ON ELECTRONIC REPRESENTATIONS IN MOLECULAR REACTION DYNAMICS

By

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This work is dedicated to Breana, Antonia, and Blake Jones.

May the love and wonder of science always be near.
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ON ELECTRONIC REPRESENTATIONS IN MOLECULAR REACTION DYNAMICS

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For many decades, the field of chemical reaction dynamics has utilized computational methods that rely on potential energy surfaces that are constructed using stationary-state calculations. These methods are typically devoid of dynamical couplings between the electronic and nuclear degrees of freedom, a fact that can result in incorrect descriptions of dynamical processes. Often, non-adiabatic coupling expressions are included in these methodologies. The Electron-Nuclear Dynamics (END) formalism, in contrast, circumvents these deficiencies by calculating all intermolecular forces directly at each time step in the dynamics and by explicitly maintaining all electronic-nuclear couplings.

The purpose of this work is to offer two new frameworks for implementing electronic representations in dynamical calculations. Firstly, a new schema is proposed for developing atomic basis sets that are consistent with dynamical calculations. Traditionally, basis sets have been designed for use in stationary-state
calculations of the structures and properties of molecules in their ground states. As a consequence of common construction techniques that utilize energy optimization methods, the unoccupied orbitals bear little resemblance to physical virtual atomic orbitals. We develop and implement a method for basis set construction that relies upon physical properties of atomic orbitals and that results in meaningful virtual orbitals. These basis sets are shown to provide a significant improvement in the accuracy of calculated dynamical properties such as charge transfer probabilities.

Secondly, the theoretical framework of END is expanded to incorporate a multi-configurational representation for electrons. This formalism, named Vector Hartree-Fock, is based in the theory of vector coherent states and utilizes a complete active space electronic representation. The Vector Hartree-Fock method is fully disclosed, with derivation of the equations of motion. The expressions for the equation of motion are derived in full and a plan for implementing the Vector Hartree-Fock formalism within the current ENDyne computer code is given.
Chemistry is the study of how atoms and molecules change with time, and fundamentally requires a dynamical description to correctly describe these changes. Experimental physical chemistry is concerned with measurement of chemical changes and the enumeration of the properties associated with these changes. Quantum chemistry, on the other hand, seeks to describe the mechanism through which chemical changes occur and to calculate properties associated with these changes as a function of fundamental properties of the molecule itself.

Virtually all of chemistry is described in the vocabulary of dynamics. Chemists speak of electron transfers, transition states, equilibria. The most fundamental measurements made in a physical chemistry laboratory involve transference of heat over time, the number of vibrations a molecule undergoes in a unit of time, the inversion of electron populations as a function of time. Chemistry is dynamic. Despite all of this, non-dynamical approaches are still most often employed when performing chemical calculations. These approximations are often sufficient for obtaining average properties, but fail to offer a deeper understanding of chemical processes that comes through dynamical methods.

Traditionally, chemists have been interested in answering two general classes of questions regarding chemical reactions. The first, “To what extent will a reaction occur?” is purely thermodynamic in nature. Provided the difference in the free energy between the product species and the reactant species is negative, the reaction has the potential to occur spontaneously to some extent. Calculations of this type are well-suited to time-independent quantum mechanics; stationary state
energy values can be calculated for various ground and excited states, which can yield (through the application of statistical thermodynamical principles) the free energies of the products and the reactants.

The second class of question that a chemist might ask is, “How fast will the reaction occur?” This type of question is kinetic in nature and relies upon some (usually detailed) knowledge of the dynamics of the reaction. This type of question is, in generally, only successfully answered using time-dependent quantum mechanical treatments. To correctly describe the kinetics of a reaction, one must first describe the interactions through and responses to inter- and intramolecular forces as a function of the time-scale of the reaction.

The focus of this dissertation is to investigate methods of improving representations of electrons for use in time-dependent dynamical calculations. Specifically, this work will investigate two sides of the very same coin. Firstly, a discussion will be made toward basis set expansion for use in construction of the electronic wave function. A new method will be proposed for the construction of dynamically consistent basis sets. Two particular features of the proposed construction method are the physical basis that underlies the method and its ease of application. Secondly, discussion will be made toward the construction of a multi-configurational wave function for use with the Electron-Nuclear Dynamics formalism. The full set of equations of motion are derived for the Vector Hartree-Fock implementation of Electron-Nuclear Dynamics in terms of a general expansion of atomic basis functions. Additionally, discussion is made as to a possible scheme for implementation.

This chapter provides a basic review of quantum molecular dynamics. Subsequently, a brief discussion is made of the general structure of the Time-Dependent Hartree-Fock method. Finally the Electron-Nuclear Dynamics formalism in its simplest form is introduced and discussed and compared to Time-Dependent Hartree-Fock.
1.1 Précis of Quantum Dynamics

The physical description of any chemical object is predicated on the concepts of a quantum mechanical state and a quantum mechanical configuration [1]. A quantum mechanical configuration is the set of all descriptive variables in the dynamical phase space (e.g., momentum and position) and/or in the electronic Hilbert space (e.g., orbital and spin angular momentum) which describes (within the completeness of the set) a given chemical object at any given instant in time, \( t = \tau \) [1]. The configuration is usually represented as a ket in Dirac notation, written as \( |\phi, t = \tau\rangle \), where \( \phi \) is a representative of the required set of descriptive variables. If \( \tau \) is specifically defined, then the configuration may be more conveniently expressed as \( |\phi\rangle \).

A quantum mechanical state, or wave-function, can also be expressed in Dirac notation, \( |\phi, t\rangle \), where \( t \) indicates the general dependence on time. The state can be defined as any subset of the complete set of configurations that contains a given configuration, \( |\phi, t = \tau\rangle \), as well as all configurations that result from the dynamical evolution of \( |\phi, t = \tau\rangle \) and all configurations that evolve into \( |\phi, t = \tau\rangle \) with the passage of time (assuming no perturbation of the system by outside influences) [1]. Some descriptions must include the time dependence explicitly in the wave-function, while others allow for the time-dependence to be treated as separable factor, depending on the appearance of time in the Schrödinger Equation [2]. For a state to be completely described, one must know the relation between all variables that determine the state at a specific time, usually denoted as time \( t = 0 \).

Investigation of chemical processes requires the knowledge of how a given state evolves with time — how the state changes dynamically. The principle tool in the descriptions of quantum chemical dynamics is the Schrödinger Wave Equation, a time-dependent differential equation of second order spatially and first order temporally. The Schrödinger Equation defines the equations of motion for a given
quantum mechanical state; once the initial state is completely described, then the
time evolution of the state as defined by the state-specific Schrödinger Equation
allows one to correctly predict the future properties of the state based on its initial
conditions. The state-specific Schrödinger Equation can be expressed in function
notation as
\[- \sum_{i=1}^{N} \frac{\hbar}{2M_i} \nabla^2_i |\phi, t\rangle \right. \left. + V(\phi, t)|\phi, t\rangle = i\hbar \frac{\partial}{\partial t} |\phi, t\rangle. \]  
(1.1)

On the left hand side of Equation (1.1), the first term is the kinetic energy of the
state; the summation is over the \(N\) particles comprising the state, \(M_i\) is the mass
of the \(i\)th particle, and \(\nabla^2_i\) is the Laplacian of the \(i\)th particle. The second term
on the left is the potential energy of the state. The potential energy of the state is
generally a complicated function of several or all of the dynamical variables and is
of particular importance to the description of quantum dynamics. One can combine
these two terms and define the action of these terms by an operator, \(\hat{H}\), called the
Hamiltonian operator. Thus, Equation (1.1) can also be written in operator form,
as
\[\hat{H} |\phi, t\rangle = i\hbar \frac{\partial}{\partial t} |\phi, t\rangle. \]  
(1.2)

Equation (1.2) is the set of equations of motion required to calculate the dynamics
of a quantum mechanical state.

1.2 Solving the Schrödinger Equation

The bulk of quantum dynamical research is involved with devising and refining
methods to solve Equation (1.2). A molecular Hamiltonian operator will take the
form (in atomic units, where \(\hbar = c = e = m = 1\))
\[\hat{H} = -\frac{1}{2} \sum_{\alpha=1}^{K} \frac{1}{M_\alpha} \nabla^2_\alpha - \frac{1}{2} \sum_{i=1}^{N} \nabla^2_i + \sum_{\alpha=1}^{K} \sum_{\beta=\alpha+1}^{K} \frac{Z_\alpha Z_\beta}{r_{\alpha,\beta}} - \sum_{\alpha=1}^{K} \sum_{i=1}^{N} \frac{Z_\alpha}{r_{i,\alpha}} + \sum_{j=1}^{N} \sum_{i=j+1}^{N} \frac{1}{r_{i,j}}, \]  
(1.3)

where the indices \(\alpha\) and \(\beta\) refer to elements of the \(K\) nuclei and \(i\) and \(j\) label
elements of the \(N\) electrons. Furthermore, \(Z_\alpha\) is the charge of nucleus \(\alpha\) and \(r_{\alpha,\beta}\),
$r_{\alpha,i}$, and $r_{i,j}$ are the distance between nuclei $\alpha$ and $\beta$, the distance between nucleus $\alpha$ and electron $i$, and the distance between electrons $i$ and $j$, respectively.

The complexity of the molecular Hamiltonian operator renders the Schrödinger equation analytically intractable for all but the simplest systems. For this reason, certain approximations must be made to simplify the system of equations. Many methods treat the nuclear and electronic degree of freedom separately, in what is usually referred to as the Born-Oppenheimer approximation. Born and Oppenheimer [4] first introduced the concept of an adiabatic separation, in which the electronic and nuclear degrees of freedom are decoupled. In a simplistic description, the mass of the electrons, $m$, is so small in comparison to the nuclei, $M$, that the electronic motion is significantly faster than the motion of the nuclei, allowing one to perform a separate electronic calculation at each nuclear configuration. The result of this approximation is that the electronic potential energy can be constructed at a large number of nuclear configurations, resulting in a potential energy surface that is a function of the nuclear coordinates. At this point, the nuclear Hamiltonian is employed in which the potential energy term is now a sum of the Coulomb repulsion of the nuclei and the specific electronic potential energy that correspond to the given nuclear configuration. This approximation gives rise to such methods as molecular dynamics (or quantum molecular dynamics if the nuclei are quantum). By employing excited state surfaces, multi-surface methods arise, such as surface hopping methods.

One immediate deficiency of these Born-Oppenheimer-type methods is the lack of dynamical coupling between the electrons and the nuclei. As a result, it is desirable to discuss methods in which no potential energy surfaces are utilized. This requires direct calculation of the potential energy between nuclei and electrons at each time-step. Such methods will be the focus of the remainder of this dissertation.
Two specific methods will be discussed. First is the Time-Dependent Hartree-Fock method. Second is the Electron-Nuclear Dynamics formalism. Both methods are time-dependent methods that do not require the calculation of potential energy surfaces.

