ATOMIC FACTORIZATION OF MOLECULAR INTERACTIONS

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Atomic Factorization of Molecular Interactions

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DEDICATION

To Robby, the laws of gravity cannot be held responsible.
To my father - Carl, my mother - Cheri, and my brother - Sean
for unfaltering love and support.
To atoms and the principles of physics,
without which this thesis would not exist.
Your mind is always occupied on something...

so it may as well be something helpful, like Mrs. Shermer, or the blanket.

–Bernard Jaffe
ABSTRACT OF THE THESIS

Atomic Factorization of Molecular Interactions
by
Julia Michelle Rossi
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The long-range dispersion interaction, or London dispersion potential, $C_6/R^6$ is numerically computed using factorized expressions relying only on the dynamic polarizabilities of the individual atoms at imaginary frequencies. The derived expressions are shown to independently agree with an alternative derivation. The dynamic dipole polarizabilities, evaluated at imaginary frequencies, are tabulated for hydrogen and lithium atoms to be used in the $C_6$ factorized expressions (which are numerically integrated by Gaussian quadrature method). This method yields $C_6$ dispersion coefficients in agreement with the latest theoretical values for the homo-nuclear atom interactions of H-H and Li-Li configurations and the hetero-nuclear interaction Li($2^2S$)-H($1^2S$). Higher energy hetero-nuclear dispersion coefficients appear to diverge from previous theoretical values possibly limiting the applicability of the current methodology. The dynamic dipole polarizabilities for the Li atom in the $2^2S$, $2^2P$, and $3^2S$ states were additionally calculated from a large basis configuration interaction calculation, encompassing frequency ranges into the positive energy continuum.
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CHAPTER 1

INTRODUCTION

The fields of ultracold atomic, molecular, and optical physics have created the new sub-field of “ultracold chemistry” comprised of new experimental techniques to measure and control molecules to amazing precision. These types of experiments are now demanding precise calculations of molecular bonding and atomic structure.

This thesis firstly aims to evaluate the atomic structure of the Li atoms, specifically, by performing calculations for the dynamic polarizabilities evaluated at real frequencies which describes the change in the energy of the atom in an electric field. The dynamic polarizability, as a function of frequency, gives insight into the varying Rydberg states of the Li atom, as well as, the specific required frequency shifts necessary for particular transitions. Specifically, the energy required to transition between the $2S$ and $3S$ Rydberg states of the Li atom is evaluated. This was motivated by recent experiments on the properties of Li $2S \rightarrow 3S$ transition.\(^1\)

For the purposes of cold atom physics, the lithium atom is advantageous to use because it only has three electrons, only one of which is a valence electron. This allows the use of a simplified atomic model system dependent on the single valence electron rather than the full three electron problem. Consequently, the calculations can be run to very high precision.\(^2\)–\(^5\) The present calculations of the dynamic polarizability, $\alpha$, for Li are based on a solution to the Schrödinger equation and are obtained at real and imaginary frequencies. The computations for real frequencies are used to validate the results against published calculations while the computations for imaginary frequencies are saved for use later in the thesis.

This thesis’ main aim is to study the interaction potentials between alkali-metal atoms interacting with atomic hydrogen. With the growing interest in ultracold chemistry, it is important to define the interaction potentials involving alkali-metal atoms which are the most controllable. The interaction potential is described by the London, or van der Waals, potential between two spherical atoms,

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots .$$  \(^{(1)}\)
The London dispersion coefficient, $C_6$, between two atoms at large separations can be factorized into the properties of the individual atoms. There are two main ways to compute $C_6$: with sum rules using either oscillator strengths $f^{k}_{ij}$, or dynamic polarizabilities $\alpha^{n}_D$ evaluated at imaginary frequencies.\(^7\) Respectively,

\[
f^{k}_{ij} = \frac{2|D^{k}_{ij}|^2 \epsilon_{ji}}{(2k + 1)(2L_i + 1)}, \tag{2}
\]

\[
\alpha^{n}_D(i\omega) = \sum_{i} \frac{f^{0i}_{0j}}{\omega_i^2 + \omega^2}, \tag{3}
\]

in which the sum rules require transition energies $\epsilon_{ji} = (E_j - E_i)$ and the $k$th multipole transition matrix element $D^{k}_{ij} = \langle \psi_i; L_i || r^k C^k(\hat{r}) || \psi_j; L_j \rangle$.

Extensive work by\(^8,^9\) to solve $C_6$ rely on second, third, and fourth-order sum rules. Out of these sum rules, the dispersion coefficient for long-range interactions is produced based on the equations:

\[
C_6 = \sum_{L_i, L_j} \frac{4!}{2L_i!2L_j!} \sum_{i,j} \int f^{L_i}_{0i} f^{L_j}_{0j} \epsilon_{0i} \epsilon_{0j} (\epsilon_{ij} + \epsilon_{0i}) \equiv \frac{3}{\pi} \int_0^\infty \alpha^{n}_D(i\omega) \alpha^{m}_D(i\omega) d\omega. \tag{4}
\]

This section of the thesis is aimed at the computation of the dispersion coefficients, particularly the interactions between the Li and H in their ground and excited $S$, $P$, and $D$-states. Instead of using oscillator strengths, the integral relationship by Casimir-Polder\(^10\) is used to redefine these sum rules in terms of $\alpha_D$, and the tensor polarizability $\alpha_T$, at imaginary frequencies, $i\omega$.

The remainder of this introduction serves to give the reader a brief history of the study of intra-molecular forces and interactions, as well as theories regarding atomic structure and inter-molecular interactions. The following chapter will first describe the theoretical aspects of calculating dynamic polarizabilities and second the atomic structure of Li in regards to Rydberg states. The third chapter derives the dynamic dipole polarizabilities and dispersion forces based on perturbation theory and the computational methods used for evaluation and validation. The fourth chapter derives $C_6$ in terms of the integral relationship developed by Casimir-Polder and dynamic dipole polarizabilities, followed by resulting computational methods for numerical integration. The fifth chapter expands the theory to include inter-molecular LiH dispersion coefficients in ground and various excited states. The sixth chapter concludes this work.
A BRIEF HISTORY OF THE THEORY OF INTER-MOLECULAR FORCES

Fritz London was one of the founding physicists responsible for the application of quantum mechanical theory to inter-molecular forces, and chemistry. Surprisingly, London first studied and worked in philosophy until 1925 when he moved to Munich to study physics with Sommerfeld. Later, in 1927, he moved to Zurich and met Walter Heitler, an unplanned coincidence that would lead to the publication on the interaction between neutral atoms and homo-polar bonds. Initially, London and Heitler aimed to calculate the interaction of the charges of two atoms (atom \( a \) and atom \( b \)). Their first results relied heavily on the attraction of two atoms due to the “Coulomb integral” which was too small a value to account for a homo-polar bond between two hydrogen atoms. The two electrons in a homo-polar bond are identical for the two atoms; therefore, the total wave function of the system can be written as the linear combination of the wave functions:

\[
\Psi = c_1 \psi_a(1) \psi_b(2) + c_2 \psi_a(2) \psi_b(1). \tag{5}
\]

To calculate \( c_1 \) and \( c_2 \), they minimized the energy

\[
E_0 = \frac{\int \Psi H \Psi d\tau}{\int \Psi^2 d\tau}, \tag{6}
\]

finding two solutions where \( \frac{c_1}{c_2} = 1 \) and \( \frac{c_1}{c_2} = -1 \) for the energy equations \( E_1 \) and \( E_2 \), respectively:

\[
E_1 = 2E_0 + \frac{C + A}{1 + S_{12}} \tag{7}
\]
\[
E_2 = 2E_0 + \frac{C - A}{1 - S_{12}} \tag{8}
\]

where the \( C \) is the Coulomb integral and \( A \) is the exchange integral. The implication of these two energy equations are wave functions of the form:

\[
\Psi_1 = \psi_a(1) \psi_b(2) + \psi_a(2) \psi_b(1) \tag{9}
\]
\[
\Psi_2 = \psi_a(1) \psi_b(2) - \psi_a(2) \psi_b(1). \tag{10}
\]

These spatial wave functions imply that \( \Psi_1 \) is the case where the electrons have anti-parallel spins (i.e. spin-singlet), corresponding to \( E_1 \), less than \( 2E_0 \), the sum of the energies of the separate hydrogen atoms, signifying attraction. The \( \Psi_2 \) represents the symmetrical
combination (spin-triplet) corresponding to $E_2$, which is greater than $2E_0$, and thus signifying repulsion.

London and Heitler recognized that the binding mechanism between two neutral hydrogen atoms relied on the pairing of electrons in an antiparallel orientation. Therefore, to form an electron pair, it was not sufficient to just have energetically available electrons, but it was necessary for the electrons to have the correct spin orientations. Heitler and London concluded homo-polar bonding was a purely quantum effect dependent on electron spin. In reaction to the publication of the Heitler-London paper, they initiated a discourse on molecular interactions and effectively founded the discipline of quantum chemistry.

**INTER-MOLECULAR FORCES**

In 1930, London drew his attention to the attractive forces between molecules in order to untangle the issues associated with the results of Debye and Keesom. The London dispersion forces, proportional to $r^{-7}$, bear his name and are the first to provide a quantum mechanical treatment of long-range attractive forces, also referred to as van der Waals forces, or induced dipole-dipole forces. At the end of the eighteenth century the van der Waals forces were originally discussed to solve the problem of capillary action. Laplace was the first to postulate that capillary action is a phenomena due to the surface tension measured as a function of the short range forces between molecules.

By 1873, van der Waals had systematically treated these forces due to an attractive long-range force despite the short-range repulsive forces. Based on the Lennard-Jones treatment of these forces, London proposed a formula for the total force that depended on the inter-molecular distance:

$$F = Ar^{-n} - Br^{-m},$$

where the first term represents the repulsive forces and the second term represents the attractive forces, demanding $n > m$.

The foundation of London’s work in the 1930s involved examining the effects of molecular dipole moments and the theories of Keesom and Debye circa 1921 and 1912, respectively. Keesom found a formula which had a distance dependence as well as an inverse of temperature dependence that arose from the thermal motion in which two molecules with permanent dipole moments develop a non-trivial attractive force. Debye calculated the force caused by induction dependent on the polarizability of the two molecules. Both explanations
relied on at least one of the interacting pair of molecules possessing a permanent dipole moment; however, not all molecules have such moments. Furthermore, van der Waals forces are additive, in that, the force between a pair of molecules is relatively unaffected by the presence of a third molecule. The alignment forces presented by Keesom, and the induction forces by Debye, are unable to express this property present in van der Waals forces.\textsuperscript{11}

London began his criticism of their theories by analyzing how electrons’ continuous motion creates a rapidly fluctuating dipole moment due to the uncertainty principle.\textsuperscript{13} Molecules lacking permanent dipoles are able to acquire an instantaneous dipole which induces an other instantaneous dipole in another molecule. London was able to show that this particular induction force, conditioned by the quantum mechanical behavior of electrons led to long-range additive attractive forces.\textsuperscript{14,15}

He calculated a second-order perturbation theory based term giving rise to a $r^{-6}$ energy dependence, for which London coined the term ”dispersion forces.” The term dispersion force arose due to the perturbation theory based terms expressed by the same oscillator strengths as those that appeared in equations for light dispersion, which will be discussed further shortly. Dispersion forces were independent of temperature giving meaningful understanding to the behavior of molecules at low temperatures. Eisenchitz and London published a paper concerning the possibility of resonance between two molecules when an energy quanta could be emitted by one and absorbed by the other.\textsuperscript{13}

A contemporary of London, Henry Margenau, remarks on his time at the Institute for Theoretical Physics at the University of Berlin with the Sterling fellowship, “My work in Berlin was dominated almost entirely by the genius of Fritz London, who had just published a first paper on the quantum theory of van der Waals forces. Realizing that the best way to learn quantum mechanics was to apply it, I extended London’s work”.\textsuperscript{11} So, this thesis now begins, as both an application of quantum mechanics and an extension of London’s dispersion forces.

**Intra-molecular Interactions**

Intra-molecular interactions and forces hold together the atoms making up a molecule or compound. There are three main types of intramolecular forces: ionic, covalent, and metallic. An ionic bond is formed by an electrostatic attraction between two oppositely charged ions while a covalent bond is a chemical bond formed by the sharing of pairs of electrons between atoms. Metallic bonds are formed between delocalized electrons through
electromagnetic interactions. Intra-molecular forces keep a molecule together while inter-molecular forces act between two molecules; therefore, this thesis focuses on inter-molecular interactions due to the instantaneous dipole-induced dipole forces e.g. London dispersion forces.

**Inter-molecular Interactions**

The interaction between molecules is due to repulsion and attraction, arising ultimately from the electrostatic interaction between the constituent particles of the two molecules. The interactions are separable into two categories: “long-range” and “short-range.” The long-range forces arise from electrostatic, induction, and dispersion forces. The electrostatic interaction arising from the static charge distributions of the two molecules are either attractive or repulsive. The induced dipole force occurs due to induction (polarization) from the attractive interaction of a permanent multipole with an induced multipole. The charge distributions of the molecules are always fluctuating as the electrons move, creating correlated motion of electrons in interacting molecules, which form instantaneous dipoles that attract each other known as dispersion forces.

The term “long-ranged” potential is generally used for potentials vanishing as a power of the distance. The values of the London dispersion coefficients $C_{2l+2}$ describe the multipolar interaction of atomic and molecular species. At large distances compared to the size of the atomic particles, the electrostatic interaction potential reduces to the interactions of their multipole moments. The primary focus of this research is to develop calculations of the long-range interactions between two hetero-nuclear atoms in arbitrary atomic states. The long-range interaction potential for two spherically symmetric atoms is called the London dispersion potential (i.e. $C_6$).

The term “short-ranged” potential refers to the distance $R$ between the nuclei when the electron shells overlap. The resulting intra-molecular forces are electrostatic in nature and increase sharply as distance decreases between atoms. A simple approximation formula for the repulsive interaction between atomic and molecular species has an exponential dependence: $A e^{-\beta r}$, in which the parameters $A$ and $\beta$ vary within the range of inter-molecular distance $\Delta R$. The representation assumes the logarithmic derivative of the potential $U$ as $\beta = d\ln U / dR$ is constant within the $\Delta R$ range. This short-ranged, repulsive exchange energy potential between two neutral (spherical) atoms is sometimes parameterized as a
Lennard-Jones potential, \( V(r) = \frac{C_{12}}{r^{12}} - \frac{C_{6}}{r^{6}} \), where the \( r^{12} \) term describes the Pauli repulsion at short range due to overlapping orbitals, and \( C_{12} \) is empirically fitted to experimental spectrum. See Figure 1 for a graphic representing the net potential energy between the attractive dispersion potential and the repulsive potential.\(^{17}\)

In the limit of \( |\vec{R}| \gg a_0 \), the long-range dispersion interaction operator can be formally expanded in a power series of \( R^{-1} \):\(^{18,20}\)

\[
V(\mathbf{R}) = \sum_{k=1}^{\infty} \sum_{k'=1}^{\infty} \frac{v_{kk'}(\hat{n})}{R^{k+k'+1}},
\]

where the operator

\[
v_{kk'}(\hat{n}) = (-1)^{k'} \left[ \frac{(2K)!}{(2k)!(2k')!} \right]^{1/2} (C^K(\hat{n}) \cdot [\mathbf{Q}^k(\mathbf{r}_a) \times \mathbf{Q}^{k'}(\mathbf{r}_b)])^K),
\]

in which \( K = k + k' \), \( \mathbf{Q}^k(\mathbf{r}) = r^k C^k(\hat{r}) \) is the operator of the multipole \((2^k\text{-pole})\) electric moment, and \( \hat{n} = \mathbf{R}/R \) in the unit vector pointing from atom (a) to a second atom (b).

The general expression for the long-range interaction between two atoms contains first-, second-, and higher-order perturbation theory based terms, written as

\[
V(R) = -\sum_{s=1}^{\infty} \frac{C_{2s+4}}{R^{2s+4}} - \sum_{s=1}^{L_a+L_b-1} \frac{C_{2s+3}}{R^{2s+3}}
\]

The dispersion coefficients are given by the \( C_n \) parameters while \( R \) is the distance between the two nuclei. The first summation is due to second-order perturbation theory, whereas the second summation is a result of the first-order interaction between two atoms. The first-order perturbation arises between two atomic states if their angular momentum is nonzero. The second summation has a finite number of terms dependent on the angular momentum on the individual atoms, \( a \) and \( b \), expressed in terms of \( L_a \) and \( L_b \), respectively.

The \( C_6 \) dispersion coefficient describes the interaction of the ionic charge \( Z e \) with the quadrupole moment of an atom and the induced dipole-dipole moments of the particles in second-order perturbation theory. Equation 1 is an averaged potential over all possible orientations of the angular momenta of the particles. The higher-order dispersion coefficients, \( C_8 \) and \( C_{10} \) represent the interactions between induced dipole-quadrupole moments, two induced quadrupole moments, and induced dipole moment with an induced octupole moment, and so on. These higher-order terms are not explored in this thesis.
Figure 1. Example intra/inter-molecular potential energy interaction graph as a function of the separation distance between atoms in units of Bohr radius ($a_0$). Non-covalent forces between two atoms, A and B, are commonly characterized in the form of the Lennard-Jones 6,12 potential, representing the energy of the van der Waals interaction between two non-polar species. The weakest type of van der Waals interaction is between spontaneously induced dipoles known as London dispersion forces. The repulsive, exchange energy is included in the Lennard-Jones potential, $V(r) = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6}$, where the $r^{12}$ term describes the Pauli repulsion at short range due to overlapping orbitals. The attractive, $r^0$ term describes the long-range dipole-dipole interactions between atoms, known as the London dispersion forces. The dispersion coefficients are calculated by second order perturbation theory and the $C_{12}$ coefficient is approximated by best fit to experimental data. Source: Prof. J.D. Cronk, Van der Waals Potential Energy, Biochemistry Dictionary, Gonzaga University.
Oscillator Strengths and Sum Rules

Eisenschitz and London\textsuperscript{13} and London\textsuperscript{14, 15} recognized the physical origin and significance of long-range interactions between atoms. They illustrated how the first term in the series, proportional to $R^{-6}$, may be expressed in terms of the dispersion $f$-values and coined the name “dispersion forces” for these interactions. Oscillator strengths or $f$-values concern the intensity of spectral transitions obtainable through experimental techniques. Oscillator strengths are a function of the atomic transition between states dependent on the change in energy between the states.\textsuperscript{7} Spontaneous emission probability per unit time for the transition from an upper state $j$ to the lower state $i$ is given by the Einstein coefficient

$$A_{ji} = \frac{4e^2\omega_{ij}^3}{3hc^3(2L_j + 1)} \cdot |\langle i | D | j \rangle|^2,$$

where the emitted photon has a frequency of $\omega_{ij} = (E_j - E_i)/h = \Delta E_{ji}/h$ and $\langle i | D | j \rangle$ is the matrix element of the atomic dipole operator. $L_j$ is the total electronic angular momentum of the $j$-state atom.

