials is beyond the scope of this work, we will briefly describe the BHS construction to illustrate the issues involved. To arrive at their pseudopotentials, BHS solve the Dirac equations in radial form for a chosen reference state of the atom (s,p,d, or f) using density functional theory and the local density approximation according to Ceperley-Alder [42] as parametrized by Perdew and Zunger [41]. From this, they obtain the self-consistent potential and the major radial all-electron wave function. The obtained potential is then modified to remove the singularity at the nucleus, to vanish at \( \infty \), and to reproduce the all-electron eigenvalue for the lowest lying state from the radial Schroedinger equation (deemed adequate outside the core region). This modification incorporates the choice of the core radius which is chosen as some fraction of the distance to the outermost peak of the all-electron wave function. The resulting radial wave function is then modified appropriately for norm conservation, referring to the corresponding all-electron wave function. Using this new wave function the radial Schroedinger equation is inverted to produce yet another potential which is then modified.
a final time to remove screening effects that were sustained from the other occupied valence states and from the exchange-correlation energy.

The final form of the potential is split into long-range Coulomb (local) and short-range $\ell$-dependent (nonlocal) parts as:

\[
V^{L}_{\text{ion}}(r) = -\frac{Z}{r}\left[\sum_{i=1}^{2} c_i \Phi \left[(\alpha_i)^{1/2} r\right]\right] \tag{C.1}
\]

and

\[
V^{NL}_{\text{eff}}(r) = \sum_{i=1}^{3} (A_i + r^2 A_{i+3}) e^{-\alpha_i r^2} \tag{C.2}
\]

where $\Phi$ is the error function and the $\{\alpha_i\}$ and $\{c_i\}$ are tabulated for the various elements with $c_1$ and $c_2$ always summing to 1. The coefficients $\{A_i\}$ are rather large and must be used with too many significant digits to be practically tabulated, so BHS instead tabulate another set of coefficients $\{C_i\}$, providing an orthogonal transformation which must be inverted to obtain the $\{A_i\}$. Equations C.1 and C.2 are analytically Fourier transformable so that their matrix elements in plane wave basis can be coded directly.

Plots of the BHS pseudopotential are shown in Figure C.1 for beryllium, lithium, and aluminum.

C.2 Application of the Pseudopotential

We now discuss the incorporation of the pseudopotential into our problem, calculating the energies and forces arising from its use\(^1\).

C.2.1 Local Contribution

The energy due to the local part of the pseudopotential is

\[
E_{\text{loc}} = \sum_{\mu=1}^{N_{\mu}} \sum_{l=1}^{N_{l}} \int_{\Omega} V^{L}_{\mu,l}(r - \mathbf{R}_{\mu,l}) n_\mu(r) \, dr
\]

\(^1\)units are in Hartrees.
Figure C.1: Total pseudopotential and local contribution plotted together and nonlocal (\( \ell \)-dependent) components of the pseudopotential plotted together for beryllium, lithium, and aluminum. Calculated from reference [64].
where the \( \mu \) refers to the species, \( N_s \) the number of species, \( \mathbf{R}_{\mu,I} \), the position of the \( I^{th} \) ion of species \( \mu \), and \( N_\mu \), the number of ions in species \( \mu \). Expanding the potential over plane waves:

\[
V^L_\mu (\mathbf{r} - \mathbf{R}_{\mu,I}) = \sum_{\mathbf{G}} \tilde{V}^L_{\mu,G} e^{i\mathbf{G} \cdot (\mathbf{r} - \mathbf{R}_{\mu,I})} \tag{C.3}
\]

and substituting into the equation for \( E_{loc} \) gives us

\[
E_{loc} = \Omega \sum_{\mathbf{G}} \left( \sum_{\mu=1}^{N_s} \tilde{V}^L_{\mu,G} S_{\mu,G} \right) \tilde{n}_G \tag{C.4}
\]

where

\[
\tilde{V}^L_{\mu,G} = \frac{1}{\Omega} \int_{\Omega} V^L_\mu (\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} \, d\mathbf{r}
\]

and the local structure factor for each species is

\[
S_{\mu,G} \equiv \sum_{I=1}^{N_\mu} e^{-i\mathbf{G} \cdot \mathbf{R}_{\mu,I}}. \tag{C.5}
\]