### 1.3 Time-Dependent Hartree-Fock (TDHF)

The TDHF method was first proposed by Dirac in 1930 [5]. The principal assumption of the TDHF method is that the self-consistent central field approximation holds. In this approximation (which is equivalent to the Hartree-Fock approximation) the total electronic wave function is composed of a product of wave functions for each electron. Furthermore, each electron moves in an average potential.

The reference state for TDHF methods is the single determinant Hartree-Fock ground state, represented as a Slater determinant (using second quantization),

$$|D\rangle = a_1^\dagger \ldots a_N^\dagger |\text{vac}\rangle. \quad (1.4)$$

The TDHF state vector has the form

$$|\Psi\rangle = e^{i\sum rs \lambda_{rs}(t)a_r^\dagger a_s}|D\rangle \quad (1.5)$$

which has a corresponding Dirac density operator of the form

$$\Gamma = e^{i\sum rs \lambda_{rs}(t)a_r^\dagger a_s}\psi_i \langle \psi_i | e^{-i\sum rs \lambda_{rs}(t)a_r^\dagger a_s}. \quad (1.6)$$

The density operator has a corresponding matrix form that is idempotent ($\Gamma^2 = \Gamma$) and the trace is equal to the number of electrons in the system [6]. The quantum mechanical Lagrangian takes the form

$$\mathcal{L} = \frac{1}{2} \left[ \langle i\hbar \frac{\partial}{\partial t} |\Psi\rangle + \langle \Psi | i\hbar \frac{\partial}{\partial t} |\Psi\rangle \right] - \langle \Psi | \mathcal{F} |\Psi\rangle, \quad (1.7)$$
where $\mathcal{F}$ is the Fock operator, which has matrix elements of the form

$$
\mathcal{F}_{rs} = h_{rs} + \frac{1}{2} \sum_{pq} \langle rs|pq \rangle \Gamma_{qp}
$$

(1.8)

where $h_{rs}$ is an element of the one-electron Hamiltonian matrix.

The equations of motion for the TDHF method are derived from the fact that the Lagrangian should be stationary with respect to small variations in the TDHF state vector, such that

$$
|\Psi\rangle \rightarrow i \sum_{rs} \delta \lambda_{rs} a_r^\dagger a_s |\Psi\rangle,
$$

(1.9)
as well as a corresponding variation in the density operator. By requiring the Lagrangian to be stationary under such an arbitrary variation, one obtains the TDHF equations of motion

$$
i \dot{\Gamma} = [\mathcal{F}, \Gamma],
$$

(1.10)

where the dot indicates the time derivative and the brackets denote the commutation relation $[a, b] = ab - ba$.

At this point, it is assumed that the time-evolution will act as a small perturbation to the Fock operator. The one-electron Hamiltonian will be perturbed such that

$$
h_{rs} \rightarrow h^0_{rs} + \delta h_{rs},
$$

(1.11)

where $h^0_{rs}$ is the one-electron Hamiltonian that corresponds to the unperturbed HF stationary ground state. The second term contains the time-dependence. Secondly, the two-electron component is perturbed through the density, such that

$$
\Gamma \rightarrow \Gamma^0 + \delta \Gamma,
$$

(1.12)

where, again, the subscript indicates the HF stationary ground state solution and the time-dependence is carried by the perturbative term. The above perturbations are then substituted into the TDHF equations of motion and, traditionally, terms
of order two or greater in the perturbations are truncated. This implementation results in a method that is linearized and limits the electron-nuclear couplings within TDHF methods [7].

Furthermore, as both components of the Fock operator depend explicitly upon the electron density, the equations of motion must be solved iteratively at each time-step. Again, this is traditionally not done. In most TDHF methods, the reference state is determined as either a configuration interaction (CI) expansion to the level of single excitations (resulting in the Tamm-Dankoff Approximation) [8] or as a perturbation expansion to the level of single and some double excitations (resulting in the Random Phase Approximation) [9]. By allowing the expansion coefficients to be time-dependent, the time-evolution of the individual orbitals is now no longer required and the single reference is used throughout the dynamics [7]. This is also a limitation to the TDHF method, as the state is not permitted dynamically outside of the limit of the single configuration included in the HF reference state.

1.4 Electron-Nuclear Dynamics (END)

The END theory is a non-adiabatic formulation allowing a complete dynamical treatment of electrons and nuclei that eliminates the need for potential energy surfaces that is equivalent to a generalized TDHF approximation. Electron-Nuclear Dynamics is derived from application of the time-dependent variational principle (TDVP) on a family of approximate state vectors parameterized in terms of Thouless coefficients. The END formalism and application of END to varied physical problems has been explained in detail in previous works [10, 11, 12, 13]. A brief account of the derivation of the END equations of motion will be provided in this section.
1.4.1 The END Equations of Motion

The derivation begins with the quantum mechanical action functional

\[ A = \int_{t_1}^{t_2} \mathcal{L} \, dt, \]  

(1.13)

where \( \mathcal{L} \) is the quantum mechanical Lagrangian, defined as

\[ \mathcal{L} = \langle \zeta | i \frac{d}{dt} - \hat{H} | \zeta \rangle \langle \zeta | \zeta \rangle. \]  

(1.14)

Here \( \zeta \) defines a complete set of time-dependent parameters that describe the particular choice of state vector and \( \hat{H} \) is the quantum mechanical Hamiltonian operator for the system. By requiring that the action remain stationary under variations of the parameters \( \zeta \), one obtains the Euler-Lagrange equations

\[ \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\zeta}_i} = \frac{\partial \mathcal{L}}{\partial \zeta_i}, \]  

(1.15)

for the set of dynamical variables \( \{\zeta_i\} \) [14]. Application of the principle of least action results in a coupled set of first-order differential equations of motion

\[ \begin{pmatrix} 0 & -iC^* \\ iC & 0 \end{pmatrix} \begin{pmatrix} \zeta \\ \dot{\zeta}^* \end{pmatrix} = \begin{pmatrix} \frac{\partial E}{\partial \zeta} \\ \frac{\partial E}{\partial \zeta^*} \end{pmatrix}, \]  

(1.16)

where

\[ E(\zeta^*, \zeta) = \frac{\langle \zeta | \hat{H} | \zeta \rangle}{\langle \zeta | \zeta \rangle} \]  

(1.17)

is the energy of the system and acts as the generator of infinitesimal time translations and where \( C \) is an invertible metric matrix with elements defined as

\[ C_{\alpha\beta} = \frac{\partial^2 \ln S}{\partial \zeta_\alpha^* \partial \zeta_\beta}. \]  

(1.18)

The metric matrices define the couplings between the dynamical variables. The argument of the logarithm in Equation (1.18) is the overlap, defined as \( S = \langle \zeta | \zeta \rangle \). The equations of motion given in Equation (1.16) are exact; any approximations
to the END formulation arise due to the choice of dynamical parameters $\zeta$ and the completeness of the electronic basis set.

### 1.4.2 Minimal Electron-Nuclear Dynamics

The minimal END theory is implemented in the ENdyne computer code. In the current version, nuclei are treated classically and electrons are represented using single Thouless determinants that are complex and single valued [15]. All electron-nuclear couplings are retained. The dynamical parameters are chosen as $\zeta=\{R_k, P_k, z_{ph}, z_{ph}^*\}$, where $R_k$ and $P_k$ are the average position and momentum of the $k$th nucleus and $z_{ph}$ and $z_{ph}^*$ (spanned by a set of atomic orbitals) are the Thouless coefficient corresponding to the $p$th atomic orbital of the $h$th spin orbital and its complex conjugate, respectively. Choosing the state to be represented as a product coherent state vector

$$|\zeta\rangle = |z; R\rangle |R, P\rangle \equiv |z\rangle |\phi\rangle$$

where the nuclear wave function is expressed as a product of traveling Gaussians

$$|\phi\rangle = \prod_k \exp \left[ -\frac{1}{2} \left( \frac{X_k - R_k}{w_k} \right)^2 + iP_k (X_k - R_k) \right]$$

taken in the narrow wave packet limit ($w_k \to 0$, for all $w_k$), and where the electronic state is represented with a single determinant electronic wave function

$$|z\rangle = \det \{ \chi_h(x_p) \}$$

allows for a consistent description of the electron-nuclear dynamics. The molecular spin orbitals in Equation (1.21), $\chi_h$, are spanned by a set of basis functions, $\{ u_h(x) \}$, that are Gaussian-type atomic orbitals (GTOs) centered on the average
nuclear positions. By making these assumptions, Equation (1.16) takes the form
\[
\begin{pmatrix}
 iC & 0 & iC_R & iC_P \\
 0 & -iC^* & -iC_R^* & -C_P^* \\
 iC_R^\dagger & -iC_R^T & C_{RR} & -I + C_{RP} \\
 iC_P^\dagger & -iC_P^T & I + C_{PR} & C_{PP}
\end{pmatrix}
\begin{pmatrix}
 \dot{z} \\
 \dot{z}^* \\
 \dot{R} \\
 \dot{P}
\end{pmatrix}
= \begin{pmatrix}
 \partial E/\partial z \\
 \partial E/\partial z^* \\
 \partial E/\partial R \\
 \partial E/\partial P
\end{pmatrix},
\] (1.22)

where the dynamic metric elements of Equation (1.22) are
\[
(C_{XY})_{ij;kl} = -2 \text{Im}\left. \frac{\partial^2 \ln S}{\partial X_{ik} \partial Y_{jl}} \right|_{R'=R},
\] (1.23)
\[
(C_{Xik})_{ph} = \left. \frac{\partial^2 \ln S}{\partial z_{ph}^* \partial X_{ik}} \right|_{R'=R},
\] (1.24)
and
\[
C_{ph;qg} = \left. \frac{\partial^2 \ln S}{\partial z_{ph}^* \partial z_{qg}} \right|_{R'=R}.
\] (1.25)

The coupling is explicit in the metric elements given in Equations (1.23) - (1.25), nuclear-nuclear coupling, non-adiabatic nuclear-electronic coupling, and pure electronic-electronic coupling, respectively.

Minimal Electron-Nuclear Dynamics is a generalization of the TDHF method [10]. The electronic and nuclear interactions are still regulated through the Fock matrix, but there are some differences in the dynamical evolution of the state. Firstly, the variation of the one-density in the END formalism is achieved through a general variation of the Thouless coefficients and is not truncated at any particular order. As a result, END is equivalent to fully non-linearized TDHF. Secondly, the reference state is permitted to change as warranted by the dynamics of the system. This provides additional flexibility to the dynamical evolution, as the reference state is not limited to a stationary state as calculated previous to the dynamical evolution.
CHAPTER 2
THEORY OF COLLISIONS

Many chemical reaction principles and results can be elucidated and obtained by virtue of so-called “scattering experiments”. The experiments most generally involve a beam of projectile species incident upon a reaction cell containing target species or upon a second beam of target species. The reactions and energy transferences occur in the volume of the reaction cell or the union volume of the crossed beams. Theoretical descriptions of such scattering phenomena are contained in the classical, quantal, and semi-classical realms of collision theory.