The absorption oscillator strength $f_{ij}(i \rightarrow j)$ is a dimensionless value which can be defined either in terms of frequency and transition matrices or as a function of $A_{ij}$.\textsuperscript{16}

$$f_{ij} = \frac{2m_e}{3h} \cdot \frac{\omega_{ij}}{(2L_i + 1)} |\langle i | D | j \rangle|^2 = \frac{m_ec^3}{2e^2\omega_{ij}^2} \cdot \frac{(2L_j + 1)}{(2L_i + 1)} A_{ji},$$

where $L_i$ is the total angular momentum of an atom in state $i$.\textsuperscript{16} In atomic units, the dipole ($k = 1$), quadrupole ($k = 2$), and octupole ($k = 3$) oscillator strengths $f_{0i}^{(k)}$ from the ground state to the $i$th excited state are defined as

$$f_{0i}^{(k)} = \frac{2|\langle \psi_0; L_0 || r^k C^k(r) || \psi_i; L_i \rangle|^2 \Delta E_{i0}}{(2k + 1)(2L_0 + 1)}$$

where the excitation energy is $\Delta E_{i0} = E_i - E_0$, $C^k$ is the spherical tensor of rank $k$.

The Thomas-Reiche-Kuhn sum rule of these dimensionless oscillator strengths for $k = 1$ only gives the number of atomic electrons, $N_e$, of the form (for the general form see Appendix A)

$$N_e = \sum_i f_{0i}^{(1)}.$$


LONG-RANGE FORCES

Inter-molecular interactions require the presence of a static multipole in at least one of the atoms. The simplest case of an atom in the \( S \)-state has a spherical charge distribution which is not at rest due to the uncertainty principle. This random motion creates instantaneous multipoles and rapidly fluctuating fields that polarize the other molecules, creating attractive forces. The theory of long-range forces can be understood by perturbation theory, specifically second order perturbation.

The sum rule for the adiabatic multipole polarizability, \( \alpha^{(k)} \) is

\[
\alpha^{(k)}(\omega = 0) = \sum_i \frac{f^{(k)}_{0i}}{\varepsilon_{0i}^2},
\]

where \( \varepsilon_{0i} = E_0 - E_i \). The frequency-dependent polarizability of an atom when \( \omega = \varepsilon_{0i} \) and \( \hbar = 1 \) is

\[
\alpha_D^n(\omega) = \sum_i \frac{f^{(1)}_{0i}}{\varepsilon_{0i}^2 - \omega^2},
\]

whereas, the imaginary polarizabilities, with \( \omega = i\omega \) are

\[
\alpha_D^n(i\omega) = \sum_i \frac{f^{(1)}_{0i}}{\varepsilon_{0i}^2 + \omega^2}.
\]

The dipole-dipole dispersion coefficient \( C_6 \) can be expressed either in terms of the oscillator \( f \)-value sum rules or integrals for the \( L_a = 0 \) and \( L_b = 0 \) case,

\[
C_6 = \frac{3}{2} \sum_{ij} \frac{f^{(1)}_{0i} f^{(1)}_{0j}}{\epsilon_{0i} \epsilon_{0j} (\epsilon_{0j} + \epsilon_{0i})} = \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_D^{bs}(i\omega) d\omega.
\]

Such expressions have been developed, for example, by Marinescu \(^9,^{22} \) and Dalgarno, \(^23 \) Yan \textit{et al.}, \(^24 \) and Marinescu and Starace. \(^25 \) The goal of the thesis is to develop the dispersion coefficient in terms of the polarizability rather than the oscillator strengths and transition energies. By using the polarizabilities, the dispersion coefficients describing the interaction between two atoms is factorized perfectly into the properties of the individual atoms.

Therefore, after a little algebra shown in Chapter 5 and substitution of the imaginary polarizabilities, Equation 22 takes the integral form. The methods outlined here are for the simplest case for the lowest energy of a spherical atom, later in the thesis terms for the excited states will be defined. The beauty of getting the \( C_6 \) parameter in terms of the polarizability is
factorizing a complicated term into the individual atoms in a “one-center” method. Other pros of this method are that the polarizability at imaginary frequencies as a function is well behaved and can be modeled easily with a trial function which yields the Slater-Kirkwood formula for a static polarizability.  

**UNITS**

The system of units depends on the context in which they are determined and used. The most widely used unit system for theoretical atomic physics and dipole polarizabilities is atomic units (au). In atomic units (au) $e$, $m_e$, $4\pi\epsilon_0$ and the Planck constant $\hbar$ effectively have the numerical value 1. In au, the polarizability has the dimension of volume and the numerical values calculated are expressed in units of $a_0^3$, where $a_0 \approx 0.052918$ nm is the Bohr radius. The experimentally determined polarizabilities are usually in units of $\text{Å}^3$, kHz (kVcm$^{-1}$)$^{-2}$, cm$^3$mol$^{-1}$ or Cm$^2$N$^{-1}$ where Cm$^2$N$^{-1}$ is the SI unit. All polarizabilities heretofore will be expressed in au. The atomic units for $\alpha$ can be converted to SI units by multiplication by 0.248832.

**OVERVIEW**

The following two chapters discuss the atomic structure and properties of H and Li, including high precision calculations of the dynamic dipole polarizabilities. A brief description of the computational methods can also be found in the atomic section of the thesis. The fourth and fifth chapters focus on the long-range interaction between two molecules; beginning with developing the theory of the $C_6$ dispersion coefficient with respect to polarizability at imaginary frequencies. Followed by the computational methods and calculations of the integrals for H, Li, and Li-H interactions.
CHAPTER 2

ATOMIC THEORY

ATOMIC STRUCTURE OF LITHIUM

The following sections will present a brief overview of the atomic structure of lithium including computational methods. In this chapter one may locate a comparison of Li energy levels which is used to introduce basic atomic theory as a foundation for use in describing the atomic and molecular interactions later.

LITHIUM ENERGY LEVELS

One of the first achievements of the quantum mechanical theory in the 1920’s, was the success of the Schrödinger equation in describing the hydrogen spectrum. Solving the Schrödinger equation for the hydrogen atom gives bound electron energy states

$$E_n = \frac{-m e^4}{8\epsilon_0^2 \hbar^2} \frac{1}{n^2} \approx -13.6eV \frac{n^2}{n^2},$$

where \(n\) is the principal quantum number.

The eigenstates of the Schrödinger equation are described by quantum numbers due to the radial and angular separation of the wavefunction in spherical coordinates,

$$\Psi_{n,\ell,m}(r, \theta, \phi) = \chi_{n,\ell}(r)Y_{\ell}^{m}(\theta, \phi),$$

where the radial portion, \(\chi_{n,\ell}(r)\) pertains to the principal quantum number, \(n\). From the polar and azimuthal coordinates \(\theta\) and \(\phi\) arise the orbital quantum number, \(\ell\), and the magnetic quantum number, \(m_\ell\), respectively. A fourth quantum number is the spin projection quantum number, \(m_s\), which is the spin of the electron within that orbital. The principal quantum number may be an integer such that \(n = 1, 2, 3, \ldots\), the orbital quantum number may be of the form \(\ell = 0, 1, 2, \ldots, n - 1\), while the magnetic quantum number is \(m_\ell = -\ell, -\ell + 1, \ldots, 0\ldots, (\ell - 1)\), \(\ell\) allowing \(2\ell + 1\) values for each \(\ell\). For electrons, the spin quantum number is \(m_s = +\frac{1}{2}, -\frac{1}{2}\). The Pauli exclusion principle is the building block of the periodic table because no two electrons can have an identical set of quantum numbers.
The electron orbitals of lithium are similarly structured to the hydrogen atom except the $1s^2$ orbital density is more tightly concentrated around the core. In order to visualize the hydrogen-like electron orbitals, Figure 2 shows a set of two-dimensional image for the probability density for the first excited state $n = 2$ of hydrogen up to $n = 4$.\textsuperscript{27} The principal, angular momentum, and magnetic quantum numbers are formatted as $(n, \ell, m_\ell)$. The spectroscopic letter code is more common for the angular momentum (orbital) quantum number such that $\ell = 0$ is the $s$ orbital, $\ell = 1$ is the $p$ orbital, and $\ell = 3$ is the $d$ orbital, etc. The magnetic quantum number, $m_\ell$, is $|m_\ell| \leq \ell$. By rotating the probability densities, shown here as cross sections of the $xz$-plane, around the $z$-axis the shape of the three dimensional probability density would appear. The ground state, or $1s^2$ orbital density state corresponds to the lowest energy state and is omitted to show only the excited hydrogen states. The higher-order orbitals contain nodes of the wavefunction where the probability density is zero, and involve spherical harmonics resulting from solutions of the Schrödinger equation.

Lithium is a hydrogen-like atom consisting of three electrons with a closed $n = 1$, $\ell = 0$ shell containing two electrons in a spin-singlet state, and one electron outside in the $n = 2, \ell = 0$ ground state configuration. One might suppose that the lithium atom would also have energy levels matching the hydrogen atom; however, this is not the case for low angular momentum states. The Grotrian energy level diagram\textsuperscript{28} shown in Figure 3, graphically exemplifies the discrepancies between the hydrogenic, $n$ dependent energy levels and the lithium energy levels. For example in H the $2S$ state has the same (non-relativistic) energy as the $2p$. It is seen in the “Rydberg” states, that for the lithium the $4s, 4p,$ and $4d$ states are converging towards hydrogenic. The lithium wavefunction with $n = 2$ and angular orbital momentum $\ell = 0$ and $\ell = 1$ correspond to the $2s$ and $2p$ states, respectively. If one were to analyze the probability density for the $2s$ and $2p$ there is a penetration into the region of occupation of the $1s$ state; therefore, the $2s$ and $2p$ electrons are exposed to the charge influence of the nucleus and more tightly bound than in the case of the hydrogen atom, and in turn lowers the associated energy states. At higher angular momentum levels, the effects of the greater nuclear charge become negligible and the lithium energy levels are closer to those for the hydrogenic model.

The electrons in an atom are affected by the interactions between the electron spin magnetic moment, $\mu_z$ and the orbital angular moment, $L$ causing a spin-orbit coupling. For the atoms considered here, the spin-orbit ($LS$) coupling is weak compared to the electrostatics
Figure 2. The cross-section of computed atomic orbital wavefunctions of a hydrogen atom orientated along the positive $z$-axis. The principal, angular momentum, and magnetic quantum numbers are listed ($n$, $\ell$, $m_\ell$) and denoted on the right corner of each atomic orbit. These images represent the probability densities where black is zero density and white is the highest density.

Source: PoorLeno, Hydrogen Density Plots, English Wikipedia.
Figure 3. Partial Grotrian diagram for lithium energy level spectra ($cm^{-1}$ and $eV$). The left axis is wave number, the right axis is $eV$. The lithium atom has a closed $n = 1$ shell with two electrons and one electron outside. The Li atom is a hydrogen-like atom, the dipole allowed (emission) transitions are indicated by the lines and the numbers on each transition are the energy differences. Of special interest are the two transitions necessary from the $2^2S$ state to the $3^2S$ state, which requires two transitions: one from $2^2S - 2^2P$ (6707) and one from $2^2P - 3^2S$ (8126).

and fine structure effects are neglected. The orbital angular momenta of the individual electrons add to form a resultant total orbital angular momentum $L$. Also, the individual spin angular momenta are coupled and produce a resultant total spin angular momentum $S$. A new total angular momentum, $J$ is the coupling of $L$ and $S$:

$$J = L + S.$$  \hspace{1cm} (25)

$L S$ coupling (or Russell-Saunders coupling) is used in this thesis.\(^3\)

**Computational Methods**

The examination of the structure of the Li atom requires a numerical treatment of the atomic system including both the core and valence electrons. A frozen-core approach partitions the electronic architecture of the atom into two categories; the core electrons and the valence electrons. The following section describes the configuration interaction and Hartree-Fock methods, and describes the transition matrix elements used for the numerical calculations and representation of the atoms and molecules in this thesis.

**Hartree-Fock and Configuration Interaction**

The main methods used for computing properties of atomic structure are Hartree-Fock (HF) and configuration interaction (CI). Here, the CI method is used to compute the valence wavefunction, requiring a solution of a variational eigenproblem. CI methods are advantageous for high-precision calculations because the results of the variational method produce the upper bound solution. The primary intention of the atomic calculations in this thesis is to describe the energy changes in processes affecting the valence-shell electrons. The approximation of including only configurations that involve the excitation of the valence-shell electrons and omits the excitations of core (inner-shell) electrons is referred to as the frozen-core (FC) approximation. This is appropriate when the core-valence correlation energies involving the inner-shell electrons are small compared to the valence energy levels. The CI program tested and validated in the present research has been written by Michael Bromley\(^{29}\) based on a code produced by Jim Mitroy.\(^{30}\)

The CI method requires the solution of a variational eigenproblem involving a superposition of configurations created by $L S$ coupling of orbitals. The time-independent
Schrödinger equation for the frozen-core model is

\[ H_n |\Psi; LS\rangle_n = E_n |\Psi; LS\rangle_n, \]  

(26)

where \( |\Psi; LS\rangle \) is the wavefunction and \( E \) is the energy of the system with (good) total angular momentum \( L \) and total spin \( S \). The non-relativistic Hamiltonian, \( H_n \), for an atom of nuclear charge, \( Z \), and with \( N_e \) electrons outside a frozen-core, is

\[
H_n = \sum_{i=1}^{N_e} \left( -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + V_{\text{dir}}(r_i) + V_{\text{exc}}(r_i) + V_{p1}(r_i) \right) + \sum_{i<j} \left( \frac{1}{r_{ij}} - V_{p2}(r_i, r_j) \right). 
\]  

(27)

The valence electron coordinate vectors are given by \( r_i \) (and \( r_j \)), the kinetic energy operator for each electron is \( -\frac{1}{2} \nabla_i^2 \). There are two Coulomb terms, the attraction between each electron and the nucleus is \( Z/r_i \), and the repulsion due to the inter-particle spacing between the electrons \( i \) and \( j \) is \( r_{ij} = |r_i - r_j| \). The core potential consists of a direct core potential \( (V_{\text{dir}}) \), a core-exchange operator \( (V_{\text{exc}}) \), both of which describe the Coulomb interaction of a single valence electron with the Hartree-Fock based frozen-core electrons, to be discussed further in the next section along with the core-polarization interaction \( (V_{p1} \text{ and } V_{p2}) \).

The desired valence wavefunction is built from a linear combination of configurations:

\[
|\Psi; LS\rangle = \sum_{I=1}^{N} c_I |\Phi_I; LS\rangle, 
\]  

(28)

where there are \( N \) configurations. In order to compute the coefficients of the wavefunction, the following matrix eigenproblem is solved,

\[
\begin{bmatrix}
H_{11} & H_{12} & \cdots & H_{1N} \\
H_{21} & H_{22} & \cdots & H_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
H_{N1} & H_{N2} & \cdots & H_{NN}
\end{bmatrix}
\begin{bmatrix}
c_{1,n} \\
c_{2,n} \\
\vdots \\
c_{N,n}
\end{bmatrix}
= E_n
\begin{bmatrix}
c_{1,n} \\
c_{2,n} \\
\vdots \\
c_{N,n}
\end{bmatrix}, 
\]  

(29)

where the matrix elements are \( H_{IJ} = \langle \Phi_I | H_n | \Phi_J \rangle \). These involve computing energy terms involving only one-valence body terms \( ( -\frac{1}{2} \nabla_i^2 , Z/r_i , V_{\text{dir}}(r_i) , V_{\text{exc}}(r_i) , V_{p1}(r_i) ) \) and two-body terms \( (V_{p2}(r_i, r_j) , \frac{1}{r_{ij}}) \). In this thesis only the one-body terms are required to be computed by the Bromley code.


**Basis Set**

In this thesis only systems with one valence electron are considered. The configurations, \( |\Phi_I; LS\rangle \) are thus only single particle orbitals with \( s = \frac{1}{2} \). The spatial portions of the single particle orbitals, \( \Phi_I(r_j) \), are a product of the radial function and spherical harmonic,

\[
\Phi_{I,\ellnm}(r, \theta, \phi) = R_{I,\ellnl}(r)Y^m_{\ell}(\theta, \phi),
\]

(30)

such that \( \langle r, \theta, \phi | \Phi_I; L \rangle = \Phi_{I,\ellnm}(r, \theta, \phi) \).

Computational methods are limited to a finite number of \( n \) and \( \ell \). The radial functions of each single particle orbital, \( R_{n,\ell} \) can be expanded into a discrete set of radial basis functions \( \chi_{n_i,\ell} \) where

\[
R_{n,\ell}(r) = \sum_{n_i} d_{n_i} r \chi_{n_i,\ell}(r),
\]

(31)

where the coefficients, \( d_{n_i} \), are the weights for each radial basis function in each orbital.