The resulting contribution to the equations of motion B.9 is

\[
\frac{\delta E_{loc}}{\delta \psi_i^*} = f_i \Omega \sum_{\mu=1}^{N_s} \sum_{l=1}^{N_\mu} V^L_\mu (\mathbf{r} - \mathbf{R}_{\mu,I}) \psi_l (\mathbf{r})
\]

\[
= f_i \Omega^{1/2} \sum_{\mu=1}^{N_s} \left[ \sum_{G'} \tilde{V}^L_{\mu,G'} S_{\mu,G'} e^{i\mathbf{G'} \cdot \mathbf{r}} \right] \sum_{G} C_{l,G} e^{i\mathbf{G} \cdot \mathbf{r}} \tag{C.6}
\]

where we recall that \( n(\mathbf{r}) = \sum f_i \psi_i \psi_i \). We need to omit the diverging Coulomb contribution from this potential at the \( \mathbf{G} = \mathbf{0} \) point, but we must retain the finite portion. Taking the Fourier transform of Equation C.1 with \( \mathbf{G} \) chosen along the \( z \)-axis:

\[
\tilde{V}^L_{\mu,G} = \frac{1}{\Omega} \int_{\Omega} V^L_\mu (\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} \, d\mathbf{r}
\]

\[
= \frac{2\pi}{\Omega} \int_0^\infty V^L_\mu (\mathbf{r}) \int_{-1}^1 e^{-iGr^2} r \, dr \, dx
\]

\[
= \frac{-2\pi Z i}{\sqrt{\pi \Omega G}} \int_0^\infty \left[ \sum_{l=1}^{2} c_l \int_0^{\sqrt{Gr}} e^{-t^2} \, dt \right] (e^{-iGr} - e^{iGr}) \, dr.
\]

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Let
\[ I = \int_0^\infty dr \int_0^{\sqrt{\alpha}r} e^{-t^2} dt \left( e^{-iGr} - e^{iGr} \right) \]
\[ = 2i \Im \left[ \int_0^\infty dr e^{-iGr} \int_0^{\sqrt{\alpha}r} e^{-t^2} dt \right] \]
\[ = \frac{2i}{\sqrt{\alpha}} \Im \left[ \int_0^\infty dr' e^{-iGr'/\sqrt{\alpha}} \int_0^{r'} e^{-t^2} dt \right] \]
\[ = \frac{2i}{\sqrt{\alpha}} \Im \left[ \int_0^\infty dt e^{-t^2} \int_0^\infty dr' e^{-Gr'/\sqrt{\alpha}} \right] \]
where we've defined \( r' = \sqrt{\alpha}r \) and changed the order and appropriately, the limits on the integration. Integrating over \( r' \) leaves us with a stereotypic contour integral:
\[ I = \frac{-2i}{G} e^{-G^2/4\alpha} \Im \left[ i \int_0^\infty e^{-(t+iG/2\sqrt{\alpha})^2} dt \right] \]
\[ = \frac{-\sqrt{\pi} e^{-G^2/4\alpha}}{G} i \]
So
\[ V_{\mu,G}^L = \frac{-2\pi Z}{\Omega G^2} \left( c_1 e^{-G^2/4\alpha_1} + c_2 e^{-G^2/4\alpha_2} \right) \]
and in the limit of \( G \to 0 \), we have:
\[ V_{\mu,0}^L = \lim_{G \to 0} \left[ \frac{-2\pi Z}{\Omega G^2} \left( c_1 \left( 1 - \frac{G^2}{4\alpha_1} \right) + c_2 \left( 1 - \frac{G^2}{4\alpha_2} \right) \right) \right] \]
\[ = \frac{\pi Z}{2\Omega} \left( \frac{c_1}{\alpha_1} + \frac{c_2}{\alpha_2} \right) - \lim_{G \to 0} \frac{2\pi Z}{\Omega G^2} \]
where it will be remembered that BHS have constructed their parameters such that \( c_1 + c_2 = 1 \). The last term is the attractive diverging Coulomb
term to be subtracted out, leaving us with
\[ V_{\mu,0}^L = \left[ \frac{\pi Z}{2\Omega} \left( \frac{c_1}{\alpha_1} + \frac{c_2}{\alpha_2} \right) \right]_\mu \] \quad (C.7)
as the local contribution at the $G = 0$ point.