2.1 Scattering Theory

While experimental results are obtained for bulk phase reactions in general, excellent theoretical descriptions of these scattering processes can be made by considering the interaction of a single projectile particle with a single target particle. At it’s simplest, classical scattering theory involves the reduction of a two-body problem into a reduced one-body problem. This transformation results in a description of the motion in the center-of-mass reference frame. This type of analysis is similar to the analysis of unbound Kepler motion, however, the nature of the central force is considerably different (though the functional form may be very similar) and all information about the orbits is lost (only the incident momentum, the final momentum, and the angle between the two is observed) [16]. In this section, we will discuss the fundamentals of classical scattering theory and methods to extend these fundamentals into the language of atomic and molecular collisions, quantum scattering theory.
2.1.1 Deflection Functions and Scattering Angles

One begins by considering a classical collision system consisting of two point masses in the laboratory frame with some undefined potential acting between them that is a function only of the separation between the particles. It will be assumed that, initially, one particle is in motion (the projectile) and one is at rest (the target). Figure 2.1 demonstrates such a collision system. The scattering axis is defined as the axis parallel to the incident motion of the projectile and containing the location of the target, as demonstrated by A in Figure 2.1. The impact parameter, labeled as $b$, is defined as the distance at which the projectile is initially located in a direction perpendicular to the scattering axis. As one can assume a spherically symmetric potential, $V(r)$, this can be in any direction perpendicular to the scattering axis.

The other principle feature of Figure 2.1 is the deflection angle, labeled as $\Psi$. The deflection angle is the angle through which the projectile is deflected by the potential, as measured in a counter-clockwise manner from the positive scattering axis. The deflection angle can be positive due to a repulsive potential (as demonstrated in A in Figure 2.2), or it can be negative due to an attractive potential (see B in Figure 2.2). Furthermore, under certain conditions, the projectile can orbit

![Figure 2.1: Diagram of a classical collision system.](image)
Figure 2.2: Three possible deflection angles. A demonstrates a positive deflection angle. B demonstrates a negative deflection angle. C demonstrates a deflection angle with magnitude greater than $2\pi$ radians (see C in Figure 2.2).

the target for one or more periods, resulting in a deflection with magnitude greater than $2\pi$ radians (see C in Figure 2.2).

It should be noted that, experimentally, it is impossible to distinguish between the three deflections shown in Figure 2.2. Experiment can only determine the angle at at which the projectile is scattered, relative to the scattering axis, and cannot elucidate whether a particle is scattered through a positive deflection, a negative deflection, or through an orbiting deflection with magnitude greater than $2\pi$ radians. Thus, we must define a parameter that corresponds to what is physically measured; a parameter called the scattering angle. The scattering angle, denoted $\theta$, 
is defined as
\[ \theta = |\Psi \text{ mod } 2\pi|. \] (2.1)

For any scattering system there exists a mapping that relates the impact parameter to a resulting scattering. This mapping is called the deflection function, \( \Theta(b) \). It is obvious from the previous paragraph that the deflection function is not an injective mapping, as more than one impact parameter may result in the same scattering angle. Furthermore, the deflection function is not a surjective mapping, as there is no guarantee that the projectile will be scattered into every angle between 0 and \( \pi \).

2.1.2 Cross Sections

While reaction rates are usually the quantities desired from “scattering experiments”, the fundamental observable of such experiments is the differential cross section \( (d\sigma/d\Omega) \). The differential cross section \( (d\sigma/d\Omega) \) is defined as
\[ \frac{d\sigma}{d\Omega} = \frac{\text{scattered current per unit solid angle}}{\text{incident current per unit area}}. \] (2.2)

At this point it becomes necessary to assume some limited quantum nature of the scattering system. Without further justification at this point in the discussion, we will introduce the general form of the scattering wave function. It is customary to choose the ansatz wave function for the target beam by considering the asymptotic regions where the effect of the scattering potential produced by the target (assumed to be finite) is negligible. In the post-scattering region, the scattered wave function will be a linear combination of incident plane wave and scattered spherical waves \( [18] \),
\[ \psi \sim e^{ik_i r} + f(\theta, \phi) \frac{e^{ik_f r}}{r}, \] (2.3)
where \( k_i \) and \( k_f \) are the magnitudes of the initial and final momenta of the projectile, respectively. Both the numerator and the denominator in Equation (2.2)
require evaluation of the probability current density, \( j \), for the wave function, defined as

\[
j = \frac{1}{2m} \left( \psi^* \nabla \psi - \psi \nabla \psi^* \right), \tag{2.4}
\]

where \( m \) is the mass of the projectile. It should be noted that vectors are denoted using boldfaced letters, while respective magnitudes are represented using non-boldfaced letters. The numerator of Equation (2.2) is found from the current density of the outgoing spherical component by the expression \( j_{\text{out}} \cdot dA \), where \( dA \) is the unit differential area normal to the solid angle subtended by \( d\Omega \). For this case, \( dA = r^2 \cdot dr \). It should be noted that, due to the area, only the \( r \) component of \( j_{\text{out}} \) is required, greatly simplifying the calculation. The denominator of Equation (2.2) is likewise found considering the current density of the incoming plane wave, \( j_{\text{in}} \). As all incident particles are considered, the denominator is just the incoming current density. Thus, the the differential cross section can now be expressed as

\[
\frac{d\sigma}{d\Omega} = \frac{j_{\text{out}} \cdot dA}{j_{\text{in}}} = \frac{k_f}{k_i} |f(\theta, \phi)|^2.
\]

(2.5)

Thus, the differential cross section depends only on the square of the amplitude of the scattered spherical wave. It should be furthermore noted that a state-to-state differential cross section may be obtained if a probability amplitude for transition is included in the scattering amplitude.

The second quantity of import in “scattering experiments” is the total cross section, \( \sigma \), defined as

\[
\sigma = \int_0^{2\pi} \int_0^\pi \frac{d\sigma}{d\Omega} \sin \theta d\theta d\phi. \tag{2.6}
\]

The total cross section depends only upon the relative kinetic energy of the colliding particles and is an effective area of scattering or reaction. If the projectile strikes within this effective area it will be scattered or reacted, however, because
of the averaging, the specific information contained within the differential cross section is lost.

2.1.3 Identical Particles

Consider the collision of two particles in the center of mass frame (Figure 2.3). To simplify the explanation, it will be assumed that axial symmetry exists, eliminating a dependence on $\phi$. Because each particle is distinguishable throughout the entire collision process, each can be determined to scatter through either and angle of $\theta$ or an angle of $\pi - \theta$. However, a interesting problem arises when identical particles are considered. Even if the particles are distinguishable at some time of separation, once the particles enter the interaction region they are no longer distinguishable. The particle scattered through angle $\theta$ is indistinguishable from the particle scattered through angle $\pi - \theta$ (Figure 2.4).
When considering identical particles, the ansatz wave function for the projectile now takes the form [19]

$$\psi \sim e^{ik_1r} + [f(\theta) \pm f(\pi - \theta)] \frac{e^{ik_2r}}{r},$$

(2.7)

where the sign is determined by whether Fermi-Dirac or Bose-Einstein statistics are employed. As the particles are identical, momentum is conserved in the collision.

From the same argument provided in Section 2.1.2, the differential cross section for identical particles in the center-of-mass frame is

$$\frac{d\sigma}{d\Omega} = |f(\theta) \pm f(\pi - \theta)|^2.$$

(2.8)

### 2.1.4 Reference Frame Transformations

One benefit of the END formalism is that calculations need not be performed in the center-of-mass frame of reference. This is beneficial as experimental results are generally reported in the lab frame. However, it was demonstrated in the previous section that the calculation of the differential cross section for the reaction of identical particles is best handled in the center-of-mass frame. Thus, a schema for transformation between lab and center-of-mass frames must be developed.

Consider the collision of two particles, as depicted in Figure 2.5. The first particle (projectile) has a mass, $m_1$, the second particle (target) has mass, $m_2$. In the lab frame, the particles have positions, $r_1$ and $r_2$, and momenta, $k_1 = m_1 \mathbf{r}_1$ and $k_2 = m_2 \mathbf{r}_2$ (where the dot indicates differentiation with respect to time). In the frame relative to the center-of-mass, the particles are defined by positions, $s_1$ and $s_2$, and momenta, $p_1 = m_1 \mathbf{s}_1$ and $p_2 = m_2 \mathbf{s}_2$. The center-of-mass for the collision system is defined as having mass, $M = m_1 + m_2$, position, $\mathbf{R}$, and momentum, $\mathbf{P} = M \dot{\mathbf{R}}$, relative to the origin.

It is evident from the definition of the system that the position of a particle in the lab frame differs from the position in the center-of-mass frame, at any time.
during the dynamics, by the position of the center-of-mass,

$$r_1 = s_1 + R.$$  \hspace{1cm} (2.9)

Differentiation of the above equation and multiplication by $m_1$ yields the relation amongst momenta,

$$k_1 = p_1 + \frac{m_1}{M}p.$$ \hspace{1cm} (2.10)

If one considers the momenta for the projectile in the two reference frames after the collision, one may obtain the relationship between the scattering angles in the two reference frames. The projectile possesses a momentum $k'_1$ in the lab frame.

Figure 2.5: Relation of collision pair and center-of-mass to origin.

Figure 2.6: Relation of the scattering angles between reference frames.
and $p_f^1$ in the center-of-mass frame. The superscript $f$ indicates a final condition.

The projectile is scattered through an angle of $\alpha$ in the lab frame and an angle of $\theta$ in the center-of-mass frame (Figure 2.6). It is evident that the transverse components of the momenta are equal,

$$p_f^1 \sin(\theta) = k_f^1 \sin(\alpha), \quad (2.11)$$

and that the longitudinal components differ by the momentum of the center-of-mass,

$$p_f^1 \cos(\theta) = k_f^1 \cos(\alpha) - \frac{m_1}{M} P. \quad (2.12)$$

Transformations between the scattering angles are obtained by taking the appropriate ratios of Equations (2.11) and (2.12). The center-of-mass scattering angle is obtained from the expression

$$\tan(\theta) = \frac{\sin(\alpha)}{\cos(\alpha) - \frac{m_1}{M} \frac{P}{k_f^1}}. \quad (2.13)$$

This generalized equation can be much simplified under two assumptions. If the particles are identical then $\frac{m_1}{M} = \frac{1}{2}$. If the target is initially stationary in the lab frame, then the magnitude of the center-of-mass momentum is equal to the magnitude of the initial momentum of the projectile ($k_i^1$) at any time during the collision. Thus, the simplified expression takes the form

$$\tan(\theta) = \frac{\sin(\alpha)}{\cos(\alpha) - \frac{1}{2} \gamma_i}, \quad (2.14)$$

where $\gamma = \frac{k_i^1}{k_f^1}$. Likewise, the reverse relation can also be obtained by inverting the ratio. The lab frame scattering angle can be obtained from the general expression

$$\tan(\alpha) = \frac{\sin(\theta)}{\cos(\theta) + \frac{m_1}{M} \frac{P}{p_f^1}}. \quad (2.15)$$
Again, the expression can be simplified. If the particles are assumed to be identical, then (as before) \( \frac{m_1}{M} = \frac{1}{2} \). Additionally, the collision is elastic in the center-of-mass frame, requiring that \( p_1 = \frac{1}{2} P \) at all times in the course of the dynamics. Thus,

\[
\tan(\alpha) = \frac{\sin(\theta)}{\cos(\theta) + 1},
\]

which indicates that \( \alpha = \frac{1}{2} \theta \).