The HF calculations for the ground states of neutral atoms express the core orbitals as a linear combination of Slater type orbitals (STOs),

\[
\chi_{n_i}(r) = \sqrt{\frac{(2\lambda_i)^{2n_i+1}}{(2n_i)!}} r^{n_i-1} e^{-\lambda_i r},
\]

(32)

where \( \lambda_i \) is a set of optimized parameters for each core orbital using the HF program of Mitroy.\(^{30}\)

For Li I the basis set is composed of the valence electron configurations constructed from Laguerre type orbitals (LTOs). LTOs consist of the product of a radial function and spherical harmonics:

\[
\Phi_{n,\ell}(r) = \chi_{n,\ell} Y^m_{\ell}(\hat{r}).
\]

(33)

The radial portion of the LTO is dependent on \( \ell \), the angular momentum of the orbital, \( \lambda \) a constant of the basis function decay, and \( L \) is an associated Laguerre polynomial in the form:

\[
\chi_{n,\ell}(r) = \sqrt{\frac{(2\lambda)^{2\ell+3}(n-\ell-1)!}{(\ell+n+1)!}} r^{\ell-1} e^{-\lambda r} L^{2\ell+2}_{n-\ell-1}(2\lambda r).
\]

(34)

Laguerre type orbitals achieve a complete basis set because each \( \chi_{n,\ell} \) is made to be orthogonal with common \( \lambda \). E.g. a helium atom ground-state calculation uses a 20 LTO set with common \( \lambda = 4.8 \) and \( L = S = J = 0 \).\(^{31}\)
The lithium basis set used here consisted of a mixture of both STOs and LTOs. A linear combination of STOs and LTOs are used to describe the valence orbitals radial dependence. This is needed to represent the orthogonality with the Hartree-Fock core orbitals, as well as for describing and wavefunction further from the nucleus. The combined STO and LTO basis produced has roughly the same total number of orbitals as the set of orbitals, \( \{ \Phi_i \} \), produced by the independent STO and LTO basis functions. The complete orbital set, \( \{ \Phi_i \} \) is used to construct a linearly independent basis set using common \( \lambda \) for the LTOs. The LTO used for lithium included \( N = 10, 20, 30, 40, 50, 60, \) and 70 orbitals for each \( \ell = 0, 1, 2, 3 \).

Table 1 shows the calculated Rydberg energies for the low-lying energy states of Li I. The \( N = 70 \) basis set is shown for all states due to the convergence of the energy towards the experimental energies (i.e. the fine-structure average) of the N.I.S.T. Atomic Database.32

**Frozen Core Electrons**

The frozen-core Hartree-Fock CI calculations presented in the following section are advantageous for modeling a large atom (greater than two electrons) where the core is frozen and the valence electrons move about in a model core potential which turn out to be a close approximation to the full electron behavior of the atom.

Referring back to the model Hamiltonian of Equation 27, the Coulombic core potential \( V_{\text{core}} \), generated by the spherical core electrons consists of the direct potential \( V_{\text{dir}} \) and the short range exchange potential \( V_{\text{exc}} \). The \( V_{\text{dir}} \) is the static Coulomb potential between the Hartree-Fock core electrons and the valence electron taking the form;

\[
\langle \phi_i | V_{\text{dir}} | \phi_j \rangle = \frac{\delta_{\ell_i \ell_j}}{2 \ell_i \ell_j} \sum_{c=1}^{N_{\text{core}}} (2L_c + 1)(2S_c + 1) \langle \phi_c | \phi_i \rangle \langle \phi_c | \phi_j \rangle \langle \phi_c | L_c S_c \rangle \frac{1}{r_{12}} | \phi_c | L_c S_c \rangle.
\]

where \( \ell_i \equiv \sqrt{2\ell_i + 1} \) and \( \ell_j \equiv \sqrt{2\ell_j + 1} \).

The short-range exchange potential is dependent on the symmetry of the core and valence electron wavefunctions, where

\[
\langle \phi_i | V_{\text{exc}} | \phi_j \rangle = \frac{\delta_{\ell_i \ell_j}}{2 \ell_i \ell_j} \sum_{c=1}^{N_{\text{core}}} \sum_{L_c, S_c} (2L_c + 1)(2S_c + 1)(-1)^{\ell_c + \ell_j + L_c + S_c} \langle \phi_c | \phi_i \rangle \langle \phi_c | \phi_j \rangle \langle \phi_c | L_c S_c \rangle \frac{1}{r_{12}} | \phi_c | L_c S_c \rangle.
\]

The \( V_{\text{core}} \) is a one-body potential since it only acts on one valence electron at a time. The alkali-metal group, like lithium, have atomic structures with only one valence electron.
Table 1. Rydberg Energy Levels of Li I Based on the NIST Atomic Spectra Database Levels Compared to the $N = 70$ Basis Set Frozen-Core Hartree Fock Configuration Interaction (CI) Calculations

<table>
<thead>
<tr>
<th>Config</th>
<th>J</th>
<th>$E^a$ (Hartree)</th>
<th>$E_{ave}^{a,b}$ (Hartree)</th>
<th>$E_{CI}$ (Hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s</td>
<td>$\frac{1}{2}$</td>
<td>-0.198142</td>
<td>-0.198142</td>
<td>-0.198141</td>
</tr>
<tr>
<td>2p</td>
<td>$\frac{1}{2}$</td>
<td>-0.130236</td>
<td>-0.130235</td>
<td>-0.130239</td>
</tr>
<tr>
<td>2p</td>
<td>$\frac{3}{2}$</td>
<td>-0.130234</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3s</td>
<td>$\frac{1}{2}$</td>
<td>-0.074182</td>
<td>-0.074182</td>
<td>-0.074169</td>
</tr>
<tr>
<td>3p</td>
<td>$\frac{1}{2}$</td>
<td>-0.057236</td>
<td>-0.057236</td>
<td>-0.057228</td>
</tr>
<tr>
<td>3p</td>
<td>$\frac{3}{2}$</td>
<td>-0.057236</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3d</td>
<td>$\frac{3}{2}$</td>
<td>-0.055606</td>
<td>-0.055606</td>
<td>-0.055611</td>
</tr>
<tr>
<td>3d</td>
<td>$\frac{5}{2}$</td>
<td>-0.055606</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4s</td>
<td>$\frac{1}{2}$</td>
<td>-0.038615</td>
<td>-0.038615</td>
<td>-0.038610</td>
</tr>
<tr>
<td>4p</td>
<td>$\frac{1}{2}$</td>
<td>-0.031975</td>
<td>-0.031975</td>
<td>-0.031970</td>
</tr>
<tr>
<td>4p</td>
<td>$\frac{3}{2}$</td>
<td>-0.031975</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4d</td>
<td>$\frac{3}{2}$</td>
<td>-0.031274</td>
<td>-0.031274</td>
<td>-0.031277</td>
</tr>
<tr>
<td>4d</td>
<td>$\frac{5}{2}$</td>
<td>-0.031274</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4f</td>
<td>$\frac{5}{2}$</td>
<td>-0.031243</td>
<td>-0.031243</td>
<td>N/A</td>
</tr>
<tr>
<td>4f</td>
<td>$\frac{7}{2}$</td>
<td>-0.031243</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5s</td>
<td>$\frac{1}{2}$</td>
<td>-0.0236367</td>
<td>-0.023637</td>
<td>-0.023634</td>
</tr>
<tr>
<td>5p</td>
<td>$\frac{1}{2}$</td>
<td>-0.020374</td>
<td>-0.020374</td>
<td>-0.020372</td>
</tr>
<tr>
<td>5p</td>
<td>$\frac{3}{2}$</td>
<td>-0.020374</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5d</td>
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<td>-0.020012</td>
<td>-0.020012</td>
<td>-0.020014</td>
</tr>
<tr>
<td>5d</td>
<td>$\frac{5}{2}$</td>
<td>-0.020012</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5f</td>
<td>$\frac{5}{2}$</td>
<td>-0.019969</td>
<td>-0.019969</td>
<td>N/A</td>
</tr>
<tr>
<td>5f</td>
<td>$\frac{7}{2}$</td>
<td>-0.019969</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$Source: NIST Atomic Spectra Database Levels.$^{32}$

$^b$Average energy of the fine-structure (very small for Li!).
simplifying the sum over all $L_cS_c$ coupled pairs formed from one core and one valence electron. In lithium, there is only one possible $L_cS_c$ because there is only one valence electron simplifying $V_{core}$ to the form:

$$\langle \phi_i | V_{\text{core}} | \phi_j \rangle = \frac{\delta_{\ell_i \ell_j}}{2\ell_i \ell_j} \sum_{c=1}^{N_{\text{core}}} (2L_c + 1)(2S_c + 1) \langle \phi_c \phi_i; L_c S_c | \frac{1}{r_{12}} | \phi_j \phi_c; L_c S_c \rangle. \quad (37)$$

The direct and exchange matrix elements are computed without approximation and simplified versions are created by invoking reduced matrix elements.

### Core Polarizations

The form of the Hamilton in Equation 27 includes the one-body polarization potential $V_{p1}$ ($V_{\text{pol}}$) and the two-body polarization $V_{p2}$ ($V_{\text{dien}}$), which is not discussed here. The polarization describes an additional attractive potential created by distortion of the core electron cloud by the valence electron(s). The semi-empirical modeling of the core polarization improves the agreement of the calculations with experiment. The one-body polarization potential $V_{p1}$ or in general $V_{\text{pol}}$ in a semi-empirical model adopted by Norcross and Seaton,\textsuperscript{33} is in the form

$$V_{p1}(r) = -\sum _{\ell m} \frac{\alpha_D}{2\ell^4} (1 - e^{-r_{\ell}/\rho_{\ell}}) |\ell m\rangle \langle \ell m| \quad (38)$$

The polarization potential correction relies on the static dipole polarizability, $\alpha_D$ of the core, which is taken from other calculations, e.g. here the Li$^+$ core. The $\rho_{\ell}$, adjustable $\ell$-dependent cutoff parameters, are tuned for experimental agreement, i.e. so the spectra match (as seen in Table 1).

### Transition Matrix Elements

The above treatment of the core-polarization means that a similar correction to the multipole operators is employed. The modified transition operator is obtained by mapping\textsuperscript{34}

$$d^1 = \sqrt{(1 - e^{-r_{\ell}/\rho_{\ell}})} r^k C^k(\hat{r}), \quad (39)$$

where $C^k(\hat{r})$ is a spherical tensor with multipole rank $k$. In order to form the transition matrices necessary to compute both polarizabilities and oscillator strengths (discussed in the next chapter), the code developed by Michael Bromley\textsuperscript{29} integrates $\langle \Phi_j | r^k C^k | \Phi_i \rangle$ and then builds the transition matrix element,

$$T_{nm} = \langle \Psi_n | r^k C^k | \Psi_m \rangle, \quad (40)$$
between eigenstates of the system in a given basis set. The transition between two electronic states is expressible in terms of the linear combinations of different configurations from an identical basis set, $|\Phi_i\rangle$, where Equation 40 is expressed in the summation

$$T_{nm} = \left(\sum_j c_{jn}^* \langle \Phi_j | \right) r^{k} C^{k} \left(\sum_i d_{im} | \Phi_i \rangle \right) = \sum_{i,j} c_{jn}^* d_{im} \langle \Phi_j | r^{k} C^{k} | \Phi_i \rangle. \quad (41)$$

Transition matrix summations can be computationally expensive due to the number of $LS$ coupled configurations possible, thereby giving rise to densely populated $c-$ and $d-$ coefficient matrices of dimension $N \times N$ and $M \times M$, respectively. The multipoles can be determined by setting the correct order rank, i.e. dipole transition is computed with rank one, $k = 1$, and the quadrupole is of rank two, $k = 2$, etc.

The CI calculations briefly outlined in this section serve as a general outline of the computational methods used for the data collected in this thesis. The author was not involved in the development or programming of the code used to create the Hartree-Fock frozen-core configuration interaction variational method of solving the eigenproblem imposed by the Schrödinger equation. For a more comprehensive description of this methodology, please see reference. Further modifications for the current research to the general HF-FC-CI code are discussed in the following sections for the present purposes of computing dynamic polarizabilities and various numerical integration techniques.

In conclusion, this chapter outlined the atomic structure and quantum mechanical nature of the Hamiltonian and the wavefunctions. In order to quantify the atomic energies, computational methods were described to build complete basis sets of radial and angular portions of the wavefunctions which are necessary for solving the time independent Schrödinger equation. The general purpose was to build the foundation for the methods to be discussed in length which exploit the general principles in order to gain a deeper understanding of atomic structure and interactions.

The next chapter will incorporate the effects of electric and magnetic fields on the elementary constituents of the atom in the quantum mechanic form, enables the calculation of polarizabilities from first principles.
CHAPTER 3
DYNAMIC DIPOLE POLARIZABILITIES AND
THE Li ATOM

The focus of the current chapter is to motivate the derivation of polarizabilities from first principles. A broad introduction to perturbation theory is generalized for an atom exposed to a uniform and oscillating electric field. Once the fundamental perturbation expansions are concluded, the concepts are expanded to an electric field with an explicit orientation with regards to a spherical atom. The reason for developing the fundamentals regarding the derivation of the dynamic dipole polarizabilities, is due to the analogous nature of an atom in an electric field with the electric field generated by other atoms. Therefore, the following discourse on the polarizabilities of atomic states builds a verifiable method to describe molecules composed of atoms with $J$, $L$, and $M$ dependences. Using reduced matrix elements, the polarizability equations are reduced to simplified versions. In order to factorize molecular interactions into the atomic constituents, the final theoretical conclusion for this chapter is to generate the $M$-dependent dynamic dipole polarizability. The computational data compiled from the Li atom is used to validate the code and compare with experimental reference.

PERTURBATION THEORY: ATOMS IN ELECTRIC FIELDS

Perturbation theory was first implemented by Schrödinger\textsuperscript{35} to calculate the Stark effect in atomic hydrogen. A system of particles having electric charge $q_i$ and position $r_i$ is placed in a uniform electric field,

$$\mathbf{F} = \varepsilon \hat{\mathbf{F}},$$ \hspace{1cm} (42)

such that the system is described by the Hamiltonian

$$H = H^0 - \varepsilon \hat{\mathbf{F}} \cdot \mathbf{d} = H^0 + H'.$$ \hspace{1cm} (43)
$H^0$ is the Hamiltonian of an unperturbed system (without an electric field), and $d$ is the dipole moment operator,

$$d = \sum_{i} q_i r_i,$$

(44)

for the number of electrons (or positrons) in the system, $N_e$ and the perturbing Hamiltonian, $H' = -\varepsilon \hat{\mathbf{F}} \cdot d$.

In order to find solutions, the energy and wavefunction are expanded in a perturbation series

$$|\Psi_n\rangle = |\Psi_n^{(0)}\rangle + \varepsilon |\Psi_n^{(1)}\rangle + \varepsilon^2 |\Psi_n^{(2)}\rangle + \cdots,$$

(45)

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots,$$

(46)

respectively, where the field strength is treated as a perturbative parameter, $\varepsilon = |\mathbf{F}|$. The superscript $k$ on each term is the power of the $k$th-order term.$^{36}$ The eigenvalue equation

$$H |\Psi_n\rangle = E_n |\Psi_n\rangle,$$

(47)

is solved to find the terms in the expansion of $|\Psi_n\rangle$, and $E_n$. The zeroth-order terms are collected in the equation

$$H^0 |\Psi_n^{(0)}\rangle = E_n^{(0)} |\Psi_n^{(0)}\rangle,$$

(48)

are independent of $H'$, and is generally assumed to be a solvable eigenproblem with corresponding eigenstates $|\Psi_n^{(0)}\rangle$ and eigenvalues $E_n^{(0)}$.

The first-order terms are collected from the expansion of Equation 47 into

$$H^0 |\Psi_n^{(1)}\rangle + H' |\Psi_n^{(0)}\rangle = E_n^{(0)} |\Psi_n^{(1)}\rangle + E_n^{(1)} |\Psi_n^{(0)}\rangle,$$

(49)

and the first-order shift in energy is (in general)

$$E_n^{(1)} = \langle \Psi_n^{(0)} | H' | \Psi_n^{(0)} \rangle = -\varepsilon \langle \Psi_n^{(0)} | \hat{\mathbf{F}} \cdot d | \Psi_n^{(0)} \rangle$$

(50)

which generates the linear Stark effect (equal to zero for lithium). By symmetry, the first-order energy term is zero for lithium. The linear Stark equation is not always zero in cases such as the $n = 2$ level mixing of hydrogen. The field is chosen where $\hat{\mathbf{F}} = [0, 0, 1]$ acting only in the
z-direction. The \( \hat{z} \) operator is a dipole operator explicitly formed by \( r^1 C_0^1 (\hat{\mathbf{r}}) = \hat{z} = \hat{r} \cos (\hat{\theta}) \), the spherical tensor of rank 1. Equation 50 becomes \( E_n^{(1)} = -\varepsilon \langle \Psi_n^{(0)} | \hat{z} | \Psi_n^{(0)} \rangle = 0 \).