### C.2.2 Nonlocal Contribution

The $\ell$-dependent pseudopotential acts on orbitals of definite $\ell$-states so the plane waves over which the KS-orbitals are expanded must in turn be expanded over products of spherical Bessel functions and spherical harmonics.

The energy is
\[ E_{NL} = \sum_{\mu=1}^{N_s} \sum_{\ell=1}^{N_\mu} f_\ell \sum_i \int_\Omega \psi_i^*(r)V_{\mu,\ell}^N L(r - R_{\mu,i})\hat{P}_\ell \psi_i(r) \, dr \]
where $\hat{P}_\ell$ is the projection operator:
\[ \hat{P}_\ell = \sum_m |\ell m><\ell m|. \]

Substituting
\[ \psi_i = \frac{1}{\sqrt{\Omega}} \sum_G C_{i,G} e^{i G \cdot r} \]
and making a variable change of $r' \equiv r - R_{\mu,i}$ we have
\[ E_{NL} = \frac{1}{\Omega} \sum_i f_i \sum_G \sum_{G'} C_{i,G}^* C_{i,G'} \sum_{\mu=1}^{N_s} [S_\mu(G - G')] \left[ \tilde{V}_{\mu,\ell}^NL(G, G') \right] \quad (C.8) \]
where we've defined a nonlocal structure factor for each species
\[ S_\mu(G - G') \equiv \sum_{I=1}^{N_s} e^{-i(G - G') \cdot R_{\mu,I}} \quad (C.9) \]
and the matrix element of the nonlocal potential for each species/$\ell$ combination
\[ \tilde{V}_{\mu,\ell}^NL(G, G') \equiv \int_\Omega e^{-iG \cdot r} V_{\mu,\ell}^NL(r)\hat{P}_\ell e^{i G \cdot r} \, dr. \quad (C.10) \]
Substituting expansions of the plane waves over products of spherical bessel functions and Legendre polynomials, that is,

\[ e^{i\mathbf{G} \cdot \mathbf{r}} = \sum_{\ell=0}^{\infty} (-i)^{\ell}(2\ell + 1)j_{\ell}(Gr)P_{\ell}(\cos \alpha) \]

gives us

\[ \hat{V}^{NL}_{\mu,\ell}(G, G') = (2\ell + 1)(2\ell' + 1) \sum_{\ell''} \sum_{\ell'''}(-i)^{\ell'}(i)^{\ell''} \]

\[ \times \int_{r} j_{\ell}(Gr)j_{\ell'}(G'\mathbf{r})V_{\mu,\ell}^{NL}(r)r^2 \, dr \]

\[ \times \int_{\Omega} P_{\ell}(\cos \alpha)\hat{P}_{\ell}P_{\ell'}(\cos \alpha') \, d\Omega \]

where \( \alpha \) and \( (\alpha') \) are the angles between \( \mathbf{r} \) and \( \mathbf{G} \) (and \( \mathbf{G}' \)). Using the spherical harmonic addition theorem