Once the scattering angle is converted to the center-of-mass frame, the deflection function and the differential cross section can be calculated. The center-of-mass frame differential cross section must then be transformed back to the lab frame. This is accomplished by realizing that fact that the number of particles scattered into a given solid angle must be conserved between the two frames [20], such that

\[
\left( \frac{d\sigma}{d\Omega} \right)_{lab} \sin(\alpha) |d\alpha| = \left( \frac{d\sigma}{d\Omega} \right)_{CM} \sin(\theta) |d\theta|,
\]

or

\[
\left( \frac{d\sigma}{d\Omega} \right)_{lab} = \left( \frac{d\sigma}{d\Omega} \right)_{CM} \left| \frac{d[\cos(\theta)]}{d[\cos(\alpha)]} \right|.
\]

The multiplicative factor in Equation (2.18) is evaluated by first applying the Law of Cosines to Figure 2.6 and substitution into Equation (2.12), yielding

\[
\cos(\alpha) = \frac{\cos(\theta) + \xi}{\sqrt{1 + \xi^2 + 2\xi \cos(\theta)}},
\]

where \( \xi = \frac{1}{2} \frac{P}{p_1} \). Now the derivative can be taken with respect to \( \cos(\theta) \),

\[
\left| \frac{d[\cos(\alpha)]}{d[\cos(\theta)]} \right| = \frac{\xi \cos(\theta) + 1}{(1 + \xi^2 + 2\xi \cos(\theta))^{3/2}}.
\]

As the numerator above never goes to zero in the domain \( \theta = [-\pi, \pi] \), Equation (2.20) can be inverted to yield the required factor,

\[
\left| \frac{d[\cos(\theta)]}{d[\cos(\alpha)]} \right| = \frac{(1 + \xi^2 + 2\xi \cos(\theta))^{3/2}}{\xi \cos(\theta) + 1}.
\]
The expression in Equation (2.21) is completely general to a collision pair. As before, simplifications can be made by considering the particles to be identical. As seen earlier, this assumption requires that $\xi = 1$. Under this assumption, the transformation from the center-of-mass frame to the lab frame takes the form

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{lab}} = 4 \cos \left( \frac{\theta}{2} \right) \left( \frac{d\sigma}{d\Omega} \right)_{\text{CM}}.$$  \hspace{1cm} (2.22)

### 2.2 Quantum Mechanical Treatment of Scattering Phenomena

To this point the description of scattering phenomena has been tacitly quantal. The scattering wave function ansatz was introduced and a discussion of the identical particle problem was made, but no reference to the Schrödinger Equation has yet been made. In this section, the differential form of the scattering Schrödinger Equation will be introduced, a derivation of the integral form of the Schrödinger Equation will be made, and this integral form will be related to the scattering amplitude. The Born Series and the various Born Approximations, a set of self-consistent solutions to the integral form of the Schrödinger Equation is then introduced. Finally, the Schiff Approximations for large and small scattering angles, which are derived from the Born Series, will be fully derived and discussed.

#### 2.2.1 The Integral Equation and its Relation to the Scattering Amplitude

The time-independent Schrödinger Equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r) = E\psi(r) \hspace{1cm} (2.23)$$

can be rewritten to take the form

$$[\nabla^2 + k^2] \psi(r) = U(r)\psi(r), \hspace{1cm} (2.24)$$

where $k = \sqrt{2mE/\hbar^2}$ is the magnitude of the momentum vector for the scattered particle and where $U(r) = 2mV(r)/\hbar^2$ is the scattering potential. Equation (2.24)
is an inhomogeneous differential equation with a solution \[23\]

\[\psi(r) = \psi_0(r) + \int G(r, r_0)U(r_0)\psi(r_0)dr_0,\] (2.25)

where \(\psi_0(r)\) and \(G(r, r_0)\) are, respectively, a general solution and the Green’s Function that corresponds to the homogeneous counterpart of Equation (2.24), which is of the form

\[\left[\nabla^2 + k^2\right] \psi_0(r) = 0.\] (2.26)

The above homogeneous differential equation is nothing more than the free particle Schrödinger Equation, and the solution is \(\psi_0(r) = e^{ikr}\). Additionally, the Equation (2.26) is in the form of the Helmholtz Equation and therefore the corresponding Green’s Function that satisfies Equation (2.25) takes the form \[24\]

\[G(r, r_0) = -\frac{e^{-ik|r-r_0|}}{4\pi|r-r_0|}.\] (2.27)

Thus, one finds that Equation (2.25) now becomes, upon substitution,

\[\psi(r) = e^{ikr} - \frac{1}{4\pi} \int \frac{e^{ik|r-r_0|}}{|r-r_0|}U(r_0)\psi(r_0)dr_0,\] (2.28)

which is the integral form of the Schrödinger Equation with scattering potential located at position \(r_0\).

It is now desirable to find an expression that relates the scattering amplitude to the integral form of the Schrödinger Equation. To accomplish this, one returns to the post-scattering conditions in which the ansatz of Equation (2.3) is assumed to hold, namely that \(r \gg r_0\). Under this requirement, the angle between \(r\) and \(r_0\) approaches zero and \(|r - r_0| \to r - r_0 \cdot \hat{r}\). This approximation allows one to express the integral form of the Schrödinger Equation as

\[\psi(r) = e^{ikr} - \frac{1}{4\pi} \frac{e^{ikr}}{r} \int e^{-ikr_0}U(r_0)\psi(r_0)dr_0.\] (2.29)
One can then immediately compare the modified integral form of the Schrödinger
Equation as given above with Equation (2.3), which demonstrates clearly that

$$f(\theta) = f(k) = -\frac{1}{4\pi} \int e^{-ikr_0}U(r_0)\psi(r_0)dr_0.$$  \hspace{1cm} (2.30)

### 2.2.2 The Born Series

Though one has now seen the solution to the scattering wave function in
Equation (2.28), the solution is analytically intractable, as the integrand itself
depends on $\psi$. Solution of the scattering wave function requires numerical integra-
tion to self-consistency. This self-consistent method yields the Born Series, with
truncations yielding the Born Approximations $[19, 21]$ of various orders.

The First Born Approximation assumes that the scattering potential has a
negligible effect on the incoming plane wave, thus the scattered wave function takes
the form

$$\psi = e^{ik_i \cdot r_1},$$  \hspace{1cm} (2.31)

The subscript on $r$ is for indexing purposes only. This term can be substituted into
Equation (2.30), and the scattering amplitude in the First Born Approximation
then becomes

$$f(k_i, k_f) = -\frac{1}{4\pi} \int e^{-ik_f \cdot r_1}U(r_1)e^{ik_i \cdot r_1}dr_1.$$  \hspace{1cm} (2.32)

In some cases conditions are such that the First Born Approximation is sufficient
for analysis, most notably when the scattering potential is not very strong and its
effective range is quite small $[19]$. However, the First Born Approximation rarely
provides adequate accuracy.

The Second Born Approximation is begun by iterating on the wave function.
The scattered wave function for the second order of approximation now becomes

$$\psi = e^{ik_i \cdot r_1} + \int G(r_1 - r_2)U(r_2)\psi(r_2)dr_2.$$  \hspace{1cm} (2.33)
Substitution of Equation (2.31) into the above equation yields the wave function in the Second Born Approximation

\[ \psi = e^{ik_i \cdot r_1} + \int G(r_1 - r_2)U(r_2)e^{ik_i \cdot r_2}dr_2 \] (2.34)

which generates the second order scattering amplitude

\[ f(k_i, k_f) = -\frac{1}{4\pi} \left[ \int e^{-ik_f \cdot r_1}U(r_1)e^{ik_i \cdot r_1}dr_1 \right. \]
\[ + \int e^{-ik_f \cdot r_1}U(r_1)G(r_1 - r_2)U(r_2)e^{ik_i \cdot r_2}dr_2dr_1 \]. (2.35)

This pattern can then be continued, and one can make successive iteration to an arbitrary degree and obtain the \( n \)th order wave function

\[ \psi = e^{ik_f \cdot r_1} + \int G(r_1 - r_2)U(r_2)e^{ik_i \cdot r_2}dr_2 \]
\[ + \int \int G(r_1 - r_2)U(r_2)G(r_2 - r_3)U(r_3)e^{ik_i \cdot r_3}dr_3dr_2 \]
\[ + \ldots + \]
\[ + \int \cdots \int G(r_1 - r_2)U(r_2)G(r_2 - r_3)U(r_3) \times \ldots \]
\[ \times G(r_{n-1} - r_n)U(r_n)e^{ik_i \cdot r_n}dr_n \ldots dr_2. \] (2.36)

The infinite Born Series is obtained by letting \( n \to \infty \) (with careful reordering of the indices). The infinite Born Series leads to a scattering amplitude with the general form

\[ f(k_i, k_f) = -\frac{1}{4\pi} \sum_{n=1}^{\infty} \int \cdots \int e^{-ik_f \cdot r_n}U(r_n)G(r_n - r_{n-1})U(r_{n-1}) \]
\[ \times \cdots \times G(r_2 - r_1)U(r_1)e^{ik_i \cdot r_1}dr_n \ldots dr_1. \] (2.37)

Now, while Equation (2.37) is exact, it is very unwieldy to solve and still depends upon the scattering potential function, a property not utilized within nor obtained from END. Furthermore, the Born Series is often afflicted with slow or no convergence [2]. So it is desirable for a number of reasons to express the Born
Series in a simplified form, in particular a form that does not depend explicitly upon the scattering potential.

2.3 Semi-Classical Treatment of Scattering Phenomena: The Schiff Approximation

The work in this section was first introduced by L. I. Schiff in 1956 [22]. This discussion is based on that paper.

The scattering potential and the projectile particle can be characterized by several physical properties. The scattering potential can be described by $V$ and $R$, which are rough indications of the strength of the potential and its effective range, respectively. Likewise, the projectile is characterized by its kinetic energy, $T$; its wave number (magnitude of the momentum), $k$; its speed, $v$; and its scattering angle, $\theta$.