The second-order energy, \( E_n^{(2)} \), determined from the eigenproblem expansion
\[
H^0 |\Psi_n^{(2)}\rangle + H' |\Psi_n^{(1)}\rangle = E_n^{(0)} |\Psi_n^{(2)}\rangle + E_n^{(1)} |\Psi_n^{(1)}\rangle + E_n^{(2)} |\Psi_n^{(0)}\rangle,
\]
is generally expressed as
\[
E_n^{(2)} = \langle \Psi_n^{(0)} | H' | \psi_n^{(1)} \rangle = \sum_{m(\neq n)} \frac{|\langle \Psi_n^{(0)} | H' | \Psi_m^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}.
\]
The other way of working with Equation 52 is that \( |\Psi_n^{(0)}\rangle \) is an eigenfunction of the Hamiltonian operator, then \( |\Psi_n^{(1)}\rangle \) satisfies
\[
(H^0 - E_n^{(0)}) |\Psi_n^{(1)}\rangle = -\hat{\mathbf{F}} \cdot \hat{\mathbf{d}} |\Psi_n^{(0)}\rangle.
\]
Using Equation 53 to create the expectation value with matrix \( \bar{\alpha}_n \), which describes the \( n \)-th unperturbed eigenstate’s second-order response,
\[
\langle \Psi_n | \hat{d} | \Psi_n \rangle = \varepsilon (\langle \Psi_n^{(0)} | \hat{d} | \Psi_n^{(1)} \rangle + \langle \Psi_n^{(1)} | \hat{d} | \Psi_n^{(0)} \rangle) = \varepsilon \bar{\alpha}_n \hat{\mathbf{F}}.
\]
The expression for \( E_n^{(2)} \) in terms of the eigenfunctions and eigenvalues of \( H^0 \) involving the ground state and some other state, \( m \) is given in terms of transition matrix elements
\[
E_n^{(2)} = -\sum_{m(\neq n)} \frac{\varepsilon^2 |\langle \Psi_n^{(0)} | \hat{d} \cdot \hat{\mathbf{F}} | \Psi_m^{(0)} \rangle|^2}{E_m^{(0)} - E_n^{(0)}} = -\frac{1}{2} |\varepsilon|^2 \hat{\mathbf{F}} \cdot \bar{\alpha}_n \hat{\mathbf{F}},
\]
where \( \bar{\alpha}_n \) is a tensor corresponding to different orientations of the atom. The second-order energy, \( E_n^{(2)} \) is the quadratic Stark effect proportional to \( |\varepsilon|^2 \). (A discussion of the tensor will be left as an exercise for the reader, e.g. with components \( \alpha_{xx}, \alpha_{xy}, \ldots, \alpha_{zz} \)).

Aligning the field in the \( z \)-direction, using the \( \hat{z} \) operator representation,
\[
\hat{\mathbf{F}} \cdot \bar{\alpha}_n \hat{\mathbf{F}} = \alpha_{zz}^n \text{ for each unperturbed eigenstate } |\Psi_n^{(0)}\rangle \text{ and } \hat{d} \cdot \hat{\mathbf{F}} = |\varepsilon|, \text{ Equation 55 yields the solution for the static dipole polarizability}
\]
\[
\bar{\alpha}_n \equiv \alpha_{zz}^n = -2 \sum_{m\neq n} \frac{|\langle \Psi_n^{(0)} | \hat{z} | \Psi_m^{(0)} \rangle|^2}{E_m^{(0)} - E_n^{(0)}}.
\]
Note that given a homogeneous electric field in the \( z \) direction, only the \( \alpha_{zz}^n \) term from the atomic polarizability tensor contributes to \( E_n^{(2)} \) while \( \alpha_{zz}^n \) is simple to compute using transition matrix elements involving the atomic orientations and \( z = r \cos \theta \).
Oscillator Strengths from Perturbation Methods

A homogeneous electric field removes the degeneracy of the atomic levels according to the direction of the electronic angular momentum $J$. The projection of the momentum $J$ in a chosen direction is called $M_J$. Unsplit levels $M_J = \pm |M_J|$ are due to the removal of the $J$ degeneracy in a homogeneous electric field which is described as the Stark effect. In a weak static electric field of strength $\varepsilon$, the lowest order perturbation energy shift of the energy level $E_n$ of state $n$ is the quadratic stark effect of Equation 55 which can be written as

$$E_n^{(2)} = -\frac{1}{2} \alpha_{zz}^n \varepsilon^2.$$  \hspace{1cm} (57)

Atomic polarizability is a function of the unperturbed atomic state $n$ and $M_J$, expressed generally with constants $\alpha_D^n$ and $\beta_T$ as follows, where $\beta_T$ is related to the tensor polarizability, $\alpha^T_n$ (which will be discussed shortly):

$$\alpha_{zz}^n = \alpha_D^n + 2\beta_T [M_J^2 - \frac{1}{3}J(J+1)].$$  \hspace{1cm} (58)

By averaging the tensor quantity, $\alpha_{zz}^n$ over all $M$-states of the $J$-level, the atomic polarizability becomes a scalar quantity. The scalar atomic polarizability is connected to the permittivity of a gas or vapor in the relationship

$$\epsilon = 1 + 4\pi N \alpha_{zz}^n,$$  \hspace{1cm} (59)

where $N$ is the number density of the gas particles.\textsuperscript{16}

Under the premise that the spin-orbit effects are small and the radial parts of the wave functions are the same for the states with different $J$, the Stark energy shifts for the different $L_0M_0$ levels in any electric field $\varepsilon$ are written as

$$E_n^{(2)} = -\frac{1}{2} \alpha_{L_0M_0}^n \varepsilon^2.$$  \hspace{1cm} (60)

This generic expression for $\alpha_D^n$ arises from second-order perturbation of an atom placed in a uniform electric field; however, this form is more a proof of concept than a utility function for the interaction between an atom and another atom’s electric field. Therefore, the following section expands the general form of $\alpha_D^n$ in order to first elaborate the $n$, $\ell$, and $m$ dependence of the eigenstates ($|\Psi_{n,\ell,m}^{(0)}$) and second to explicitly define the polarizability in $J$, $L$, $S$, and $M$ representations.
In terms of the second-order perturbation theory, the energy shift from the electric field, $\epsilon$ along the $z$ direction is

$$E^{(2)}_n = \frac{1}{2} \sum_{m \neq n} \frac{2 \langle \psi_n; L_n M_n | \sum_i r_i C_0^1(\hat{r}_i) | \psi_m; L_m M_m \rangle \langle \psi_m; L_m M_m | \sum_i r_i C_0^1(\hat{r}_i) | \psi_n; L_n M_n \rangle \epsilon^2}{(E_n - E_m)} \quad (61)$$

The LS coupled absorption oscillator strength, $f_{0n}$ for a dipole transition from the ground state, $n = 0$ to level $n$ is defined in a $J-$representation is

$$f_{0n} = \frac{2 |\langle \psi_0 || r C_0^1(\hat{r}) || \psi_n \rangle|^2 (E_n - E_0)}{3(2J_n + 1)}, \quad (62)$$

where $C_1(\hat{r}) = \cos \hat{\theta}$ is the spherical tensor of rank 1. The LS coupling form of the oscillator strength is obtained by replacing the total angular momentum with the orbital angular momentum, and relies on reduced matrices.

**Reduced Matrix Elements via the Wigner-Eckart Theorem**

The eigenfunction $|\Psi_i\rangle$ describes an atomic state with quantum numbers $n_i$, $\ell_i$, and $m_i$, such that an expanded version of the eigenfunction is written in equivalent form as $|n_i, \ell_i, m_i\rangle$. The Wigner-Eckart theorem allows for the separation of the angular momentum, $m$, quantum number from the matrix elements for spherical tensor operators, $T^k_q$.

$$\langle n, \ell, m|T^k_q|n', \ell', m'\rangle = (-1)^{\ell - m} \begin{pmatrix} \ell & k & \ell' \\ -m & q & m' \end{pmatrix} \langle n, \ell||T^k||n', \ell'\rangle. \quad (63)$$

The bracketed quantity is a scalar defined as the Wigner 3-\( j \) symbol, and is related to the Clebsch-Gordan coefficients, $\langle j_1 m_1 j_2 m_2 | j_3 - m_3 \rangle$, shown through

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m_3}}{\sqrt{2j_3 + 1}} \langle j_1 m_1 j_2 m_2 | j_3 - m_3 \rangle. \quad (64)$$

The reduced matrix element appears as a double-bar matrix element independent of $m$ and $q$. By applying the Wigner-Eckart theorem to the transition matrix element (Equation 56), the sum over states $m$ collapses $q = m = m'$,

$$\sum_m |\langle n, \ell, m|z|n', \ell', m'\rangle|^2 = -\frac{1}{3} |\langle n, \ell||r C_1(\hat{r})||n', \ell'\rangle|^2. \quad (65)$$
For fixed $m$, and any $\ell$, the reduced matrix elements for the static dipole polarizability are expressed as,

$$\alpha^n_D = -\frac{2}{3} \sum_{m \neq n} \frac{|\langle n, \ell_n | \sum_i r_i \mathbf{C}^1(\hat{r}_i) | m, \ell_m \rangle|^2}{E_m - E_n},$$  \hspace{1cm} (66)$$

where $m$ now denotes the index of the final states.

**Atomic Polarizabilities**

By implementing perturbation theory, generic expressions for the oscillator strengths and atomic polarizabilities have been identified. These expressions rely heavily on the eigenfunctions describing the atomic state. The use of reduced matrix elements allows the separation of angular momentum quantum number, $m$ alleviating the $M$ dependance. The following section will build the polarizabilities with various combinations of $M$, $L$, $S$, and $J$ dependance. The decomposition of polarizabilities into different forms of coupling, e.g. $LS$ coupling, are useful depending on the atomic calculations. For this thesis, $M$-dependent $LS$ coupled polarizabilities are necessary.

Using the definition of the oscillator strength and the average energy shifts, $\epsilon_{0n} = (E_0 - E_n)$, yields the following sum rule:

$$\alpha^n_D = \sum_{M_0 = -L_0}^{L_0} \frac{\alpha^n_{L_0 M_0}}{(2L_0 + 1)} = \sum_m f_{0m} \epsilon_{0m}^2,$$  \hspace{1cm} (67)$$

which includes the valence and core excitations. The $f$-value distribution for the core was estimated using a method described in Appendix A.

For a state with a non-zero angular momentum $J$, the polarizability depends on the magnetic projection $M$ defined as,

$$\alpha^n = \alpha^n_D + \alpha^n_T \frac{3M^2 - J(J + 1)}{J(2J + 1)},$$  \hspace{1cm} (68)$$

where $\alpha^n_D$ is the scalar polarizability and $\alpha^n_T$ is the tensor polarizability. In terms of the reduced matrix elements of the electric-dipole operator, the scalar polarizability $\alpha_D$ of the atom with a total angular momentum $J$ is written as

$$\alpha^n_D = \frac{2}{3(2J + 1)} \sum_m \frac{|\langle \psi_n | r \mathbf{C}^1(\hat{r}) | \psi_m \rangle|^2}{E_m - E_n}. \hspace{1cm} (69)$$
In the $J$ representation the tensor polarizability is defined by

$$\alpha^n_T = N_J \times \sum_m (-1)^{J_n + J_m} \begin{pmatrix} J_n & 1 & J_m \\ 1 & J_n & 2 \end{pmatrix} \frac{|\langle \psi_n | r C^1 (\hat{r}) | \psi_m \rangle|^2}{E_m - E_n},$$  \hspace{1cm} (70)

where $N_J = 4 \left( \frac{5 J (2 J + 1)}{6 (J_n + 1)(2 J_n + 1)(2 J_n + 3)} \right)^{1/2}$.

For the purpose of the calculations presented in this thesis, it is necessary to define the polarizabilities in strict $L S$ coupling. For a state with orbital angular momentum $L \rightarrow L_n$, the tensor polarizability $\alpha^n_{\tau, L}$ is expressed as:

$$\alpha^n_{\tau, L} = \sum_m \left[ \begin{pmatrix} L_n & 1 & L_m \\ -L_n & 0 & L_n \end{pmatrix}^2 - \frac{1}{3(2 L_n + 1)} \right] \times \frac{2 |\langle \psi_n | r C^1 (\hat{r}) | \psi_m \rangle|^2}{(E_n - E_m)}.$$  \hspace{1cm} (71)

In the $J$ and $L$ representations, the tensor polarizabilities $\alpha_2$ and $\alpha_{2,L}$ are related through the following term as,

$$\alpha^n_T = \alpha^n_{\tau, L} (-1)^{S + L + J + 2 (2 J + 1)} \begin{pmatrix} S & L & J \\ 2 & J & L \end{pmatrix} \times \begin{pmatrix} J & 2 & J \\ -J & 0 & J \end{pmatrix} \begin{pmatrix} L & 2 & L \\ -L & 0 & L \end{pmatrix}^{-1}.$$  \hspace{1cm} (72)

As an example, the atomic state of $L = 1$ and $J = 3/2$, equation (72) gives $\alpha^n_T = \alpha^n_{\tau, L}$, and for atomic state $L = 1$, $S = 1$ and $J = 1$, equation (72) gives $\alpha^n_T = -\alpha^n_{\tau, L}/2$.

The polarizability is expressed in $M$-dependent terms as

$$\alpha^n_{L_n, M_n} = \sum_m \left( \begin{pmatrix} L_n & 1 & L_m \\ -M_n & 0 & M_m \end{pmatrix}^2 - \frac{1}{3(2 L_n + 1)} \right) \times \frac{2 |\langle \psi_n | L_n | \sum_i r_i C^1_i (\hat{r}) | \psi_m \rangle|^2}{(E_n - E_m)}.$$  \hspace{1cm} (73)

where $n = 0$. The $M$-dependent part of the polarizability is a tensor of rank 2, it is commonly defined in terms of $\alpha^n_{\tau, L_n, L_n}$,

$$\alpha^n_{\tau, L_n, M_n} = \alpha^n_{\tau, L_n L_n} \times (-1)^{L_n - M_n} \begin{pmatrix} L_n & 2 & L_n \\ -M_n & 0 & M_n \end{pmatrix} \times \frac{3 M_n^2 - L_n (L_n + 1)}{L_n (2 L_n - 1)},$$  \hspace{1cm} (74)

where

$$\alpha^n_{\tau, L_n L_n} = \sum_m \left[ \begin{pmatrix} L_n & 1 & L_m \\ -L_n & 0 & L_n \end{pmatrix}^2 - \frac{1}{3(2 L_n + 1)} \right] \times \frac{2 |\langle \psi_n | L_n | \sum_i r_i C^1_i (\hat{r}) | \psi_m \rangle|^2}{(E_n - E_m)}.$$  \hspace{1cm} (75)
In terms of \( f \)-value sums

\[
\alpha_{T, L_0 L_a}^n = -\left( \sum_{m, L_m = 0} f_{0m} \frac{2 \Delta E_{nm}}{\epsilon_{0m}^2} - \frac{1}{2} \sum_{m, L_m = 1} f_{0m} \frac{2 \Delta E_{nm}}{\epsilon_{0m}^2} + \frac{1}{10} \sum_{m, L_m = 2} f_{0m} \frac{2 \Delta E_{nm}}{\epsilon_{0m}^2} \right),
\]

(76)

where the core does not make a contribution to the tensor polarizability since it equally impacts the different \( M \)-levels, which will show up again later in this thesis.

**Dynamic Fields**

For the purposes of cold atom physics, the Li atom is advantageous to use because it only has three electrons. Consequently, the calculations can be run to high precision. The present calculations of the dynamic polarizability for Li are based on a solution to the non-relativistic Schrödinger equation using time-dependent perturbation methods and are obtained here at real frequencies.

Dynamic polarizability is a measurement of the reaction of an atom to an external electric field. At real frequencies, the dynamic polarizability can be expressed in terms of a sum over all intermediate states, including the continuum. It may also be expressed in terms of the dynamic scalar and tensor dipole polarizabilities, \( \alpha_D^n(\omega) \) and \( \alpha_T^n(\omega) \), respectively. In terms of the reduced matrix elements of the dipole transition operator, \( T_1 = \sum_i q_i R_i Y_{10}(\hat{R}_i) \), the dynamic scalar and tensor dipole polarizabilities are also expressed by:

\[
\alpha_D^n(\omega) = \sum_{L_a} \alpha_D(L_a, \omega),
\]

(77)

\[
\alpha_T^n(\omega) = \sum_{L_a} W(L, L_a) \alpha_D(L_a, \omega),
\]

(78)

where

\[
\alpha_D^n(L_a, \omega) = \frac{8\pi}{9(2L_n + 1)} \sum_{m(\neq n)} \frac{\Delta E_{nm} | \langle nL_n | T_1 | mL_a \rangle |^2}{\Delta E_{nm}^2 - \omega^2},
\]

(79)

and

\[
W(L_n, L_a) = (-1)^{L_n + L_a} \sqrt{\frac{30(2L_n + 1) L_a (2L_n - 1)}{(2L_n + 3)(L_n + 1)}} \times \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ L_n & L_n & L_a \end{array} \right\}.
\]

(80)

The initial state eigenfunction, \( |nL_n\rangle \), is the state with principal quantum number \( n \), angular momentum quantum number \( L_n \), and energy \( E_n^{(0)} \). The state with principal quantum number \( m \), angular momentum quantum number \( L_a \), and energy \( E_m^{(0)} \), is the \( m \)th intermediate
eigenfunction $|mL_a\rangle$. The transition energy between the initial and $n$th intermediate state is
$\Delta E_{mn} = E_m^{(0)} - E_n^{(0)}$. As defined by Zhang and Yan, $q_i$ are the charges of the particles and $R_i$ is direction of the induced dipole.

For the case where $L = 0$,

$$\alpha^n_D(\omega) = \alpha_D(P, \omega), \tag{81}$$
$$\alpha^n_T(\omega) = 0; \tag{82}$$

whereas, for the case $L = 1$,

$$\alpha^n_D(\omega) = \alpha_D(S, \omega) + \alpha_D(P, \omega) + \alpha_D(D, \omega), \tag{83}$$
$$\alpha^n_T(\omega) = -\alpha_D(S, \omega) + \frac{1}{2}\alpha_D(P, \omega) - \frac{1}{10}\alpha_D(D, \omega). \tag{84}$$

The scalar and tensor polarizabilities can be related to the polarizabilities of the magnetic sub-levels, $2 \alpha^n_{D,M}(\omega)$,

$$\alpha^n_{D,0}(\omega) = \alpha^n_D(\omega) - 2\alpha^n_T(\omega) \tag{85}$$
$$\alpha^n_{D,\pm 1}(\omega) = \alpha^n_D(\omega) + \alpha^n_T(\omega). \tag{86}$$

**Ground State Dynamic Polarizabilities**

Figure 4 shows the dynamic dipole polarizability $\alpha^n_D(\omega)$ of the lithium ground state, $2^2S$ ($n = 2s$) as a function of photon energy $\omega$ (a.u.). The computations were run with basis sets with $\ell = 1, 2, 3$ and mixed STO and LTO with $N = 10, 20, 30, 40, 50, 60, 70, 80$ and 100. As seen in Figure 4, as the basis set size increased, the higher order excitation energies are picked up. The ionization potential for lithium occurs at $\omega = 0.198142$ a.u. The polarizability is very susceptible to small changes in the physical energies at photon energies close to the $n^2P$ excitation energies. The singularities in the polarizability at the $2^2S \rightarrow n^2P$ frequencies lie between 0.06 and 0.07 (au) where the exact excitation energy for this transition is at $\omega = 0.067907$ a.u.