\[ P_{\ell}(\cos \alpha) = \frac{4\pi}{2\ell + 1} \sum_{m} Y_{\ell m}(\theta_G, \phi_G)Y_{\ell m}^{*}(\theta, \phi) \]

\[ = \frac{4\pi}{2\ell + 1} \sum_{m} Y_{\ell m}(\theta_G, \phi_G) < \ell m| \]

where \( \theta_G, \phi_G \) are the angles specifying the direction of \( \mathbf{G} \), we can replace the Legendre polynomials in the angular part of the integral, giving us (where we have operated with \( \hat{P}_{\ell} \))

\[ \left( \frac{4\pi}{2\ell + 1} \right)^2 \sum_{m} Y_{\ell m}(\theta_G, \phi_G)Y_{\ell m}^{*}(\theta_G', \phi_G')\delta_{\ell\ell'}\delta_{m'\ell}\delta_{m''m'} \]

\[ = \frac{4\pi}{2\ell + 1} P_{\ell}(\cos \gamma)\delta_{\ell\ell'}\delta_{m'\ell}\delta_{m''m'} \]

where \( \gamma \) is the angle between \( \mathbf{G} \) and \( \mathbf{G}' \), and where we have used the addition theorem in reverse. This gives us, for the matrix element

\[ \hat{V}^{NL}_{\mu,\ell}(G, G') = 4\pi(2\ell + 1) \]

\[ \times \int j_{\ell}(Gr)j_{\ell}(G'\mathbf{r})V_{\mu,\ell}^{NL}(r)r^2 \, dr P_{\ell}(\cos \gamma) \quad (C.11) \]
and the energy is then

\[ E_{NL} = \frac{1}{\Omega} \sum_i f_i \sum_G \sum_G' C_{i,G}^* C_{i,G'} \tilde{V}_{eff}^{NL}(G, G') \]  \hspace{1cm} (C.12)

where \( \tilde{V}_{eff}^{NL}(G, G') \) is the total effective nonlocal potential modified by the structure factor:

\[ \tilde{V}_{eff}^{NL}(G, G') \equiv \sum_{\mu=1}^{N_x} [S_{\mu}(G - G')] [\tilde{V}^{NL}_{\mu,L}(G, G')] . \]  \hspace{1cm} (C.13)

To obtain the contributions to the equations of motion, just substitute for \( C^*_{i,G} \) in Equation C.12 with

\[ C^*_{i,G} = \frac{1}{\sqrt{\Omega}} \int_\Omega \psi_i^*(r) e^{i\mathbf{G} \cdot \mathbf{r}} \, d\mathbf{r} \]

and

\[ \frac{\delta E_{NL}}{\delta \psi_i^*(r)} = \frac{1}{\sqrt{\Omega}} \sum_i f_i \sum_L C_{i,G} \tilde{V}_{eff}^{NL}(G, G') e^{i\mathbf{G} \cdot \mathbf{r}}. \]  \hspace{1cm} (C.14)

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VITA

Andrew Marc Kolchin graduated from the State University of New York at Stony Brook in May 1982 receiving bachelor's degrees in physics and in mechanical engineering. He worked for some years as a process engineer in various phases of electronic packaging and metal deposition first at Hughes Aircraft Corp. in Tucson and then at Action Technologies in Boulder before beginning his graduate work at Louisiana State University.

In 1994, he received a master's degree in physics. In 1998, he earned a master's degree in systems science, developing codes to set up scenes consisting of hierarchical models with realistic rendering via recursive ray-tracing. He will receive the doctoral degree in physics in August 2000 for which he has developed codes to optimize the atomic and electronic structures of material systems. His main interests include electronic structure, optimization problems, and algorithms for realistic rendering and animation in computer graphics. He is a member of the American Physical Society and the Association for Computing Machinery (SIGGRAPH).
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Title of Dissertation: Atomic and Electronic Properties of Neutral and Cationic Metallic Clusters

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