These characteristics provide a qualitative means by which to discuss the scattering process. For example, the First Born Approximation is valid under conditions when the scattered wave is insignificantly perturbed by the scattering potential (c.f. Equation (2.31)). This can be expressed in a qualitative manner by the magnitude of $V$ being very small compared to the collision energy (weak scattering potential) or by the magnitude of $R$ being very small (short range scattering potential). Schiff provides a general condition under which the First Born Approximation is valid as given by the expression $(|V| R)/(\hbar v) << 1$ [22].

The Schiff Approximation provides an approximate scattering amplitude for large collision energy collisions. Specifically, the assumptions imposed are that $|V|/T << 1$, that $\theta$ be very large or very small in comparison to $\sqrt{1/(kR)}$, and that the scattering potential be slowly varying when compared to the incoming wavelength. In contrast with the First Born Approximation, the Schiff Approximation is valid for any magnitude of $(|V| R)/(\hbar v)$ [22].
2.3.1 Schiff Scattering Amplitude for Large Angles

The Schiff Approximation consists of approximately representing each of the terms in the Born series using the stationary state approximation [22, 23, 24]. One begins the derivation with the infinite Born series, Equation (2.37), rewritten slightly to the form

\[
f(k_i, k_f) = -\frac{1}{4\pi} \sum_{n=1}^{\infty} \prod \int e^{-i(k_f \cdot r_n - k_i \cdot r_1)} U(r_n) G(r_n - r_{n-1}) U(r_{n-1}) \times \cdots \times G(r_2 - r_1) U(r_1) dr_n \cdots dr_1.
\] (2.38)

A change of variables is made, such that \( \rho_{n-1} = r_n - r_{n-1} \), so that \( r_n = \rho_{n-1} + r_{n-1} \). The argument of the exponential term can be expanded iteratively as

\[
-k_f \cdot r_n + k_i \cdot r_1 = -k_f \cdot (\rho_{n-1} + r_{n-1}) + k_i \cdot (r_2 - \rho_1)
\]
\[
= -k_f \cdot \rho_{n-1} - k_f \cdot (\rho_{n-2} + r_{n-2}) + k_i \cdot (r_3 - \rho_2) - k_i \cdot \rho_1
\]
\[
\vdots
\]
\[
= -k_f \cdot \rho_{n-1} - k_f \cdot \rho_{n-2} - k_f \cdot \rho_{n-3} - \cdots - k_f \cdot \rho_{m} + k_i \cdot (\rho_{m-1} - r_{m-1}) - \cdots - k_i \cdot \rho_2 - k_i \cdot \rho_1
\]
\[
= -k_f \cdot \rho_{n-1} - k_f \cdot \rho_{n-2} - k_f \cdot \rho_{n-3} - \cdots - k_f \cdot \rho_{m} + q \cdot r_m - k_i \cdot \rho_{m-1} - \cdots - k_i \cdot \rho_2 - k_i \cdot \rho_1,
\] (2.39)

where \( q = k_i - k_f \) is the momentum transfer for the collision process. To complete the transformation of variables in Equation (2.38), one must calculate the Jacobian of the transformation, specifically

\[
J = \begin{vmatrix}
\frac{\partial \rho_1}{\partial r_1} & \frac{\partial \rho_2}{\partial r_1} & \ldots & \frac{\partial \rho_{m-1}}{\partial r_1} & \frac{\partial \rho_{m+1}}{\partial r_1} & \frac{\partial \rho_{m+2}}{\partial r_1} & \ldots & \frac{\partial \rho_{n-2}}{\partial r_1} & \frac{\partial \rho_{n-1}}{\partial r_1} \\
\frac{\partial \rho_1}{\partial r_2} & \frac{\partial \rho_2}{\partial r_2} & \ldots & \frac{\partial \rho_{m-1}}{\partial r_2} & \frac{\partial \rho_{m+1}}{\partial r_2} & \frac{\partial \rho_{m+2}}{\partial r_2} & \ldots & \frac{\partial \rho_{n-2}}{\partial r_2} & \frac{\partial \rho_{n-1}}{\partial r_2} \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\frac{\partial \rho_1}{\partial r_n} & \frac{\partial \rho_2}{\partial r_n} & \ldots & \frac{\partial \rho_{m-1}}{\partial r_n} & \frac{\partial \rho_{m+1}}{\partial r_n} & \frac{\partial \rho_{m+2}}{\partial r_n} & \ldots & \frac{\partial \rho_{n-2}}{\partial r_n} & \frac{\partial \rho_{n-1}}{\partial r_n}
\end{vmatrix},
\] (2.40)
noting that the \( r_m \) row and column are omitted. The derivatives take the general form

\[
\frac{\partial \rho_f}{\partial r_g} = \begin{cases} 
-1 & \text{for } f = g \\
1 & \text{for } f = g - 1 \\
0 & \text{otherwise}
\end{cases}
\]  

(2.41)

From this, it can be justified that the Jacobian matrix has the values of \(-1\) along the diagonal, the values of \(1\) for each element immediately below the diagonal, and the value \(0\) elsewhere. From this is can be seen that the determinant takes the value \( J = \pm 1 \). Therefore,

\[
d\rho_{n-1}...d\rho_1 = dr_n...dr_{m+1}dr_{m-1}...dr_1,
\]

(2.42)

and the limits of integration do not change.

The change of variables may now be accomplished, transforming Equation (2.38) into the following form

\[
f(k_i, k_f) = -\frac{1}{4\pi} \sum_{n=1}^{\infty} \sum_{m=1}^{n} \int ... \int e^{i[-k_f^j \rho_{n-1} - ... - k_f^j \rho_{n+1} + q_m - k_i] \rho_m - k_i \rho_n - ... - k_i \rho_1]}
\times U(r_m + \rho_{n-1} + \rho_{n-2} + ... + \rho_m)G(\rho_{n-1})
\times U(r_m + \rho_{n-2} + \rho_{n-3} + ... + \rho_m)G(\rho_{n-2})
\times ... 
\times U(r_m + \rho_m)G(\rho_m)U(r_m)G(\rho_{m-1})U(r_m - \rho_{m-1})G(\rho_{m-2})
\times ... 
\times U(r_m - \rho_{m-1} - \rho_{m-2} - ... - \rho_3)G(\rho_2)
\times U(r_m - \rho_{m-1} - \rho_{m-2} - ... - \rho_2)G(\rho_1)
\times U(r_m - \rho_{m-1} - \rho_{m-2} - ... - \rho_1)
\times dr_md\rho_{n-1}d\rho_{n-1}...d\rho_2d\rho_1.
\]  

(2.43)
where the fact that
\[ r_f = \begin{cases} 
  r_m + \rho_{f-1} + \rho_{f-2} + \ldots + \rho_m & \text{for } f > m \\
  r_m - \rho_{m-1} - \rho_{m-2} - \ldots - \rho_1 & \text{for } f < m 
\end{cases} \]  
was used to indicate the \( \rho \) dependence of the potential terms. The second summation (over \( m \)) arises from the stationary phase approximation. The majority of the integral will come from the regions where the phase is stationary, specifically where the derivative of the phase with respect to the wave vector is zero [24]. Thus, one must sum over all of these stationary phase points to completely enumerate the integral.

Now, recognizing that the transformed Green’s function for the scattering amplitude equation now takes the form
\[ G(r_n - r_{n-1}) \rightarrow G(\rho_{n-1}) = -\frac{e^{ik_f \rho}}{4\pi \rho}, \]  
the above equation can be partitioned into the form
\[ f(k_i, k_f) = -\frac{1}{4\pi} \sum_{n=1}^{\infty} \sum_{m=1}^{n} \left\{ \left( -\frac{1}{4\pi} \right)^{n-1} \int e^{iqr_m} dr_m \times \right. \]
\[ \left. \int \rho_{n-1}^{-1} e^{i(k_f \rho_{n-1} - k_f \rho_{n-1})} g(\rho_{n-1}) d\rho_{n-1} \right. \]
\[ \left. \int \rho_{n-2}^{-1} e^{i(k_f \rho_{n-2} - k_f \rho_{n-2})} g(\rho_{n-2}) d\rho_{n-2} \times \ldots \right. \]
\[ \left. \int \rho_2^{-1} e^{i(k_f \rho_2 - k_f \rho_2)} g(\rho_2) d\rho_2 \times \int \rho_1^{-1} e^{i(k_f \rho_1 - k_f \rho_1)} g(\rho_1) d\rho_1 \right\}. \]  
In Equation (2.46), the terms \( g(\rho_j) \) represent a product of all \( U \) terms that depend explicitly upon \( \rho_j \). Thus, for an elastic scattering process, the scattering amplitude has been reduced to a product of integrals of the form
\[ I = \int \rho^{-1} g(\rho) e^{i(k_f \rho - k_f \rho)} d\rho. \]  
(2.47)
To evaluate this integral, one needs to transform to spherical polar coordinates 
\((\rho, \theta, \phi)\) where \(\theta\) measures the angle of \(k\) with respect to \(\rho\),
\[
I = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty \rho g(\rho, \theta, \phi) e^{i(k\rho - k\rho \cos \theta)} d\rho,
\]
where the scalar product is geometrically evaluated. One can now make the familiar change of variable \(\mu = \cos \theta\), where \(d\mu = -\sin \theta d\theta\). Substitution (with appropriate change of limits) yields
\[
I = \int_0^{2\pi} d\phi \int_{-1}^1 d\mu \int_0^\infty \rho g(\rho, \mu, \phi) e^{ik\rho(1-\mu)} d\rho.
\]
One can now integrate by parts with respect to \(\mu\), resulting in the expression
\[
I = \int_0^{2\pi} d\phi \int_0^\infty \rho d\rho \left\{ \frac{i}{k\rho} g(\rho, \mu, \phi) e^{ik\rho(1-\mu)} \right|_1^1 - \int_{-1}^1 \frac{i}{k\rho} \frac{\partial g(\rho, \mu, \phi)}{\partial \mu} e^{ik\rho(1-\mu)} d\mu \right\}.
\]
Integrating the second term in the braces will bring down another factor of \(1/(k\rho)\). By applying the limits on the first term, one can write
\[
I = \int_0^{2\pi} d\phi \int_0^\infty \rho d\rho \left\{ \frac{i}{k\rho} [g(\rho, 1, \phi) - g(\rho, -1, \phi)e^{ik\rho}] \right\} + O(k^{-2}).
\]
As the collision energy is assumed to be large \((k >> 1)\), one can reasonably expect the magnitude of \(k\rho\) to be somewhat greater than 1. Thusly, the exponential will be highly oscillatory and subsequent integration over \(\rho\) will result in a negligible contribution to \(I\). As a result, one can omit this term, as well as the terms of order \(k^{-2}\) and higher. Furthermore, if one assumes a spherically symmetric scattering potential, the value of \(\phi\) becomes arbitrary and integrates out to a factor of \(2\pi\). Thus,
\[
I \approx \frac{2\pi i}{k} \int_0^\infty g(\tilde{k}\rho) d\rho.
\]
The \(\tilde{k}\rho\) arises due to the facts that \(\mu = 1\) \((\theta = 0)\) and that \(\phi\) is arbitrary, and so the potential term now depends only on the magnitude of \(\rho\) in the direction of the
scattered momentum. So, the integration over the angles serves to transform the
dependence on the vector $\rho$ in the scattering potential into a dependence upon the
magnitude of $\rho$ in the direction of the momentum.