**Excited State Dynamic Polarizabilities**

The scalar ($\alpha^n_D(\omega)$) and tensor ($\alpha^n_T(\omega)$) dipole polarizabilities for the excited $2^2P$ state of the Li atom are graphed in Figure 5. The structure of the dynamic polarizability is complicated since the scalar and tensor polarizabilities create singularities associated with downward and upward transitions. The tensor polarizability becomes large in the vicinity of
Figure 4. Dynamic dipole polarizability, $\alpha_D^2(\omega)$, of the Li atom in the ground $2^2S$ state for various sized basis sets of $N = 10, 20, 60, \text{ and } 100$. 

\[ \text{Figure 4. Dynamic dipole polarizability, } \alpha_D^2(\omega), \text{ of the Li atom in the ground } 2^2S \text{ state for various sized basis sets of } N = 10, 20, 60, \text{ and } 100. \]
Figure 5. Dynamic dipole polarizabilities, $\alpha^{2p}_D(\omega)$ (color:red/dark line) and $\alpha^{2p}_T(\omega)$ (color:green/light line) (a.u.) of the Li atom in $2^2P$ state for various sized basis sets of $N = 10, 20, 60,$ and $100$. 
the $2^2S$, $3^2S$ and $3^2D$ transitions, where a single transition dominates in Equation 84. Again the computation is generated with basis sets of varying size, $N = 10, 20, 30, 40, 50, 60, 70, 80,$ and 100. The scalar and tensor polarizabilities are of opposite parity. The $S$ and $D$ state transitions are the main contributors to the polarizabilities, as seen from the sign change in Equation 84 and Equation 83.

The Li ground state $2^2S$ and $2^2P$ dynamic dipole polarizability is validated with the values determined by Li-Yan Tang et al.\textsuperscript{2} In the publication,\textsuperscript{2} $\alpha_n^D(\omega)$ is computed for photon energies ranging from $\omega = 0$ (au) up to $\omega = 0.8$ (au). The current dynamic dipole polarizabilities presented in this work are computed from photon energies extending into the continuum at $\omega = 0.25$ (au). The validation with currently acceptable values of the dynamic dipole polarizabilities ensures proper orbital configurations and the ability to properly map the transition energies.

Figure 6 shows the dynamic dipole polarizability $\alpha_n^D(\omega)$ of the lithium $3^2S$ ($n = 3s$) as a function of photon energy $\omega$ (au). The computations were run with basis sets with

![Figure 6. Dynamic dipole polarizability, $\alpha_{3s}^D(\omega)$ (in a.u.) of the Li atom in $3^2S$ state for various sized basis sets of $N = 10, 20, 60,$ and 100.](image-url)
\( \ell = 1, 2, 3 \) and mixed STO and LTO with \( N = 10, 20, 30, 40, 50, 60, 70, 80 \) and 100. By examining Figure 6, as the number of orbitals increased, the higher order excitations energies create more discrepancies in the predicted energies of the singularities. Referring back to the Grotrian diagram (Figure 3), the lowest order allowed transitions are the \( 3^2 S \) to the \( 3^2 P \) and \( 4^2 P \) states located at the first two singularities, respectively.

**Numbers for the Experimentalists**

The numerical calculations for the ground state and first two excited states of Li are shown in Figure 4, Figure 5, and Figure 6. The insights gained for the Li transitions are validated\(^2\) and further satisfy the proper allowed transitions as shown in Figure 3. The convergence of the dynamic dipole polarizabilities are validated by increasing the orbital basis set in orders of 10. Experimentalists are interested in understanding the transition between the \( 2^2 S \) to \( 3^2 S \) Li states. The polarizability difference between the \( 2^2 S \) and the \( 3^2 S \) states of Li is graphed in Figure 7. The difference references the transition energy between the two states. The experimentalists\(^1\) have successfully excited a ground state atom to the \( 3^2 S \) state using a method of hitting the atom with a laser with energies of 0.075 au. (2.033 eV) and 0.062 au. (1.687 eV). The two laser system involves a shift of \( \lambda_1 = 735 \, \text{nm} \) and \( \lambda_2 = 610 \, \text{nm} \).

The theoretical interpretation is the solution of the dynamic dipole polarizabilities as a function of photon energy. The vertical lines on Figure 7 reference the two experimental lasers at 0.075 and 0.062 au. The first laser with photon \( \lambda_1 \) is an intermediate transition to an energy just below the \( 2^2 P \) state. The second laser wavelength \( \lambda_2 \) pumps the energy of the Li atom to the \( 3^2 S \) state. The two-photon transition is accurately described through the theoretical methods resulting in Figure 7 summarizing the specific transition.
Figure 7. The polarizability difference between the $2^2 S$ and the $3^2 S$ states of Li. The vertical lines are photon energies of 0.075 and 0.062 a.u.
CHAPTER 4

THE THEORY OF LONG-RANGE DISPERSION INTERACTIONS

Previous theoretical expressions for computing the values of the dispersion coefficient $C_6$ are discussed at length. Theoretical sections are followed by new $C_6$ integral equations combining the Casimir-Polder relationship and expressions of the dynamic polarizabilities of the individual atom. The chapter concludes with numerical integration techniques used for validation with the currently accepted values from several published papers.

**Theory**

In the limit of $|\vec{R}| \gg a_0$, the dispersion interaction operator can be expanded in a power series of $R^{-1}$.

\[
V(\vec{R}) = \sum_{k=1}^{\infty} \sum_{k'=1}^{\infty} \frac{v_{kk'}(\hat{n})}{\vec{R}^{k+k'+1}},
\]

where $|\vec{R}|$ is the distance between two nuclei, while

\[
v_{kk'}(\hat{n}) = (-1)^{k'} \left[ \frac{(2L)!}{(2k)!((2k')!)!} \right]^{1/2} (C^K(\hat{n}) \cdot [Q^k(\vec{r}_a) \times Q^{k'}(\vec{r}_b)]^K),
\]

where $K = k + k'$, $Q^k(\vec{r}) = \gamma^k C^k(\hat{r})$ is the operator of the multipole $(2^k$-pole) electric moment, and $\hat{n} = \vec{R}/R$ is the unit vector pointing from atom $a$ to a second atom $b$.

The general expression for the long-range interaction between atoms contains first-order and second-order perturbation theory calculations and is written

\[
V(r) = -\sum_{s=1}^{\infty} \frac{C_{2s+4}}{R^{2s+4}} - \sum_{s=1}^{L_a+L_b-1} \frac{C_{2s+3}}{R^{2s+3}} - \frac{C_5}{R^5} - \frac{C_6}{R^6} - \frac{C_7}{R^7} - \frac{C_8}{R^8} - \cdots
\]

The even power terms arise from the second-order perturbation theory; whereas the second summation results from the first-order interaction between two atoms. The first-order perturbation that arises between two atomic states exists only if the orbital angular momentum of each atom is nonzero. The second summation has a finite number of terms dependent on the angular momentum of the individual atoms, $a$ and $b$, expressed in terms of $L_a$ and $L_b$, respectively.
PREVIOUS $C_6$ DISPERSION COEFFICIENT CALCULATIONS

Dispersion coefficients are often expressed in terms of oscillator strengths. There is an absorption oscillator strength $f_{0n}^{(k)}$ of multipole $k$ for transitions from $0 \rightarrow n$ which can be expressed as per Equation 62 from the previous chapter,

$$f_{0n}^{(k)} = \frac{2 | \langle \psi_0; L_0 | r^k C^k(\hat{r}) | \psi_n; L_n \rangle |^2 \varepsilon_{n0}}{(2k + 1)(2L_0 + 1)},$$  \hspace{1cm} (90)

where $\varepsilon_{n0} = E_n - E_0$ is the excitation energy of the transition.$^{21}$ In this expression, $C^k$ is the spherical tensor of rank $k$. The dipole-dipole dispersion parameter, $C_6$ between two atoms $a$ and $b$ using oscillator strength sum rules is$^{40,41}$

$$C_6 = \frac{3}{2} \sum_{i \in a, j \in b} \frac{f_{0i}^{(1)} f_{0j}^{(1)}}{\varepsilon_{0i} \varepsilon_{0j} (\varepsilon_{0j} + \varepsilon_{0i})}. \hspace{1cm} (91)$$

The generalized sum rules include the sum over excitations to bound states and excitations into the continuum states. Other sum rules for atom-atom adiabatic dispersion parameters are outside the scope of the research presented in this thesis, and include the dispersion parameter, $C_8$, which has dipole-quadrupole terms

$$C_8 = \frac{15}{2} \sum_{ij} \frac{f_{0i}^{(1)} f_{0j}^{(2)}}{\varepsilon_{0i} \varepsilon_{0j} (\varepsilon_{0j} + \varepsilon_{0i})} + \frac{15}{2} \sum_{ij} \frac{f_{0i}^{(2)} f_{0j}^{(1)}}{\varepsilon_{0i} \varepsilon_{0j} (\varepsilon_{0j} + \varepsilon_{0i})} \hspace{1cm} (92)$$

and the dispersion parameter, $C_{10}$ with dipole-octupole and quadrupole-quadrupole terms

$$C_{10} = 7 \sum_{ij} \frac{f_{0i}^{(1)} f_{0j}^{(3)}}{\varepsilon_{0i} \varepsilon_{0j} (\varepsilon_{0j} + \varepsilon_{0i})} + 7 \sum_{ij} \frac{f_{0i}^{(3)} f_{0j}^{(1)}}{\varepsilon_{0i} \varepsilon_{0j} (\varepsilon_{0j} + \varepsilon_{0i})} + \frac{35}{2} \sum_{ij} \frac{f_{0i}^{(2)} f_{0j}^{(2)}}{\varepsilon_{0i} \varepsilon_{0j} (\varepsilon_{0j} + \varepsilon_{0i})}. \hspace{1cm} (93)$$

The remainder of this thesis will omit dispersion parameters containing the quadrupole, octupole, or higher terms and focus only on the dipole-dipole dispersion parameter, $C_6$. The references for these equations are in Mitroy et al.$^{21}$ Marinescu and Dalgarno,$^{23}$ Marinescu, Babb, and Dalgarno,$^{22}$ Yan et al.$^{24}$ and Marinescu and Starace.$^{25}$

CASIMIR-POLDER IDENTITY RELATIONSHIP FOR DISPERSION COEFFICIENT CALCULATION

The aim of the current research presented in this thesis is to derive the dispersion coefficient of $C_6$ in terms of the dynamic polarizability involving states with $L > 0$. The approach by Casimir and Polder depends on the identity,

$$\frac{1}{A + B} = \frac{2}{\pi} \int_0^\infty \frac{AB}{(A^2 + \omega^2)(B^2 + \omega^2)} d\omega, \hspace{1cm} (94)$$
to express the oscillator strengths in terms of the dynamic polarizability, $\alpha^D_n$ at imaginary frequencies. The identity is applied to the formula for the excitation energies found to directly correlate to the oscillator strengths. Notice that the denominator of Equation 91 contains $(\varepsilon_{0j} + \varepsilon_{0i})$ which can be factorized into two terms $(\varepsilon_{0i}^2 + \omega^2)(\varepsilon_{0j}^2 + \omega^2)$ using the identity Equation 94 such that

$$\frac{1}{(\varepsilon_{0j} + \varepsilon_{0j})} = \frac{2}{\pi} \int_0^\infty \frac{\varepsilon_{0j}\varepsilon_{0j}}{(\varepsilon_{0j} + \omega^2)(\varepsilon_{0i} + \omega^2)} d\omega. \tag{95}$$

The $C_6$ dispersion coefficient given by Equation 91, can then be put in terms of this new identity

$$C_6 = \frac{3}{2\pi} \sum_{ij} \int_0^\infty \frac{f_{0i}^{(1)} f_{0j}^{(1)} \varepsilon_{0j}\varepsilon_{0i}}{(\varepsilon_{0j}^2 + \omega^2)(\varepsilon_{0i}^2 + \omega^2)} d\omega. \tag{96}$$

Distributing the summations inside the integral and cancellation of terms yields

$$C_6 = \frac{6}{2\pi} \int_0^\infty d\omega \sum_i \frac{f_{0i}^{(1)}}{(\varepsilon_{0i}^2 + \omega^2)} \sum_j \frac{f_{0j}^{(1)}}{(\varepsilon_{0j}^2 + \omega^2)}. \tag{97}$$

The dynamic polarizabilities in terms of frequency, $\omega$, and oscillator strength are

$$\alpha^D_n(\omega) = \sum_i \frac{f_{0i}^{(1)}}{\varepsilon_{0i}^2 - \omega^2} = \sum_i \frac{2 | \langle \psi_i; L_i || r^1 C^1(\hat{\mathbf{r}}) || \psi_j; L_j \rangle |^2 \varepsilon_{ji}}{3(2L_i + 1)(\varepsilon_{0i}^2 - \omega^2)}, \tag{98}$$

$$\alpha^D_n(i\omega) = \sum_i \frac{f_{0i}^{(1)}}{\varepsilon_{0i}^2 + \omega^2} = \sum_i \frac{2 | \langle \psi_i; L_i || r^1 C^1(\hat{\mathbf{r}}) || \psi_j; L_j \rangle |^2 \varepsilon_{ji}}{3(2L_i + 1)(\varepsilon_{0i}^2 + \omega^2)}. \tag{99}$$

Substituting these dynamic dipole polarizabilities into the dipole-dipole term (Equation 97) yields

$$C_6 = \frac{3}{\pi} \int_0^\infty \alpha^D_n(i\omega) \alpha^D_n(i\omega) d\omega. \tag{100}$$

The dispersion energy coefficient between two atoms, $a$ and $b$, is now expressed in terms of dynamic dipole polarizability at imaginary frequencies, $i\omega$ and simplified for spherical atoms ($L = 0$).

**Dynamic Dipole Polarizabilities at Imaginary Frequencies**

Chapter 5 contains validation for the computation of the dynamic dipole polarizability at imaginary frequencies; however, it is important to illustrate the general functional form of
the values to establish the reasons for choosing the numerical integration methods in the next section. The following figures show that the dynamic dipole polarizability at imaginary frequencies is well-behaved. The curves follow the characteristic of a Lorentzian as expected.\(^7\)

Figure 8 shows the dynamic scalar and tensor dipole polarizabilities \(\alpha_n^D(i\omega)\) and \(\alpha_n^T(i\omega)\) of the hydrogen atom in states \(1^2S, 2^2S, 2^2P,\) and \(3^2S\) as a function of photon energy \(\omega\) (a.u.). The computations were run with a basis sets containing \(\ell = 1, 2,\) and 3 and mixed STO and LTO with \(N = 50\). As seen in Figure 8, the static dipole polarizability increases with excited states. Of important note, the value of the ground state static dipole polarizability, \(\alpha_{1s}^D(i\omega)\), at \(\omega = 0\) is 4.5 a.u.

![Figure 8](image)

**Figure 8.** Dynamic static and tensor dipole polarizability of the hydrogen atom at imaginary frequencies, \(\alpha_n^D(i\omega)\) and \(\alpha_n^T(i\omega)\). At \(\omega = 0\), \(\alpha_{1s}^D(i\omega)\) is equal to the static dipole polarizability 4.5 a.u.

Figure 9 shows the dynamic scalar and tensor dipole polarizabilities \(\alpha_n^D(i\omega)\) and \(\alpha_n^T(i\omega)\) of the lithium atom in states \(2^2S, 2^2P\) and \(3^2S\) as a function of photon energy \(\omega\) (a.u.). The computations were run with a basis sets containing \(\ell = 1,\) and 2 and mixed STO and LTO with \(N = 50\). As seen in Figure 9, the static dipole polarizability increases with excited states but maintains the same general curvature. Of important note, the value of the ground state static dipole polarizability, \(\alpha_{2s}^D(i\omega)\), at \(\omega = 0\) is 164.04 a.u.
Figure 9. Dynamic dipole polarizability of the lithium atom at imaginary frequencies, $\alpha_D^n(i\omega)$ and $\alpha_T^n(i\omega)$. At $\omega = 0$, $\alpha_D^{2s}(i\omega)$ is equal to the static dipole polarizability 164.04 a.u.

**Computational Methods for Numerical Integration of $C_6$**

The basic computational methods are discussed in Chapter 2. The program computes $\alpha_D^n$ evaluated at imaginary frequencies, $i\omega$ through a simple sign flip,

$$\alpha_D^n(i\omega) = \sum_{m(\neq n)}^{\infty} \frac{f_{nm}}{\varepsilon_{nm}^2 + \omega^2}. \quad (101)$$

The current computation for calculating $C_6$ requires numerical solutions for improper integrals. Three methods were used to attempt numerical calculations. The first technique involved the closed Newton-Cotes formula with four points known as the Boole’s Rule. The second integration method subdivided the frequencies into panels of 16-point Gaussian Quadrature and summation over all the panels. The integral involves spanning frequencies from zero to infinity, it is necessary to transform the grid in order to achieve higher accuracy. By using the third method, the resulting transform and integration is comparable to method of a 50-point gauss-legendre quadrature.
Composite Boole’s Rule

The first approach for the numerical integration of the dipole polarizability with respect to the frequency is Boole’s Rule approximation. The Newton-Cotes like formula is in the generic form:

\[
\int_{x_1}^{x_5} f(x) \, dx \approx \sum_{j=1}^{N} w_j f(x_j) = \frac{2}{45} h(7f_1 + 32f_2 + 12f_3 + 32f_4 + 7f_5) - \frac{8}{945} h^7 f^{(6)}(\xi).
\]

(102)

The formula presents a number of disadvantages to accurately integrate the \( C_6 \) formulas. The first main drawback is the necessity to subdivide frequencies ranging from \( 0 \to \infty \) into 5-point numerical values. The grid is split into 5-point sections, each of which are summed in order to approach \( w = \infty \). Use of composite Boole’s Rule (CBR) integration scheme introduced a large error term because at long ranges it has power series decay (not exponential decay). The Newton-Cotes like formula is used for finite integrals and is a poor model to represent an upper limit of \( \infty \). This method provided the least accurate numerical solution for the integration.