Now, returning to Equation (2.46) one finds that integration of the angular
dependence results in the equation

$$f(k_i, k_f) = -\frac{1}{4\pi} \sum_{n=1}^{\infty} \sum_{m=1}^{n} \left\{ \left( -\frac{i}{2k} \right)^{n-1} \int e^{i\mathbf{q} \cdot \mathbf{r}_m} d\mathbf{r}_m \int_0^\infty g(\hat{k}_f \rho_{n-1}) d\rho_{n-1} \times \int_0^\infty g(\hat{k}_f \rho_{n-2}) d\rho_{n-2} \times \cdots \right\} .$$

The individual $g$ terms can be factored back to their respective $U$ terms, with the $\rho$
dependences replaced by $\hat{k}\rho$ dependences. Specifically, one finds that

$$f(k_i, k_f) = -\frac{1}{4\pi} \sum_{n=1}^{\infty} \sum_{m=1}^{n} \left\{ \left( -\frac{i}{2k} \right)^{n-1} \int d\mathbf{r}_m \int_0^\infty d\rho_1 \cdots \int_0^\infty d\rho_{n-1} e^{i\mathbf{q} \cdot \mathbf{r}_m} \times U \left( \mathbf{r}_m + \hat{k}_f (\rho_{n-1} + \rho_{n-2} + \cdots + \rho_m) \right) \times \cdots \right\} .$$

At this point, a second change of variables can be made, such that

$$s_j = \begin{cases} 
\rho_j + \rho_{j+1} + \cdots + \rho_{m-2} + \rho_{m-1} & \text{for } j < m \\
\rho_m + \rho_{m+1} + \cdots + \rho_{j-2} + \rho_{j-1} & \text{for } j > m \\
\rho_m & \text{for } j = m 
\end{cases}$$

There are two recursion relations that arise, specifically $s_j = \rho_j + s_{j+1}$ for $j < m$
and $s_j = s_{j-1} + \rho_j$ for $j > m$. It is clear from following the previous analysis
that the Jacobian is unity, but the lower limits of integration must be transformed.

When integrating over $\rho_j$ for $j < m$, one finds that the lower limit of $\rho_j = 0$
transforms to $s_{j+1}$. Likewise, when one integrates over $\rho_j$ for $j > m$, one finds
that the lower limit transforms to $s_{j-1}$. Therefore, the change of variables may be
imposed, transforming Equation (2.54) into the form

\[
f(k_i, k_f) = -\frac{1}{4\pi} \sum_{n=1}^{\infty} \sum_{m=1}^{n} \left\{ \left( -\frac{i}{2k} \right)^{n-1} \int_{s_1} ds_1 U(r_m - \hat{k_i}s_1) \times \int_{s_2} ds_2 U(r_m - \hat{k_i}s_2) \times ... \times \int_{s_m} ds_m U(r_m - \hat{k_i}s_m) \times \int_{s_{m-1}} ds_{m-1} U(r_m - \hat{k_i}s_{m-1}) \times \int_{s_{m-2}} ds_{m-2} U(r_m - \hat{k_i}s_{m-2}) \times ... \times \int_{s_2} ds_2 U(r_m + \hat{k_f}s_2) \times \int_{s_1} ds_1 U(r_m + \hat{k_f}s_1) \right\}. \tag{2.56}
\]

At this point, the above equation can be partitioned into two parts, the part explicitly depending upon the scattered direction (\(\hat{k_f}\)) and the part depending explicitly upon the incident direction (\(\hat{k_i}\)). If one considers the product depending only on the incident direction, then yet another substitution can be made, such that

\[
W_j = \int_{s_j}^{\infty} U(r_m - \hat{k_i}s_{j-1}) \, ds_{j-1}, \tag{2.57}
\]

and

\[
W_0 = \int_{0}^{\infty} U(r_m - \hat{k_i}s_{m-1}) \, ds_{m-1}. \tag{2.58}
\]

Thus, calling the product in question \(K\), one finds that

\[
K = \int_{s_2}^{\infty} ds_1 U(r_m - \hat{k_i}s_1) \int_{s_3}^{\infty} ds_2 U(r_m - \hat{k_i}s_2) \times ...
\]

\[
\times \int_{s_{m-1}}^{\infty} ds_{m-2} U(r_m - \hat{k_i}s_{m-2}) \int_{0}^{\infty} ds_{m-1} U(r_m - \hat{k_i}s_{m-1}) \int_{s_{m-2}}^{\infty} ds_{m-2} U(r_m + \hat{k_f}s_{m-2}) \times ...
\]

\[
= \int_{0}^{W_0} dW_{m-1} \int_{0}^{W_{m-1}} dW_{m-2} \times ... \int_{0}^{W_3} dW_2 \int_{0}^{W_2} dW_1. \tag{2.59}
\]
The expression for $K$ can now be integrated, with the following results:

\[
K = \int_0^W dW_m \int_0^{W_{m-1}} dW_{m-2} \times \cdots \int_0^{W_3} dW_2 \int_0^{W_2} dW_1
\]

\[
= \int_0^W dW_m \int_0^{W_{m-1}} dW_{m-2} \times \cdots \int_0^{W_4} dW_3 W_2^2
\]

\[
= \frac{1}{2} \int_0^W dW_m \int_0^{W_{m-1}} dW_{m-2} \times \cdots \int_0^{W_5} dW_4 W_3^3
\]

\[
::: = \frac{1}{2 \times 3} \int_0^W dW_m \int_0^{W_{m-1}} dW_{m-2} \times \cdots \int_0^{W_6} dW_5 W_4^3
\]

\[
::: = \frac{1}{2 \times 3 \times \cdots \times (m-3) \int_0^W dW_m \int_0^{W_{m-1}} dW_{m-2} W_{m-3}^2
\]

\[
= \frac{1}{2 \times 3 \times \cdots \times (m-3) \times (m-2) \int_0^W dW_m W_{m-2}^{m-1}
\]

\[
= \frac{1}{2 \times 3 \times \cdots \times (m-3) \times (m-2) \times (n-1) W_0^{m-1}
\]

\[
= [(m-1)!]^{-1} \left[ \int_0^\infty U \left( r_m - \hat{k}_s \right) ds \right]^{m-1}
\]

A similar substitution can be made for the product involving the direction of scattered momentum, allowing for the evaluation of these $n - m$ integrals,

\[
\int_0^\infty ds_m U \left( r_m - \hat{k}_f s_m \right) \int_0^\infty ds_{m+1} U \left( r_m + \hat{k}_f s_{m+1} \right) \times ...
\]

\[
\times \int_0^\infty ds_{n-2} U \left( r_m + \hat{k}_f s_{n-2} \right) \times \int_0^\infty ds_{n-1} U \left( r_m + \hat{k}_f s_{n-1} \right)
\]

\[
= [(n-m)!]^{-1} \left[ \int_0^\infty U \left( r_m + \hat{k}_f s \right) ds \right]^{n-m}
\]

The scattering amplitude can then be expressed using these terms,

\[
f(k_i, k_f) = -\frac{1}{4\pi} \sum_{n=1}^\infty \sum_{m=1}^n \left\{ \left( -\frac{i}{2k} \right)^{n-1} \int dr_m e^{i q r_m} U \left( r_m \right)
\]

\[
\times [(m-1)!]^{-1} \left[ \int_0^\infty U \left( r_m - \hat{k}_i s \right) ds \right]^{m-1}
\]

\[
\times [(n-m)!]^{-1} \left[ \int_0^\infty U \left( r_m + \hat{k}_f s \right) ds \right]^{n-m}
\]

\[
(2.62)
\]
At this point, the above equation can be further simplified, but cannot be made devoid of its dependence upon the scattering potential, which was the intention. However, a second approximation can be made which will allow a general expression that does not depend explicitly upon the scattering potential.

2.3.2 Schiff Scattering Amplitude for Small Angles

The above expression for the scattering amplitude is valid under conditions that \( k \) is large, so that the second term in Equation (2.51) is negligible and that the scattering angle is large, requiring that the \( n \) different stationary phase points are distinct. For this discussion, one begins with the assumption that the scattering angle is very small, such that \( \theta << (kR)^{-1/2} \). This results in two specific requirements. First, the \( n \) distinct stationary phase points now converge to a single point, thus eliminating the requirement for summation over \( m \). Secondly, the scalar product in the exponential of Equation (2.62) can be written in its Cartesian components,

\[
e^{i\mathbf{q} \cdot \mathbf{r}_m} = e^{i(q_x x_m + q_y y_m + q_z z_m)}.
\]

(2.63)

Since the scattering angle is assumed to be so small, the angle between \( \mathbf{k}_i \) and \( \mathbf{k}_f \) is nearly zero, ensuring that \( q_z \) is negligible. This can be explicitly demonstrated if one requires that \( \hat{k}_i \) coincide with the z-axis. Thus,

\[
q_z = \mathbf{q} \cdot \hat{k}_i
= (\mathbf{k}_i - \mathbf{k}_f) \cdot \hat{k}_i
= \mathbf{k}_i \cdot \hat{k}_i - \mathbf{k}_f \cdot \hat{k}_i
= k_i - k_f \cos \theta
= k_f (1 - \cos \theta)
\approx k_f \left[ 1 - \left( 1 - \frac{\theta^2}{2} \right) \right]
\approx \frac{k_f \theta^2}{2}.
\]

(2.64)
In the above demonstration, the fifth line was obtained by virtue of the fact that $k_i = k_f$ for elastic scattering. Furthermore, the sixth line was obtained by employing the Maclaurin series representation of $\cos \theta$ with truncation at the second term. It becomes clear that, because $\theta$ is so small, the longitudinal component of the momentum transfer is negligible, as would be expected physically.

This is not true of the transverse components of the momentum transfer. Again, one must consider the momentum transfer,

$$q \cdot q = q_x^2 + q_y^2,$$

where the longitudinal component has been omitted. Using the definition of the momentum transfer, one finds that

$$q_x^2 + q_y^2 = (k_i - k_f)^2$$

$$= k_i^2 + k_f^2 - 2k_i k_f \cos \theta$$

$$= 2k_f^2 - 2k_f^2 \cos \theta$$

$$\approx 2k_f^2 (1 - \cos \theta)$$

$$\approx 2k_f^2 \left( \frac{\theta^2}{2} \right)$$

$$\approx k_f^2 \theta^2.$$  

Thus, it is clear that the transverse components of the momentum transfer are both of the order of $\sim k\theta$ and cannot be neglected. Converting to Cartesian components, the scattering amplitude now becomes

$$f(k_i, k_f) = -\frac{1}{4\pi} \sum_{n=1}^{\infty} \left\{ \left( \frac{-i}{2k} \right)^{n-1} \int_{-\infty}^{\infty} dx_m \int_{-\infty}^{\infty} dy_m e^{i(q_x x_m + q_y y_m)} \right. $$

$$\times \int_{-\infty}^{z_m} d\tilde{z} U(x_m, y_m, z_m) [(m - 1)!]^{-1} \left[ \int_{-\infty}^{\tilde{z}_m} U(x_m, y_m, \tilde{z}) d\tilde{z} \right]^{m-1} \left. $$

$$\times [(n - m)!]^{-1} \left[ \int_{z_m}^{\infty} U(x_m, y_m, z) dz \right]^{n-m} \right\}. \quad (2.67)$$
To obtain the above form, it must be recognized that the first integral over $s$ in Equation (2.62) represents the pre-scattering trajectory while the second integration over $s$ represents the post-scattering trajectory. As the scattering angle is so small, these to wave-vectors are effectively the same. Therefore, instead of integrating over two different trajectories one can integrate a single trajectory for both regions ($-\infty$ to $z_m$ and then $z_m$ to $\infty$).

The integration over $z_m$ is of principle interest, so one can define it as $M$, such that

$$M = \int_{-\infty}^{\infty} dz_m U(x_m, y_m, z_m) \left[ (m - 1)! \right]^{-1} \left[ \int_{-\infty}^{z_m} U(x_m, y_m, z) \, dz \right]^{m-1} \times [(n - m)!]^{-1} \left[ \int_{z_m}^{\infty} U(x_m, y_m, z) \, dz \right]^{n-m}.$$  

(2.68)

One can then introduce the notation that

$$w = \int_{-\infty}^{z_m} U(x_m, y_m, z) \, dz$$

(2.69)

and

$$a = \int_{-\infty}^{\infty} U(x_m, y_m, z) \, dz.$$  

(2.70)

In order to be able to integrate over $w$, one must evaluate the derivative of $w$ with respect to $z_m$,

$$\frac{dw}{dz_m} = \frac{d}{dz_m} \int_{-\infty}^{z_m} U(x_m, y_m, z) = U(x_m, y_m, z_m).$$  

(2.71)

Therefore, it is clear that $dw = dz_m U(x_m, y_m, z_m)$. Finally, the new limits of integration must be evaluated, leading one to find that

$$w = \begin{cases} 
\int_{-\infty}^{-\infty} U(x_m, y_m, z) = 0 & \text{for } z_m = -\infty \\
\int_{-\infty}^{\infty} U(x_m, y_m, z) = a & \text{for } z_m = \infty
\end{cases}$$

(2.72)
Thus, the integral over $z_m$ now can be rewritten as

$$M = [(m - 1)! (n - m)!]^{-1} \int_0^a w^{m-1}(a - w)^{n-m}dw. \quad (2.73)$$

This equation must now be integrated by parts through $m - 1$ iterations. For the first integration, one can let $u = w^{m-1}$ and $dv = (a - m)^{n-m}dw$. Thus,

$$M = \frac{1}{(m - 1)! (n - m)!} \int_0^a w^{m-1}(a - w)^{n-m}dw \quad (2.74)$$

For the second integration, one can let $u = w^{m-2}$ and $dv = (a - w)^{n-(m-1)}dw$, such that

$$M = \frac{1}{(m - 2)! (n - (m - 1))!} \int_0^a w^{m-2}(a - w)^{n-(m-1)}dw. \quad (2.75)$$

Following this pattern, one finds that after $m - 1$ integrations, $M$ takes the form

$$M = \frac{1}{(n - 1)!} \int_0^a (a - w)^{n-1}dw. \quad (2.76)$$

The final integration can now be performed, yielding the following expression,

$$M = \frac{1}{(n - 1)!} \int_0^a (a - w)^{n-1}dw$$

$$= \frac{1}{(n - 1)!} \frac{-1}{n} (a - w)^n \bigg|_0^a$$

$$= a^n \frac{1}{n!}.$$

$$= a^n \frac{1}{n!}.$$
The scattering amplitude is no longer dependent upon \( m \), as should be expected. Thus,

\[
\begin{align*}
   f(k_i, k_f) &= -\frac{1}{4\pi} \sum_{n=1}^{\infty} \left( -\frac{i}{2k} \right)^{n-1} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{i(q_x x + q_y y)} a^n n! \\
   &= -\frac{1}{4\pi} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{i(q_x x + q_y y)} \sum_{n=1}^{\infty} \left( -\frac{i}{2k} \right)^{n-1} a^n n! \\
   &= \frac{k}{2i\pi} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{i(q_x x + q_y y)} \sum_{n=1}^{\infty} \left( -\frac{i a}{2k} \right)^n \frac{1}{n} \\
   &= \frac{k}{2i\pi} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{i(q_x x + q_y y)} \left( e^{-\frac{i a}{2k} - 1} \right) \\
   &= \frac{ik}{2\pi} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{i(q_x x + q_y y)} \left( 1 - \exp \left[ -\frac{i}{2k} \int_{-\infty}^{\infty} U(x, y, z) dz \right] \right).
\end{align*}
\]

(2.78)

At this point, it should be noted that the integration over \( x \) and \( y \) is taken over the plane perpendicular to the scattering axis. In the limit of an axially symmetric scattering potential, \( x \) and \( y \) can be represented by the impact parameter, \( b = \sqrt{x^2 + y^2} \), and the azimuthal angle, \( \phi \), such that \( x = b \cos \phi \) and \( y = b \sin \phi \). Thus, the transformation to cylindrical coordinates renders the scattering amplitude into the form

\[
\begin{align*}
   f(k_i, k_f) &= \frac{ik}{2\pi} \int_{0}^{2\pi} d\phi \int_{0}^{\infty} e^{i(q_x b \cos \phi + q_y b \sin \phi) b} db \left( 1 - \exp \left[ -\frac{i}{2k} \int_{-\infty}^{\infty} U(b, z) dz \right] \right).
\end{align*}
\]

(2.79)

Now, as the scattering potential is spherically symmetric, the momentum transfer will always be parallel with \( b \). As a result, the expression \( q_x b \cos \phi + q_y b \sin \phi \) will have the same value regardless of the value of \( \phi \). Therefore, one can choose any value of \( \phi \), and then sum all of the contributions from 0 to \( 2\pi \). Specifically, if one allows \( \phi = \phi' = 0 \), then \( q_x = q \) and \( q_y = 0 \). Consequently,

\[
q_x b \cos \phi + q_y b \sin \phi = q b \cos \phi'.
\]

(2.80)
The integral over $\phi$ now takes the form of the zeroth-order Bessel function [14],

$$\int_0^{2\pi} e^{qb\cos\phi} d\phi = 2\pi J_0(qb).$$

(2.81)

The small angle Schiff Approximation to the scattering amplitude can now be expressed as

$$f(k_i, k_f) = ik \int_0^\infty J_0(qb) \left(1 - \exp \left[ -\frac{i}{2k} \int_0^\infty U(b, z) \, dz \right] \right) bdb.$$

(2.82)

Unfortunately, the scattering amplitude is still an explicit function of the scattering potential, a term that is not obtained during an END calculation. This expression can, however, be transformed into one that does not depend on the scattering potential [23]. If one assumes that $r$ is the position of the projectile at any point during the trajectory, then the fact that the scattering angle is very small requires that

$$r \cdot r = (z + b) \cdot (z + b),$$

(2.83)

where $z$ is the position of the projectile along the scattering axis. As the impact parameter is perpendicular to the scattering axis, it is clear that $r^2 = z^2 + b^2$. From this, one finds that

$$dz = \frac{dr}{\left[1 - \left(\frac{b}{r}\right)\right]^{1/2}}.$$

(2.84)

Therefore, the argument of the exponential now becomes

$$\frac{1}{2k} \int_{-\infty}^\infty U(b, z) = \frac{1}{2k} \int_{-\infty}^\infty \frac{U(r)}{\left[1 - \left(\frac{b}{r}\right)\right]^{1/2}} dr$$

$$= \frac{1}{k} \int_0^\infty \frac{U(r)}{\left[1 - \left(\frac{b}{r}\right)\right]^{1/2}} dr,$$

(2.85)

where the fact that the limits of integration remain the same when the transformation from $z$ to $r$ is made. Furthermore, the symmetry of the scattering potential was utilized in the second step. The above expression is the Massey-Mohr approximation for the semi-classical phase shift, $\delta(b)$, in the small scattering angle
limit [21, 25, 26] which is the semi-classical analog of the Kennard approximation for classical scattering processes [23, 27]. Specifically, the Massey-Mohr approximation is given the form [23]

\[ \delta(b) \approx -\frac{k}{2} \int_{b}^{\infty} \left( \frac{U}{k^2} \right) \left[ 1 - \left( \frac{b}{r} \right)^2 \right]^{1/2} \, dr. \] (2.86)

In the asymptotic limit, \( r \gg b \), therefore,

\[ \frac{1}{2k} \int_{-\infty}^{\infty} U(b, z) \approx -2\delta(b). \] (2.87)

Finally, this means that the Schiff Approximation scattering amplitude for small angle scattering takes the form [23, 28]

\[ f(k_i; k_f) \approx ik \int_{0}^{\infty} J_0(qb) (1 - \exp[-2i\delta(b)]) b \, db. \] (2.88)

While Equation (2.88) no longer depends explicitly upon the potential, it has introduced the semi-classical phase shift, which itself is not a value provided by END calculations. This is easily remedied, though, by the fact that the semi-classical phase shift is directly related to the deflection function by the expression [19, 21, 23]

\[ \Theta(b) = \frac{2}{k} \frac{d\delta(b)}{db}. \] (2.89)

The Schiff Approximation provides an effective method for calculating the scattering amplitude without any prior knowledge of the scattering potential. The principle power of the Schiff Approximation is the fact that it explicitly contains all of the terms in the infinite Born series. Furthermore, the Schiff Approximation provides good differential cross sections in the region of small scattering angle, which the region most often reported by experimental studies.
Quantum mechanical calculations on molecular systems are traditionally divided into two general categories, the localized valence bond-type (VB) calculations and the delocalized molecular orbital-type (MO) calculations. In many ways, these two descriptions serve as complements to each other. Where VB methods, in general, provide more visual physical descriptions, such as molecular geometries, they generally fail with important properties, such as paramagnetism and bond strengths. The MO method tends to provide a more rigorous quantum mechanical description of molecules, such as electron delocalization over the entirety of a molecule and variations in bond strengths, but generally offers little in the way of physically intuitive descriptions of the molecular system. Both classes of methods are formulated from rather coarse approximations, and, as a consequence, each possesses deficiencies, in particular with relation to electron correlation. The VB methods tend to over-estimate electron correlation, while MO methods tend to under-estimate correlation effects [29]. While each has its strengths and weaknesses, and while each converges to a common molecular wave function representation in the absence of their respective generalized approximations, a large community of quantum chemists has chosen to employ MO methods for quantum chemical calculations. The MO method, and its application in the Hartree-Fock approximation, will be the focus of this chapter.