Composite 16-point Gaussian Quadrature

The second numerical integration method we attempted is the use of Gaussian quadrature in order to give freedom to choose specific abscissas and weighting coefficients. Gaussian quadrature chooses optimal points for evaluation and weights such that the integral is approximated by a summation as follows:

\[
\int_{a}^{b} f(x) \, dx \approx \sum_{j=1}^{N} w_j f(x_j),
\]

(103)

where \( x_j \) are the abscissas, and \( w_j \) are a set of weights. For the purposes of validating the integration, a region spanning 1600 frequency \( \omega \) points is chosen. The 1600 point grid is subdivided into 16-point Gaussian Quadrature trying to overcome the error and compensate for the difference between the finite integration techniques and the actual improper integration required for the atomic factorization of interest to the research in the present thesis. Using the composite method, the 16-point Gaussian quadratures are simply summed up to tabulate the integral \( I = \int_{0}^{\infty} \alpha(i\omega) \, d\omega \). In this method the integration is replaced by a finite composite sum \( I = \sum_{k=1}^{100 \times N_q} w_k \alpha(i\omega_k) \) over values of \( \alpha(i\omega_k) \) tabulated at certain frequencies \( \omega_k \) yielding a
$N_g$-point quadrature repeated 100 times, where each term in the sum is weighted by factors $\omega_k$.

### Gauss-Legendre Quadrature

The tabulated grid points and weights are obtained with the Gauss-Legendre abscissas $x_k$ and weights $g_k$ defined on the interval $(0, 1)$ with $N_g = 50$ points. The weights and abscissas are generated in a computational routine. In the dynamic polarizabilities involve integration of a product of $\alpha(i\omega)$ with a smoothly behaving function $f(\omega)$,

$$I = \int_0^\infty f(\omega)\alpha(i\omega)\,d\omega.$$  

Using Gaussian quadrature, the integration is replaced by the finite sum

$$I = \sum_{k=1}^{N_g} w_k f(\omega_k)\alpha(i\omega_k)$$  

where $N_g = 50$. The basis of used the mapping of function $\omega_k = 2 \tan(\pi/2x_k)$, such that $\omega$ samples the entire integration range. The Gaussian-Legendre weights are redefined, $w_k = g_k \pi / \cos(\pi/2x_k)^2$. The results of the Gauss-Legendre quadrature and respective transform are used for validation of the $z$-transformation tabulated in the following section.

### Transform

The improper integral requires a grid of $(0, \infty)$; however, the gaussian quadrature requires a finite grid. The grid transformation used in this thesis redefines the spacing in terms of a $z$ parameter within $(0, 1)$. For any $N_g$-point quadrature, the transform is $z = \omega_k/N_g$.

Using the Gauss-Legendre abscissas $\omega_k$ and weights $g_k$, the weights are defined in terms of $z$ as

$$W_k = g_k (1 - z)^2.$$  

The integral $I = \int_0^\infty \alpha(i\omega)\,d\omega$ is replaced by the finite sum

$$I = \sum_{k=1}^{N_g} W_k \alpha(i\omega_k).$$  

In order to validate the accuracy of the computational methods; the results from the CBR with 400 points, the composite 16-point Gaussian quadrature (CGQ) with 1600 points, the Gauss-Legendre quadrature (GLQ) with 50 points, and the transformed grid (TG) with 50 points are computed using the same computational algorithms to solve for $\alpha(i\omega)$. The comparison of the different computational methods is tabulated in Table 2.

The $z$-transform computational method used for the calculations are presented in the next section. By transforming the integration grid to a finite interval, the finite summation
Table 2. Comparison of Computational Finite Sum Methods
Approximating the Improper Integral for Evaluating $C_6$

<table>
<thead>
<tr>
<th>Configuration</th>
<th>CBR(^a)</th>
<th>CGQ(^b)</th>
<th>GLQ(^c)</th>
<th>TG(^d)</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6$ (a.u.)</td>
<td>$C_6$ (a.u.)</td>
<td>$C_6$ (a.u.)</td>
<td>$C_6$ (a.u.)</td>
<td>$C_6$ (a.u.)</td>
<td></td>
</tr>
<tr>
<td>H(1s)-H(1s)</td>
<td>—</td>
<td>6.4987</td>
<td>6.4983</td>
<td>6.4990</td>
<td>6.499(^{44})</td>
</tr>
<tr>
<td>Li(2s)-Li(2s)</td>
<td>1388.68</td>
<td>1388.95</td>
<td>1389.40</td>
<td>1394.95</td>
<td>1394.60(^5)</td>
</tr>
<tr>
<td>Li(2s)-H(1s)</td>
<td>—</td>
<td>66.1078</td>
<td>66.3586</td>
<td>66.5717</td>
<td>66.5400(^5)</td>
</tr>
</tbody>
</table>

\(^a\)400-point composite Boole’s rule(CBR).
\(^b\)16-point composite Gaussian quadrature(CGQ) over a grid of 1600 points.
\(^c\)50-point Gauss-Legendre quadrature(GLQ) method outlined by Derevianko.\(^43\)
\(^d\)z-transformed gaussian quadrature (TG) using 50 points.

converges at a faster rate and requires fewer abscissas for computation. In order to achieve reasonable convergence of the composite 16-point Gaussian quadrature, 100 grids were necessary, totaling 1600 points to compute the finite summation. Composite Boole’s rule converged with 400 points; however, higher order states are affected by the high error term. Gaussian quadrature and Boole’s rule both require truncation of the infinite interval to a finite interval; therefore, the numerical value in the truncated region adds a significant amount of error to the finite sums. In the work of Derevianko, Porsev, and Babb,\(^43\) the transformation to a finite interval involves the additional fitting of the polarizability to a smoothly behaving function. Using the same abscissas, weights, and transformations, the code presented in this thesis computed the corresponding $\alpha(i\omega_k)$ values verifying the same results as Derevianko et al.\(^43\) The $z$-transform is beneficial due to the low error involved in transformation of the interval and the low number of abscissas points required to achieve convergence.

Another validation for the $z$-transformation computational method for evaluating the improper integral is a comparison of varying Li basis sets. For the computation, the hydrogen basis set is $L = 3$ containing $\ell = 0, 1, 2, 3$ with $N = 50$ while the lithium basis set is either $L = 2$, contains $\ell = 0, 1, 2$, or $L = 3$ with varying values of N to test the convergence (see Table 3). The $C_6$ parameter is computed for interactions between the ground state of H and the ground state of Li and the excited state Li($3s$) as well as the interaction between two ground state Li atoms (Li($2s$)-Li($2s$)). Note the difference between the evaluated quantities in Table 3 without core contribution and with core contribution. The addition of core
Table 3. Comparison of the Convergence of the $z$-Transformed Gaussian Quadrature Using Various Basis Sets for the Lithium Atom

<table>
<thead>
<tr>
<th></th>
<th>$N$</th>
<th>$C_6$ (a.u.)</th>
<th>$C_6$ (a.u.)</th>
<th>$C_6$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Li(2s)-Li(2s)</td>
<td>H(1s)-Li(2s)</td>
<td>H(1s)-Li(3s)</td>
</tr>
<tr>
<td>Without Core</td>
<td>20</td>
<td>1388.980962</td>
<td>66.11545200</td>
<td>432.5659635</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1388.963462</td>
<td>66.11492275</td>
<td>433.1275398</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1388.963455</td>
<td>66.11492252</td>
<td>433.1276724</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1388.963454</td>
<td>66.11492247</td>
<td>433.1276726</td>
</tr>
<tr>
<td>With Core</td>
<td>20</td>
<td>1394.961171</td>
<td>66.57205951</td>
<td>432.9070591</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1394.947286</td>
<td>66.57167630</td>
<td>433.5842738</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1394.947279</td>
<td>66.57167610</td>
<td>433.5844260</td>
</tr>
<tr>
<td>Actual$^{18}$</td>
<td></td>
<td>1394.6</td>
<td>66.54</td>
<td>514.9</td>
</tr>
</tbody>
</table>

contributions in the computations is a significant to accurately represent the atom. It appears, using $L = 3$ containing higher order angular momentum terms gives a more accurate representation of the ground state. However, the higher order lithium state (Li(3s)) diverges from the currently accepted $C_6$ values. In conclusion of this discourse about finite sum computational methods, the method for transforming the infinite interval of the improper integral to a finite integral over $[0, 1]$ using the $z$-transform and a $N_g = 50$ Gauss-Legendre quadrature finite summation is a verified means for numerical analysis.
CHAPTER 5

ATOMIC INTERACTIONS OF EXCITED STATES

The current chapter begins with a brief overview of the theory of molecular interactions characterized by London dispersion forces. Theoretical sections are followed by new $C_6$ integral equations combining the Casimir-Polder integral form and expressions of the dynamic polarizabilities of the individual atom. The new method for calculating these lowers the computational cost as well as factorizes the inter-molecular force between two atoms into the attributes of the individual atoms. Therefore, the dynamic polarizabilities evaluated at imaginary frequencies for the hydrogen and lithium atoms are tabulated independently of each other. The $C_6$ expression is an improper integral over all frequencies from zero to infinity. The method for numerical calculations requires a grid transformation over a finite interval and evaluated using a Gaussian quadrature fifty point summation. The chapter is concluded with the resulting $C_6$ computations using the Hartree-Fock frozen core configuration interaction computational methods and basis sets consisting of Slater and Laguerre type orbitals in comparison to currently accepted published results for $C_6$.

MOLECULAR WAVEFUNCTIONS

In order to build the foundation for describing molecular wavefunctions, a synthesis of several sources was used. The reason for the variety of expressions to describe molecular symmetries and how the wavefunctions interact is due to the diversity of fields responsible for their development, i.e. chemistry papers advocate $\Sigma$, $\Pi$, $\Delta$, and higher order symmetry, while some physics papers use the molecular term symbol having the general form $^{2S+1}A_{\pm}$ or $^g/u$. Although symbolically different, in one way or another, the notation contains the same basic molecular configuration information. For this thesis, the molecular wavefunctions are in terms of $M$ and use a format consistent with a distillation of several publications in order to represent molecular interactions succinctly.

The general form of the zeroth order wave function for the a system of two unlike atoms $a$ and $b$, in states with angular momentum $l_a$ and $l_b$, with a total magnetic quantum
number $M$ is:

$$
\Psi^{(0)}(M) = \sum_{m_a=-l_a}^{+l_a} \sum_{m_b=-l_b}^{+l_b} \delta_{m_a+m_b,M} C_{m_a,M} \times \Psi_{n_a l_a, m_a}(r_a) \Psi_{n_b l_b, m_b}(r_b),
$$

(106)

where $C_{m_a,M}$ in the expansion is constant. $\Psi_{n_a}$ has an energy eigenvalue of $E_{n_a}$, and $\Psi_{n_b}$ has an energy eigenvalue of $E_{n_b}$. In the case where one atom $a$ is in an $S$ state while atom $b$ is in an arbitrary state, the wave function for any $M$ becomes

$$
\Psi^{(0)}(M) = \Psi_{n_a 0, 0}(r_a) \Psi_{n_b l_b, M}(r_b),
$$

(107)

where the general form is

$$
\Psi^{(0)}(M) = \Psi_{n_a l_a, m_a}(r_a) \Psi_{n_b l_b, m_b}(r_b),
$$

(108)

with $M = m_a + m_b$. The electron-electron operator conserves $M$ but not $m_a$ or $m_b$, giving $V_{m_a m_b m'_a m'_b}^{(1)}$.

The systematics of an individual electron in a diatomic molecule is characterized by four quantum numbers. The $\pm \lambda$ of the electron angular momentum along the molecular axis passing through the two nuclei take the values $\lambda = 0, 1, 2, \ldots$ and corresponding electrons called the $\sigma, \pi, \delta, \ldots$ electrons. The electron component along the inter-molecular axis is the spin, $m_s = \pm 1/2$. The principle quantum number, $n$ and the angular momentum $l$ of the electronic state, when the inter-molecular distance $R$ approaches infinity ($R \to \infty$), denoted by $\lambda nl$ ($\sigma 2s, \pi 3p$ orbitals), or in a combined atom, $R \to 0$, denoted by $nl \lambda$ ($1s \sigma, 2p \pi$ orbitals). If the electrons have the same $n$ and $l$ they are equivalent to the number of $\sigma$ electrons which is $\leq 2$ according to the Pauli principle. In the case of homo-nuclear molecules the states of the individual electrons are distinguished by their wavefunctions symmetry reflecting the result of the coordinate inversion in the midpoint between the nuclei: even ($g$) state wavefunctions ($\sigma_g, \pi_g$, etc.) are unchanged when the coordinates of the electrons change sign, while odd ($u$) state wavefunctions change sign ($\sigma_u, \pi_u$, etc.). Even $l$ correspond to the states $s \sigma, d \sigma \rightarrow \sigma_g$, and odd $l$ correspond to the states $p \sigma \rightarrow \sigma_u, p \pi \rightarrow \pi_g$. The classification of the $g$ and $u$ symmetry is only useful for diatomic particles with one electron.

The states of a diatomic molecule can be characterized as a whole with the quantum numbers, $M_L, M_S$, and $\Omega$. The total orbital angular momentum, $M_L$ along the inter-molecular axis. $M_L$ has values $M_L = 0, \pm 1, \pm 2, \pm 3, \ldots$ and corresponding molecular states designated
The energy in the electric field of the nuclei depend on the value \( \Lambda = |M_L| \); therefore, \( \Sigma \) states are not degenerate, but \( \Pi, \Delta, \) etc states are doubly degenerate since \( M_L \) has two values \( +\Lambda \) and \( -\Lambda \). The quantum number, \( M_S \) of the electron spin \( S \), has integer or half-integer value according to whether there is an even or odd number of electrons in the molecule.

For \( P - P \) case is where atom \( a \) and atom \( b \) are both in a \( P \) state. The values of \( M \) are -2, -1, 0, 1, and 2; however the -1 and -2 cases can be reduced from \( M=1,2 \) by symmetry. There is only one term that appears in the wave function of the \( \Delta \) system where \( M=2 \). In the \( M = 1 \) case, there are two occurrences of the \( \Pi \) state. Whereas the \( M=2 \) case has three possible \( m \) combinations for the \( \Sigma \) symmetry, which forms two \( \Sigma^+ \) states and one \( \Sigma^- \) state.

For the \( P - P \) case, the overall values of \( M \) are 0, 1, and 2 (the -1 and -2 cases can be deduced from \( M = 1, 2 \) by symmetry). The \( \Delta \) system only has one term but there are two \( \Pi \) states that can occur. There are three possible \( m \) combinations for the \( \Sigma \) symmetry from which two positive symmetry \( \Sigma^+ \) states and one negative symmetry \( \Sigma^- \) state. The states with \( m_a = -m_b \neq 0 \) are in pairs compactly written as

\[
\Psi^+ = \frac{1}{\sqrt{2}} (\Psi_{n_a l_a m_a} \Psi_{n_b l_b - m_a} + \Psi_{n_a l_a - m_a} \Psi_{n_b l_b m_a}),
\]

\[
\Psi^- = \frac{1}{\sqrt{2}} (\Psi_{n_a l_a m_a} \Psi_{n_b l_b - m_a} + \Psi_{n_a l_a - m_a} \Psi_{n_b l_b m_a}).
\]

The \( \Psi_{n_a l_a,0} \Psi_{n_b l_b,0} \) state is a \( \Sigma^+ \) state.

It is possible to write a coupled state,

\[
\Psi^{(0)}(L, M) = \Psi_{n_a l_a, n_b l_b, LM}(r_a, r_b) = \sum_{m_a, m_b} \langle l_a m_a | l_b m_b | L M \rangle \Psi_{n_a l_a m_a}(r_a) \Psi_{n_b l_b m_b}(r_b),
\]

such that the molecular wave functions can be written in terms of coupled states giving the zeroth-order wave function as

\[
\Psi^{(0)}(M) = \sum_{L=|l_a - l_b|} C_{L,M} \Psi_{n_a l_a, n_b l_b, LM}(r_a, r_b).
\]
**C6 for Molecular Configurations in Terms of Oscillator Strengths**

For the smallest multipole van der Waals coefficient $C_6$ can be expressed in terms of oscillator strengths,\textsuperscript{18}

$$V_{m_am_b,m'_{a'}} = -\sum_{n_{c,d}} \frac{135}{2R^6} \frac{\tilde{p}^2_{a,b} f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} (\Delta E_{ca} + \Delta E_{db})}$$

$$\times \sum_{\mu_1 \mu_2} \sum_{m_{c,d}} \left( \begin{array}{ccc} 1 & 1 & 2 \\ -\mu_1 & \mu_1 & 0 \\ -\mu_2 & \mu_2 & 0 \end{array} \right)$$

$$\times \left( \begin{array}{ccc} l_a & 1 & l_c \\ -m_a & -\mu_1 & m_c \\ -m_b & \mu_1 & m_d \end{array} \right)$$

$$\times \left( \begin{array}{ccc} l_c & 1 & l_a \\ -m_c & -\mu_2 & m_{a'} \\ -m_d & \mu_2 & m_{b'} \end{array} \right).$$

(113)

There exist exact formulas for this potential expression which can be deduced with sums involving products of six $3jm$ symbols.\textsuperscript{49} By evaluating Equation 113 numerically, the coefficients of $C_6$ are as follows:\textsuperscript{18} The $^1\Sigma$ symmetry for an $as - bs$ configuration is

$$C_6 = \frac{3}{2} \sum_{l_c=1,l_d=1} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} (\Delta E_{ca} + \Delta E_{db})}$$

(114)

The $^1\Sigma I$ and $^1\Sigma \Sigma$ symmetries for an $as - bp$ configuration are

$$C_6 = \frac{3}{4} \sum_{l_c=1,l_d=0} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} (\Delta E_{ca} + \Delta E_{db})} + \frac{15}{8} \sum_{l_c=1,l_d=1} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} (\Delta E_{ca} + \Delta E_{db})}$$

$$+ \frac{57}{40} \sum_{l_c=1,l_d=2} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} (\Delta E_{ca} + \Delta E_{db})}$$

(115)

and

$$C_6 = 3 \sum_{l_c=1,l_d=0} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} (\Delta E_{ca} + \Delta E_{db})} + \frac{3}{2} \sum_{l_c=1,l_d=1} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} (\Delta E_{ca} + \Delta E_{db})}$$

$$+ \frac{33}{20} \sum_{l_c=1,l_d=2} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} (\Delta E_{ca} + \Delta E_{db})}$$

(116)
respectively. The value of $C_6$ for the $as - bd$ configuration is dependent on various numerical factors multiplying the sums, $c_1$, $c_2$, and $c_3$, such that

$$C_6 = c_1 \sum_{n_c,n_d}^{l_c=1,l_d=1} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db}(\Delta E_{ca} + \Delta E_{db})} + c_2 \sum_{n_c,n_d}^{l_c=1,l_d=2} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db}(\Delta E_{ca} + \Delta E_{db})} + c_3 \sum_{n_c,n_d}^{l_c=1,l_d=3} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db}(\Delta E_{ca} + \Delta E_{db})};$$

(117)

The numerical values $c_1$, $c_2$, and $c_3$ are $\frac{3}{4}$, $\frac{9}{4}$, and $\frac{9}{7}$ for the $^1\Delta$ symmetry; $\frac{15}{8}$, $\frac{9}{8}$, and $\frac{45}{28}$ for the $^1\Pi$ symmetry; $\frac{9}{7}$, $\frac{3}{4}$, and $\frac{12}{7}$ for the $^1\Sigma$ symmetry, respectively. See Appendix A for treatment of the core contribution to the $C_6$ expressions.

The previous dispersion coefficients for $C_6$ use approaches pertaining to the long-range interactions between two hetero-nuclear atoms in arbitrary atomic states. Although, the $C_6$ dispersion coefficient for two spherically symmetric atoms in their ground states is the same, the higher order state configurations require additional cross terms due to degeneracy of identical atom states. For the purpose of this research paper, only spherical atoms, specifically lithium and hydrogen are used and the dispersion coefficients between these two hetero-nuclear atoms.

**Casimir-Polder Identity Integrals for Excited State Dispersion Coefficients**

In order to solve for the higher order terms, we need to solve $M$ states tensor polarizability, $\alpha_{T,L_0,L_0}^n$ for the $s$, $p$, and $d$ states in terms of $f$-value sums. The $s$ state is given by

$$\alpha_{T,L_0,L_0}^n = \left( \sum_{i,L_i=0} f_{0i} - \sum_{i,L_i=1} f_{0i} \right)
\left( \sum_{i,L_i=0} \frac{f_{0i}}{\epsilon_{0i}^2} + \sum_{i,L_i=1} \frac{f_{0i}}{\epsilon_{0i}^2} + \sum_{i,L_i=2} \frac{f_{0i}}{\epsilon_{0i}^2} \right),$$

(118)

$$\alpha_{T,L_0,L_0}^n = - \sum_{i,L_i=1} \frac{f_{0i}}{\epsilon_{0i}^2},$$

(119)

the $p$ state is

$$\alpha_{T,L_0,L_0}^n = \left( \sum_{i,L_i=0} f_{0i} \frac{1}{\epsilon_{0i}^2} - \frac{1}{2} \sum_{i,L_i=1} f_{0i} \frac{1}{\epsilon_{0i}^2} + \frac{1}{10} \sum_{i,L_i=2} f_{0i} \frac{1}{\epsilon_{0i}^2} \right),$$

(120)
and the $d$ state dipole tensor polarizability in terms of $f$-value sums is

$$\alpha_{T, L_0 L_0}^n = - \left( \sum_{i, L_i = 0} \frac{f_{0i}}{\epsilon_{0i}} - \sum_{i, L_i = 1} \frac{f_{0i}}{\epsilon_{0i}} + \frac{2}{7} \sum_{i, L_i = 2} \frac{f_{0i}}{\epsilon_{0i}} \right). \tag{121}$$

A simplified version of the $f$-value sums is $\alpha_{D}^s = (1, 1, 1)$, $\alpha_{T}^s = (0, -1, 0)$, $\alpha_{T}^p = (-1, \frac{1}{2}, -\frac{1}{10})$, and $\alpha_{T}^d = (-1, 1, -\frac{2}{7})$. To solve for the numerical values $A$ and $B$ for the integrals where

$$C_6 = \frac{2}{\pi} A \int_0^\infty \alpha_{D}^a \alpha_{D}^b d\omega + \frac{2}{\pi} B \int_0^\infty \alpha_{D}^a \alpha_{T}^b d\omega, \tag{122}$$

it requires solving the system of equations, i.e.

$$A \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} + B \begin{pmatrix} 0 \\ -1 \\ 0 \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

such that $A - B = \frac{3}{2}$ but $B = 0$ for the $as - bs$ configurations. The $as - bp$ configuration with $1,3 \Pi$ is solved by the system of equations,

$$A \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} + B \begin{pmatrix} -1 \\ \frac{1}{2} \\ -\frac{1}{10} \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} \frac{3}{4} \\ \frac{15}{8} \\ \frac{57}{40} \end{pmatrix}$$

$$\Longrightarrow A = \frac{3}{2} \text{ and } B = \frac{3}{4}. \tag{123}$$

Similarly, for the $1,3 \Sigma$,

$$A \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} + B \begin{pmatrix} -1 \\ \frac{1}{2} \\ -\frac{1}{10} \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 3 \\ \frac{3}{4} \\ \frac{33}{26} \end{pmatrix}$$

$$\Longrightarrow A = \frac{3}{2} \text{ and } B = -\frac{3}{2}. \tag{124}$$

By the method outlined above, the $C_6$ dispersion coefficient for the $as - bs$ configuration of two hetero-nuclear atoms $a$ and $b$ in the $1,3 \Sigma$ symmetry is

$$C_6 = \frac{3}{\pi} \int_0^\infty \alpha_{D}^{as}(i\omega) \alpha_{D}^{bs}(i\omega) d\omega. \tag{125}$$
For two hetero-nuclear atoms in the $as - bp$ configuration, there are two symmetries $1^3\Pi$ and $1^3\Sigma$, which give the respective dispersion coefficients:

\[
C_6 = \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_D^{bp}(i\omega) \, d\omega + \frac{3}{2\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_T^{bp}(i\omega) \, d\omega,
\]

(126)

\[
C_6 = \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_D^{bp}(i\omega) \, d\omega - \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_T^{bp}(i\omega) \, d\omega.
\]

(127)

For two hetero-nuclear atoms in the $as - bd$ configuration, there are three possible symmetries $1^3\Delta$, $1^3\Pi$ and $1^3\Sigma$. The dispersion coefficients are (respective to the symmetries):

\[
C_6 = \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_D^{bd}(i\omega) \, d\omega + \frac{3}{2\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_T^{bd}(i\omega) \, d\omega,
\]

(128)

\[
C_6 = \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_D^{bd}(i\omega) \, d\omega - \frac{3}{4\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_T^{bd}(i\omega) \, d\omega,
\]

(129)

\[
C_6 = \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_D^{bd}(i\omega) \, d\omega - \frac{3}{2\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_T^{bd}(i\omega) \, d\omega.
\]

(130)

For two hetero-nuclear atoms in the $as - bf$ configuration, there are four symmetries $1^3\Phi$, $1^3\Delta$, $1^3\Pi$ and $1^3\Sigma$, where the respective dispersion coefficients are:

\[
C_6 = \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_D^{bf}(i\omega) \, d\omega + \frac{3}{2\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_T^{bf}(i\omega) \, d\omega,
\]

(131)

\[
C_6 = \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_D^{bf}(i\omega) \, d\omega
\]

(132)

\[
C_6 = \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_D^{bf}(i\omega) \, d\omega - \frac{9}{10\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_T^{bf}(i\omega) \, d\omega,
\]

(133)

\[
C_6 = \frac{3}{\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_D^{bf}(i\omega) \, d\omega - \frac{6}{5\pi} \int_0^\infty \alpha_D^{as}(i\omega) \alpha_T^{bf}(i\omega) \, d\omega.
\]

(134)

Chu et al.\(^8\) developed a concise version using the $C_6$ dispersion coefficient calculated by methods found in Stone\(^4\) dependent on the second order interaction between an $S$-state and an open-shell atom with total orbital angular momentum $L$, where $M$ is the projection of the angular momentum on the internuclear axis.

\[
C_6(L, M) = \frac{2}{\pi} \int_0^\infty \alpha_{zz}(L, M; i\omega) \tilde{\alpha}_{He}(i\omega) \, d\omega + \frac{1}{\pi} \int_0^\infty \alpha_{XX}(L, M; i\omega) \tilde{\alpha}_{He}(i\omega) \, d\omega,
\]

(135)

in this form, the $2(2L + 1)$ polarizabilities can be expressed as $\alpha_D(L, i\omega)$, the dipole-dipole scalar polarizability at imaginary frequencies, and $\alpha_T(L, i\omega)$, the tensor dipole polarizability. They describe a dispersion coefficient, $C_{6,0}(L)$ that depends on $\alpha_D(L, i\omega)$

\[
C_{6,0}(L) = \frac{3}{\pi} \int_0^\infty \alpha_D(L; i\omega) \tilde{\alpha}_{He}(i\omega) \, d\omega
\]

(136)
and the $C_{6,2}(L)$ term dependent on $\alpha_T(L, i\omega)$

$$C_{6,2}(L) = -\frac{3(2L + 3)}{2\pi L} \int_0^\infty \alpha_T(L; i\omega)\tilde{\alpha}_D^H(i\omega) \, d\omega.$$  \hspace{1cm} (137)

Combining $C_{6,0}(L)$ and $C_{6,2}(L)$, all dispersion coefficients may be described as

$$C_6(L, M) = C_{6,0}(L) - \frac{3M^2 - L(L + 1)}{(2L - 1)(2L + 3)}C_{6,2}(L).$$  \hspace{1cm} (138)

The formulas derived in this section were used to compute the $C_6$ dispersion coefficients between various ground and excited states of the Li and H atoms. The evaluation of these formulas requires calculation of $\alpha_D(L, i\omega)$ and $\alpha_T(L, i\omega)$, and a numerical integration method with respect to $\omega$. The following section will focus on the computational methods required to evaluate numerical values of the $C_6$ dispersion coefficients.

**CALCULATIONS**

The present thesis reports the values of the $C_n$ coefficients between different combinations of the low-lying states of a pair of hetero-nuclear lithium and hydrogen atoms. Dynamic dipole polarizabilities describe the response of atoms to applied electric fields and are useful for application in computing the long-range dispersion interactions. By evaluating the dynamic dipole and tensor polarizabilities as functions of imaginary frequencies for the individual atoms, the long-range dispersion interaction, $C_6$, between two atoms is calculated. By using Casimir-Polder method and identity relationship, evaluation of the $C_6$ dispersion interaction is factorized into the individual atom’s dynamic dipole and tensor polarizabilities as functions of imaginary frequencies.

In order to accurately factorize the polarizability functions, it is necessary to ensure the basis set is an accurate representation of the atom. Comparisons of the resulting evaluations of the dynamic dipole polarizability as a function of imaginary frequencies for the ground state hydrogen atom are listed in Table 4. The data is based on a 50-point Gauss-Legendre summation of a transformed grid, frequencies $\omega = 0, 1.06, \text{ and } 4.098$ are compared for different basis sets of $N = 20, 30, 40, \text{ and } 50$. The transform summation and corresponding dispersion coefficients $C_6$ for two ground state hydrogen atoms, $1^2S - 1^2S$, are listed in comparison to the $C_6$ sum computed with the sum rules in the code. The dispersion coefficient $C_6$ between the ground state hydrogen atoms at large internuclear distances are tabulated as well in order to illustrate the effect of the factorized summation suggested in evaluation of $C_6$ presented in this thesis.
Table 4. Comparison of $\alpha_{1s}^D(i\omega)$ for Hydrogen Evaluated at Various Frequencies $\omega$ and Basis Set Sizes $N$ With Corresponding Dispersion Coefficients $C_6$ for Two Ground State Hydrogen Atoms

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>$N^a$</th>
<th>$N^a$</th>
<th>$N^a$</th>
<th>$N^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000000</td>
<td>4.500000</td>
<td>4.500000</td>
<td>4.500000</td>
<td>4.500000</td>
</tr>
<tr>
<td>1.064193</td>
<td>6.7214587(-1)</td>
<td>6.7214587(-1)</td>
<td>6.7214587(-1)</td>
<td>6.7214587(-1)</td>
</tr>
<tr>
<td>4.098177</td>
<td>5.7519324(-2)</td>
<td>5.7519324(-2)</td>
<td>5.7519324(-2)</td>
<td>5.7519324(-2)</td>
</tr>
<tr>
<td>$C_6^b$</td>
<td>6.499026705</td>
<td>6.499026705</td>
<td>6.499026705</td>
<td>6.499026705</td>
</tr>
<tr>
<td>$C_6^c$</td>
<td>6.499026705</td>
<td>6.499026705</td>
<td>6.499026705</td>
<td>6.499026705</td>
</tr>
</tbody>
</table>

$^a$The numbers in the parentheses denote powers of ten.

$^b$ $C_6$ using 50-point transform summation rules and Casimir-Polder relationship.

$^c$ $C_6$ computed by sum rules in the code.

The ground state of hydrogen is well represented by the basis function irrespective of the value $N$; however, the impact of the size of the basis set increases at higher order atomic states. Table 5 compares the dynamic and tensor polarizabilities, $\alpha_D$ and $\alpha_T$ as functions of imaginary frequencies, $i\omega$ for the hydrogen atom in the first excited state $2^2P$. Again, the values of $\alpha_D$ and $\alpha_T$ are listed at frequencies $\omega = 0, 1.064, 4.098$ for basis sets varying in size $N = 20, 30, 40, 50$. The values are erratic at lower basis set sizes $N = 20, 30$, while the values converge for $N = 40, 50$. The identity found by Casimir-Polder was used for solving the dispersion interaction between atom $A$ and $B$ is a combination of the integrals in the form $\int_0^\infty \alpha_D^A(i\omega)\alpha_D^B(i\omega)d\omega$ and $\int_0^\infty \alpha_T^A(i\omega)\alpha_T^B(i\omega)d\omega$. The dispersion interaction $C_6$ is calculated with the Casimir-Polder identity integrals and the 50-point transform summations are $\sum_{k=0}^{50} g_k(1 - z)^2 \alpha_D^A(i\omega)\alpha_D^B(i\omega)$ and $\sum_{k=0}^{50} g_k(1 - z)^2 \alpha_T^A(i\omega)\alpha_T^B(i\omega)$, respectively. The Gauss-Legendre weights are $g_k$ and $z = w_k/50$, where $w_k$ are the abscissas.

Despite the variations in the polarizability at the select frequencies, $\omega$, the 50-point Gauss-Legendre quadrature summations yield equivalent results independent of the basis set size. The hydrogen validations for the dispersion interaction, $C_6$, represent calculations of the ground $1^2S$ state and the higher order $2^2P$ state of hydrogen. In Table 5 the transform summations for two hydrogen atoms in the ground and excited $2P$ state, $1^2S - 2^2P$, are listed for $\int \alpha_D^{1s}(i\omega)\alpha_D^{2p}(i\omega)d\omega$ and $\int \alpha_T^{1s}(i\omega)\alpha_T^{2p}(i\omega)d\omega$. The Casimir-Polder relationship allows the
Table 5. Comparison of $\alpha_2^p(i\omega)$ and $\alpha_2^p(i\omega)$ for Hydrogen at Various Frequencies $\omega$ and Basis Set Sizes $N$ With Corresponding Transform Summations for $\int \alpha_1^s(i\omega)\alpha_2^p(i\omega)d\omega$ and $\int \alpha_1^s(i\omega)\alpha_2^p(i\omega)d\omega$

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>$N^a$</th>
<th>$N^a$</th>
<th>$N^a$</th>
<th>$N^a$</th>
</tr>
</thead>
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<tr>
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<td>5.9545(-2)</td>
<td>5.9545(-2)</td>
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</table>

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
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<th>$N^a$</th>
<th>$N^a$</th>
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</thead>
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<tr>
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<td>-20.00</td>
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<td>-5.9246(-5)</td>
<td>-5.9246(-5)</td>
<td>-5.9246(-5)</td>
</tr>
</tbody>
</table>

$\int \alpha_1^s \alpha_2^p d\omega$ \(b\) using 50-point transform summation rules and Casimir-Polder relationship.

$\int \alpha_1^s \alpha_2^p d\omega$ \(c\) using 50-point transform summation rules and Casimir-Polder relationship.

\(a\)The numbers in the parentheses denote powers of ten.

\(b\) $\int \alpha_1^s \alpha_2^p d\omega$ using 50-point transform summation rules and Casimir-Polder relationship.

\(c\) $\int \alpha_1^s \alpha_2^p d\omega$ using 50-point transform summation rules and Casimir-Polder relationship.

factorization of the integrals into functions of the individual atoms’ dynamic and tensor polarizabilities; therefore, the $C_6$ dispersion coefficient between two atoms is calculated in a relatively simple summation.

Table 6 lists the $C_6$ dispersion coefficients calculated using the methods described in the present thesis. The various symmetries involved in the system configurations correspond to different combinations with certain coefficient weightings in the Casimir-Polder relationship Equations 125, 127, 130, and 134. The two atoms used in the current research are hydrogen and lithium. The chosen basis sets contain $\ell = 0, 1, 2,$ and $3$ ($L = 3$) corresponding to a complete set of $S, P, \text{and} D$ states with sizes $N = 50$. The calculation of $C_6$ for the homo-nuclear atoms H-H and Li-Li are listed in ground state and low level excited state interactions. The alkali-metal combination of Li-H between $1^2S$ ground state hydrogen and states of ground and low level excited states of Li. The calculated values are compared to published results in the correspondingly cited references.\(^{5,24,43,44,48,50}\) Appendix B is an integral summation matrix allowing for the quick calculation of $C_6$ by plugging in the
Table 6. The Dispersion Coefficients $C_6$ Between Li, H and the Lower Alkali-Metal Combination Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Symmetry</th>
<th>$C_6$ (a.u.)</th>
<th>$C_6$ (a.u.) $[References]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH $1s - 1s$</td>
<td>$^1S\Sigma$</td>
<td>6.499</td>
<td>6.499 $[44]$</td>
</tr>
<tr>
<td>HH $1s - 2s$</td>
<td>$^1S\Sigma$</td>
<td>55.25</td>
<td>55.25 $[44]$</td>
</tr>
<tr>
<td>HH $1s - 2p$</td>
<td>$^1S\Sigma$</td>
<td>83.62</td>
<td>83.63 $[44]$</td>
</tr>
<tr>
<td>HH $1s - 2p$</td>
<td>$^1P\Sigma$</td>
<td>71.82</td>
<td>71.82 $[44]$</td>
</tr>
<tr>
<td>HH $2s - 2s$</td>
<td>$^1S\Sigma$</td>
<td>853.75</td>
<td>853.75 $[44]$</td>
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<tr>
<td>HH $1s - 3s$</td>
<td>$^1S\Sigma$</td>
<td>180.32</td>
<td></td>
</tr>
<tr>
<td>HH $3s - 3s$</td>
<td>$^1S\Sigma$</td>
<td>20804.26</td>
<td></td>
</tr>
<tr>
<td>LiLi $2s - 2s$</td>
<td>$^1S\Sigma$</td>
<td>1394.9</td>
<td>1394.6 $[5]$</td>
</tr>
<tr>
<td>LiLi $2s - 3s$</td>
<td>$^1S\Sigma$</td>
<td>$1.3423 \times 10^4$</td>
<td>1.3850 $\times 10^4$ $[5]$</td>
</tr>
<tr>
<td>LiLi $3s - 3s$</td>
<td>$^1S\Sigma$</td>
<td>$2.1177 \times 10^5$</td>
<td>$1.9591 \times 10^5$ $[5]$</td>
</tr>
<tr>
<td>LiLi $4s - 4s$</td>
<td>$^1S\Sigma$</td>
<td>$5.7531 \times 10^6$</td>
<td>$4.6129 \times 10^6$ $[5]$</td>
</tr>
<tr>
<td>LiH $2s - 1s$</td>
<td>$^1S\Sigma$</td>
<td>66.57</td>
<td>66.54 $[5]$</td>
</tr>
<tr>
<td>LiH $3s - 1s$</td>
<td>$^1S\Sigma$</td>
<td>433.58</td>
<td>514.90 $[5]$</td>
</tr>
<tr>
<td>LiH $2p - 1s$</td>
<td>$^1S\Sigma$</td>
<td>58.29</td>
<td>160.10 $[5]$</td>
</tr>
<tr>
<td>LiH $2p - 1s$</td>
<td>$^1P\Sigma$</td>
<td>59.99</td>
<td>85.43 $[5]$</td>
</tr>
<tr>
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<td>$^1S\Sigma$</td>
<td>402.78</td>
<td></td>
</tr>
<tr>
<td>LiH $3p - 1s$</td>
<td>$^1P\Sigma$</td>
<td>431.69</td>
<td></td>
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<tr>
<td>LiH $3d - 1s$</td>
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<td>53.07</td>
<td>715.0 $[5]$</td>
</tr>
<tr>
<td>LiH $3d - 1s$</td>
<td>$^1P\Sigma$</td>
<td>82.18</td>
<td>633.8 $[5]$</td>
</tr>
<tr>
<td>LiH $3d - 1s$</td>
<td>$^1\Delta$</td>
<td>169.52</td>
<td>390.1 $[5]$</td>
</tr>
</tbody>
</table>

The corresponding integrals into Equations 125, 127, 130, and 134 relating to the system configuration and symmetry of two hetero-nuclear atoms hydrogen and lithium.

The dispersion coefficient $C_6$ for the homo-nuclear interactions between hydrogen atoms are in agreement with currently acceptable values. The case for the homo-nuclear interaction between two ground state lithium atoms is the only computed dispersion coefficient that agrees with Zhang, Mitroy, and Bromley. For the long-range dispersion interactions for two hetero-nuclear atoms hydrogen and lithium, the ground state atomic interactions calculated agree with Zhang, Mitroy, and Bromley and Yan et al.; however, the
higher order states of lithium diverge from references Zhang, Mitroy, and Bromley\textsuperscript{5} and Zhu, Zhou, and Yan.\textsuperscript{50} The methods used by Zhang, Mitroy, and Bromley\textsuperscript{5} and Zhu, Zhou, and Yan\textsuperscript{50} for calculating the long-range dispersion coefficients are based on oscillator strength summations, not the explicit calculations of dipole and tensor polarizabilities used in this current research. Further analysis is necessary to resolve the discrepancies between the dynamic dipole polarizability summations for $C_6$ and the oscillator strength summation method for $C_6$ calculations.
CHAPTER 6
CONCLUSION

Through the discourse of the present thesis, two main conclusions are apparent. The first is the demonstrated ability to calculate dynamic dipole and tensor polarizabilities at real and imaginary frequencies using Hartree-Fock frozen core configuration interaction with a basis set described by a combination of Slater type and Laguerre type orbitals. The second conclusion is the demonstrated ease of factorizing the long-range dispersion force coefficient $C_6$ between two atoms into the integrals containing the dynamic dipole and tensor polarizabilities evaluated at imaginary frequencies of the individual atoms.

The dynamic dipole polarizabilities are related to the second order perturbation of the Schrödinger equation. The Hamiltonian is perturbed when atoms are placed in an uniform electric field, which yields high precision frequency standards for describing optical transitions. Given the sophistication of the computations, the dynamic dipole polarizabilities are analytically represented for frequencies ranging from $\omega = 0$ into the continuum $\omega = 0.25$ for $^7\text{Li} \, 2^2S$, $2^2P$, and $3^2S$ states. The values are in the non-relativistic limit showing the transition frequencies expected based on NIST$^{32}$ as well as higher order transitions and erratic behavior at frequencies approaching the continuum.

Based on the experimental current research on the absolute frequency measurements on the $2S - 3S$ transition of lithium-7.$^1$ The frequencies of the $2S - 3S$ two-photon transition for the stable lithium isotopes were measured using advanced experimental techniques requiring a cavity-enhanced Doppler-free laser excitation controlled by a femtosecond frequency comp. The experimental measurements of the transition equated photon transitions of $E_2 = 0.075$ Hartree and $E_1 = 0.062$ Hartree. The dynamic dipole polarizability difference between the $2^2S$ and $3^2S$ lithium-7 atom illustrates the transition rates in Figure 7. The vertical lines are the change in the dynamic dipole polarizability at $E_1$ and $E_2$. The high precision of the theoretical calculations presented in Chapter 2 are beneficial to experimentalists in order to diffuse the discrepancy between the most current measured and theoretical values.
The primary aim of the current research is the calculation of the long-range interactions between two hetero-nuclear atoms in arbitrary atomic states. For two spherically symmetric atoms, the long-range interaction potential is expressed with dispersion coefficients given by $C_n$ parameters as a function of $R^n$ distance between two nuclei. The main focus is to use the current computational methods and achieve high precision values of the dispersion coefficient $C_6$ for the homo-nuclear interaction of hydrogen and lithium as well as the hetero-nuclear interaction between hydrogen and lithium. The derivation of the $C_6$ dispersion coefficient equations are Equations 125, 127, 130, and 134 are dependent on the configuration and symmetries of the two atom systems.

The $C_6$ parameter is related to the dynamic polarizabilities, $\alpha^{n_D}$ and $\alpha^{n_T}$ of the individual atoms evaluated at imaginary frequencies. The computation of the polarizabilities at imaginary frequencies turns out to only require a sign change and is not as computationally laborious as oscillator strength calculations requiring knowledge of all atomic transitions. By expressing the dispersion coefficient in terms of polarizability and relying on the integral identity described by Casimir-Polder’s, the $C_6$ dispersion coefficient between atoms $A$ and $B$ takes the form $c \int_0^\infty \alpha^{n_D}_A(i\omega)\alpha^{n_D}_B(i\omega)d\omega$ and $d \int_0^\infty \alpha^{n_D}_A(i\omega)\alpha^{n_T}_B(i\omega)d\omega$, where $c$ and $d$ are weighting factor dependent on the symmetry of the atomic configuration. Numerical integration methods require a grid transformation to a finite interval and the Gaussian quadrature, requiring a reasonably straightforward summation for evaluating the integrals.

Chapter 5 lists the tabulated $C_6$ compared to currently accepted and published values. The homo-nuclear atom interaction for H-H and Li-Li configurations for different symmetries and energy state combinations are found in Table 6. In the table, the $C_6$ for the hetero-nuclear atom interactions for configurations of Li-H are also tabulated. The lowest energy configuration for Li-H is in agreement with published values based on sum rules of oscillator strengths; however, higher order energy configurations diverge from the expected values. Appendix B is an integral summation matrix used for computing the $C_6$ dispersion coefficient by multiplying by the appropriate symmetry configuration weighting. Linear combinations of the integrals multiplied by weighting coefficients give all the low level configuration states.

A major goal of future research efforts will include figuring out the convergence of the higher order configuration states of the $C_6$ parameter describing long-range hetero-nuclear interactions. The same equations and methodology outlined in the pages of this thesis are applicable to other alkali metal atoms and can be tabulated using the same code. Larger atoms
may require relativistic techniques to achieve the correct dispersion force values. Other future research will include the optimization of choosing the Laguerre type orbital $g$ parameter to describe the various atomic states. Another future research goal is to apply the $C_6$ expressions to the long-range molecular interaction of the $H_2$ molecule with an alkali-metal atom. Evaluation of the $C_6$ parameter will require computation of the dynamic polarizabilities of the $H_2$ molecule, adding to the expanding interest in inter-molecular forces at long-ranges.
REFERENCES


J.-M. Zhu, B.-L. Zhou and Z.-C. Yan, “Long-range interactions for H(1s)-He(1s), H(1s)-Li(2P) and He(1S)-Li(2P),” J. Phys. B 34, 1535 (2001).
APPENDIX A

TREATMENT OF CORE EXCITATION
TREATMENT OF CORE EXCITATION

Calculations involving sum rules use core and valence excitation contributions requiring diagonalizing the Hamiltonian in a very large basis. The method described using sum rules is a brute-force calculation. The valence excitation f-value sum rules are found as described in Chapter 3; however, the core contribution is computed with the sum rule for the polarizability,

$$\alpha_{\text{core}} = \sum_{i \in \text{core}} \frac{N_i}{(\epsilon_i + \Delta)^2}, \quad (139)$$

where \(N_i\) is the number of electrons in the core orbital, \(\epsilon_i\) is the Koopman energy, and \(\Delta\) is an energy shift parameter chosen to fit other core polarizability estimates. Equation 139 and

$$\ell N \langle r^{2\ell-2} \rangle = \sum_i f_i^{(\ell)} \quad (140)$$

are used to estimate an \(f^{(\ell)}\)-value distribution function. The expression reduces for the dipole case \(\ell = 1\) to the Thomas-Reiche-Kuhn sum rule,

$$N = \sum_i f_i^{(1)} \quad (141)$$

where \(N\) is the total number of electrons and \(\langle r^{2\ell-2} \rangle\) is the expectation value of the ground state wave function. Assuming the contribution of each closed subshell \((N_i)\) is equal to the number of electrons in the subshell multiplied by the mean value of \(r^{2\ell-2}\) for the subshell, where \(\langle r^{2\ell-2} \rangle\) is computed using the Hartree-Fock (HF) wave function. The excitation energy for each subshell is set to Koopman energy, \(\epsilon_i\) plus an energy shift; therefore, the expression

$$\alpha_{\text{core}}^{(\ell)} = \sum_i \frac{\ell N_i r_i^{2\ell-2}}{(\epsilon_i + \Delta^{(\ell)})^2}, \quad (142)$$

is used to fix \(\Delta^{(\ell)}\) to fit the computed polarizability values to the known theoretical values. The \(C_6\) parameter for atoms \(a\) and \(b\) can be partitioned into

$$C_6 = C_6^c + C_6^w + C_6^{cv}, \quad (143)$$
where
\[ C_6^w = \frac{3}{2} \sum_{i \in \text{core:a}} \sum_{j \in \text{core:b}} \frac{N_i N_j}{(\epsilon_i + \Delta_a^{(1)})(\epsilon_j + \Delta_b^{(1)})}, \tag{144} \]
\[ C_6^{cw} = \frac{3}{2} \sum_{i \in \text{core:a}} \sum_{j \in \text{val:b}} \frac{N_i f_{0j}}{(\epsilon_i + \Delta_a^{(1)})\epsilon_{0j}(\epsilon_i + \Delta_a^{(1)} + \epsilon_{0j})} \]
\[ + \frac{3}{2} \sum_{i \in \text{val:a}} \sum_{j \in \text{core:b}} \frac{f_{0i} N_j}{\epsilon_{0i}(\epsilon_j + \Delta_b^{(1)})(\epsilon_{0i} + \epsilon_j + \Delta_b^{(1)})}, \tag{145} \]

and
\[ C_6^v = \frac{3}{2} \sum_{i,j \in \text{val}} \frac{f_{0i} f_{0j}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j} + \epsilon_{0i})}. \tag{146} \]

From the core contribution expressions, the relative contributions of the core to \( \alpha^{(\ell)} \) get smaller as \( \ell \) increases because of the weighting factor, \( \ell r_i^{(2\ell-2)} \). Note that for this thesis all polarizabilities (real and imaginary) were computed with modified Equation 142:
\[ \alpha_D^{(\ell)}(\omega) = \alpha_{\text{valence}}^{(\ell)}(\omega) + \alpha_{\text{core}}^{(\ell)}(\omega) = \alpha_{\text{valence}}^{(\ell)}(\omega) + \sum_i \frac{\ell N_i r_i^{2\ell-2}}{(\epsilon_i + \Delta^{(\ell)})^2 - \omega^2}. \tag{147} \]

The same methodology is used for the tensor polarizability, \( \alpha_T^{(\ell)}(\omega) \).
APPENDIX B
INTEGRAL SUMMATION MATRICES
INTEGRAL SUMMATION MATRICES

The following three tables are matrices of the integral calculations
\[ \int \alpha_s^D(i\omega)\alpha_{D/T}^{s,p,d,f}(i\omega)d\omega \] for the different molecular configuration of H-H, Li-Li, and Li-H. By locating the spherical \( S \)-state of the particular atom, i.e. \( \alpha_s^D \) of interest along the top row of each matrix, and locating the proper atom along the left side column, \( \alpha_{D/T}^{s,p,d,f} \), the intersecting matrix element is the value of \[ \int \alpha_s^D(i\omega)\alpha_{D/T}^{s,p,d,f}(i\omega)d\omega. \] In referencing Chapter 5, the coefficients for the different molecular symmetries can be applied in order to calculate the dispersion coefficient, \( C_6 \). Tables 7, 8, 9, and 10 use a 50 point transform numerical integration method to solve \[ \int \alpha_n^D\alpha_{D/T}^nd\omega. \] The calculated (rounded) terms are required for solving the dispersion coefficients given the proper coefficient for the various symmetries Chapter 5. Integral summation matrices only have elements when one atom is in the \( \ell = 0, s \) state.

Table 7. H-H Integral Summation Matrix

<table>
<thead>
<tr>
<th></th>
<th>( \alpha_1^{sH} )</th>
<th>( \alpha_2^{sH} )</th>
<th>( \alpha_3^{sH} )</th>
<th>( \alpha_4^{sH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_1^{sH} )</td>
<td>6.81</td>
<td>57.86</td>
<td>188.83</td>
<td>435.49</td>
</tr>
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<td>( \alpha_2^{sH} )</td>
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<td>894.04</td>
<td>3882.95</td>
<td>10147.79</td>
</tr>
<tr>
<td>( \alpha_2^{pH} )</td>
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<td>1271.23</td>
<td>5612.97</td>
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<td>( \alpha_2^{pH} )</td>
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<td>( \alpha_3^{sH} )</td>
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<td>3882.91</td>
<td>21786.19</td>
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<td>( \alpha_3^{pH} )</td>
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<td>4814.294</td>
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Table 8. Li-Li Integral Summation Matrix

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<th>$\alpha_{4s Li}^{4s}$</th>
<th>$\alpha_{5s Li}^{5s}$</th>
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<td>$\alpha_{D}^{2s}$</td>
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<td>0.00</td>
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<td>2719619.89</td>
<td>18854569.47</td>
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Table 9. Li-H Integral Summation Matrix for $1^2S$, $2^2S$, $3^2S$, and $4^2S$ Hydrogen States

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<th>$\alpha_{D}^{3sH}$</th>
<th>$\alpha_{D}^{4sH}$</th>
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Table 10. Li-H Integral Summation Matrix for $^{2}S$, $^{3}S$, $^{4}S$, and $^{5}S$ Lithium States

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<th>$\alpha_{D}$</th>
<th>$\alpha_{T}$</th>
<th>$\alpha_{D}$</th>
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<tbody>
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<td>$\alpha_{2sLi}^{2pH}$</td>
<td>1625.1</td>
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<td>67064.1</td>
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