Some address must be made toward notation. The literature of ab initio quantum chemistry, as with most other fields, is not completely consistent. While it is not crucial to describe a set of canonical variables, clarification of symbolic
Table 3.1: Notation employed in this review.

<table>
<thead>
<tr>
<th>Term</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi$</td>
<td>Exact electronic wave function</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>Generally approximated electronic wave function</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Electronic spin-orbital</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Spatial electronic factor</td>
</tr>
<tr>
<td>$\alpha,\beta$</td>
<td>Spin electronic factor</td>
</tr>
<tr>
<td>$\phi$</td>
<td>General electronic basis function</td>
</tr>
<tr>
<td>$dV$</td>
<td>Element of spatial volume (no spin included)</td>
</tr>
<tr>
<td>$dr$</td>
<td>Element of volume (spin included)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Uppercase Roman indices</th>
<th>Nuclear indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowercase Roman indices</td>
<td>Molecular orbital expansion coefficients</td>
</tr>
<tr>
<td>Lowercase Greek indices</td>
<td>Atomic orbital expansion coefficients</td>
</tr>
</tbody>
</table>

notation up front is the most lucid manner of handling the issue. The notation of Szabo [30] will be most closely followed, with minor adjustments as needed. Table 3.1 provides an exhaustive list of notation used in this chapter.

3.1 The Hartree-Fock Approximation

The MO method in quantum chemical calculations of molecular systems has become synonymous with the Hartree-Fock (HF) approximation. In this section, the HF approximation and the HF wave functions will be introduced. Additionally, the concept of electron correlation and the correlation effects will be addressed. Finally, an in depth discussion of HF basis sets will be made.

3.1.1 Partitioning of the Molecular Wave Function

In Section 1.2, the non-relativistic molecular Hamiltonian operator was introduced, with the explicit form

$$\hat{H} = -\frac{1}{2} \sum_{A=1}^{K} \frac{1}{M_A} \nabla_A^2 - \frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{A=1}^{K} \sum_{B=A+1}^{K} \frac{Z_A Z_B}{r_{A,B}} - \sum_{A=1}^{K} \sum_{i=1}^{N} \frac{Z_A}{r_{A,i}} + \sum_{j=1}^{N} \sum_{i=j+1}^{N} \frac{1}{r_{i,j}}, \quad (3.1)$$

where the indices $A$ and $B$ refer to elements of the $K$ nuclei and $i$ and $j$ label elements of the $N$ electrons. Furthermore, $Z_A$ is the charge of nucleus $A$ and $r_{A,B}$, $r_{A,i}$, and $r_{i,j}$ are the distance between nuclei $A$ and $B$, the distance between nucleus
and electron $i$, and the distance between electrons $i$ and $j$, respectively. The complicated coupling between the nuclear and the electronic degrees of freedom cause the Schrödinger equation to be practically insoluble by direct methods. To simplify the problem, the Born-Oppenheimer (BO) approximation was introduced, in which the nuclear degrees of freedom are assumed to vary on a much larger time-scale than the electronic degrees of freedom. In essence, the BO approximation allows for a “clamped nucleus” model, in which the nuclei are fixed in space and the electronic degrees of freedom are allowed to vary on this fixed nuclear framework. As the nuclei are motionless, the nuclear kinetic energy terms (the first summation in Equation (3.1), above) become identically zero. This assumption decouples to nuclear degrees of freedom from the nuclear degrees of freedom. The resulting form of the Schrödinger equation is now called the electronic Schrödinger equation and takes the form

$$\hat{H}_{el} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{A=1}^{K} \sum_{B=A+1}^{K} \frac{Z_A Z_B}{r_{A,B}} - \sum_{A=1}^{K} \sum_{i=1}^{N} \frac{Z_A}{r_{i,A}} + \sum_{j=1}^{N} \sum_{i=j+1}^{N} \frac{1}{r_{i,j}}. \quad (3.2)$$

It is the solutions to this equation with which the majority of quantum chemistry is focused.

Following the example of Löwdin [31], one can partition the electronic Hamiltonian operator into three parts,

$$\hat{H}_{el} = h^0 + \sum_{i=1}^{N} h^1_i + \sum_{i=1}^{N} \sum_{j=i+1}^{N} h^2_{i,j}. \quad (3.3)$$

In the above equation, the term $h^0$ is the nuclear repulsion (or zero-electron Hamiltonian) term, which depends only upon the fixed nuclear degrees of freedom and is defined as

$$h^0 = \frac{1}{2} \sum_{A=1}^{K} \sum_{B=A+1}^{K} \frac{Z_A Z_B}{r_{A,B}}. \quad (3.4)$$
The second term in Equation 3.3, $h^1_i$, is the one-electron Hamiltonian. The one-electron Hamiltonian includes the additive kinetic energies of the individual electrons as well as instantaneous attractive potentials between the $N$ electrons and the $K$ nuclei and takes the form

$$h^1_i = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{K} \frac{Z_A}{r_{i,A}}$$

(3.5)

The final term, $h^2_{i,j}$, is the two-electron Hamiltonian, which generates the instantaneous repulsive forces between each individual electron and the remaining molecular electrons. The two-electron Hamiltonian takes the form

$$h^2_{i,j} = \frac{1}{r_{i,j}}$$

(3.6)

The terms denoted by $h^0$ result in a constant for a given nuclear configuration, and therefore will not have any bearing on our choice of molecular wave function. Rather, the total energy will only be increased by the fixed potential energy values associated with $h^0$.

The above partitioning of the molecular Hamiltonian operator in Equation (3.3) allows one to write the molecular wave function as a product wave function of the form

$$\Phi_{el}(\{r_i\}; \{r_A\}) = \Phi_1(\{r_i\}; \{r_A\})\Phi_2(\{r_i\}; \{r_A\})$$

(3.7)

where the factor wave functions are eigenfunctions of the operators in Equation 3.3, specifically,

$$\mathcal{H}_{el}\Phi_1 = \mathcal{E}_1 \Phi_1,$$

(3.8)

$$\mathcal{H}_{el}\Phi_2 = \mathcal{E}_2 \Phi_2,$$

(3.9)

where $\mathcal{E}_1$, and $\mathcal{E}_2$ are the energy eigenvalues. The total energy for the given nuclear configuration, $\mathcal{E}$, becomes the sum of the energy eigenvalues and the nuclear
potential energy defined by $h^0$,

$$\mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2 + V_{\text{nuc}}.$$  

(3.10)

The major focus of quantum chemistry involves the solution of Equations (3.3), (3.7), and (3.10), and we will use these equations as the starting point for the discussion of the Hartree-Fock approximation.

### 3.1.2 The Hartree-Fock Wave Function

The HF approximation begins with the assumption that the total electronic wave function can be approximated by a product of one-electron wave functions. Furthermore, one must assume that the potential experienced by a given electron is an average of the potentials produced by the remaining electrons [29]. In this approximation, the term $h^0$ and the $N$ different $h^1$ terms are maintained, but the $\frac{N}{2}(N-1)$ two-electron terms are replaced by $N$ additional one electron terms. By replacing the two-electron terms with one-electron terms, the HF approximation does not explicitly treat the instantaneous interaction of individual electrons. Rather, each electron is treated as if it were influenced by an average field produced by the other electrons in the molecule. This approximation allows for relatively accurate quantum chemical calculations despite the gross approximations imposed, though several important physical descriptions are omitted. These correlation effects will not be discussed in this chapter.

The new electronic Hamiltonian can be rewritten in the form

$$\hat{\mathcal{H}}_{\text{el}} = \sum_{i=1}^{N} \left[ h^1_i + V_{i}^{HF} \right],$$

(3.11)

where $h^1_i$ is the one-electron Hamiltonian (as previously defined) and $V^{HF}$ is the new HF one-electron potential energy term (to be defined later in this section). Because the zero-electron Hamiltonian only adds a constant factor to the electronic
energy, it is omitted. The most striking benefit of this reformulation of the electronic Hamiltonian is the fact that, because the Hamiltonian operator is now a sum of one-electron terms, one can approximate a single \( N \)-electron wave function as a product of \( N \) one-electron wave functions (called a Hartree product),

\[
\Psi^{HP}(\{x_i\}; \{r_A\}) = \prod_{j=1}^{N} \chi_j(\{x_i\}; \{r_A\}),
\]

which is an eigenfunction of the one-electron Hamiltonian,

\[
\mathcal{H}_{el}^{HP} = E\Psi^{HP}.
\]

As before, the eigenvalue is the energy of the system.

The wave function defined in Equation (3.12) is a product of a set of \( N \) spin-orbitals, \( \chi_j \), which are themselves eigenfunctions of the respective one-electron Hamiltonians,

\[
[h^1_j + V^{HF}_j] \chi_j = \epsilon_j \chi_j,
\]

where \( \epsilon_j \) is the energy eigenvalue of the \( j \)th orbital. The total energy, \( E \), is a sum of the orbital energies,

\[
E = \sum_{j=1}^{N} \epsilon_j.
\]

The electronic Hamiltonian in Equation (3.11) does not have a spin dependence, therefore a transformation from spatial electronic coordinates, \( \{r_i\} \), to spatial-spin coordinates, \( \{x_i\} \) by employing a product form of the spin-orbitals does not change the energy eigenvalues of Equation (3.13). Thus, in the absence of relativistic effects, the \( N \) spin-orbitals can be represented by a product of a spatial-dependent factor, \( \psi_j(\{r_i\}) \), and a spin-dependent factor, either “spin up”, \( \alpha(\omega) \), or “spin down”, \( \beta(\omega) \), such that

\[
\chi_j = \begin{cases} 
\psi_j(\{r_i\})\alpha(\omega) \\
\psi_j(\{r_i\})\beta(\omega)
\end{cases}.
\]
The variable \( \omega \) represents the general spin variable. It should be noted that the product wave functions indicated in the above equation have the same spatial factors with varying spin factors. This is consistent with restricted HF method. Allowing each spin-orbital to have a unique spin AND spatial factor results in the unrestricted HF method. [30].

The partitioning of the spin-orbitals given by Equation (3.16) satisfies the Pauli exclusion principle by allowing two spin-orbitals to have the exact same spatial factor, but opposite spins (that is, one molecular orbital with a paired set of electrons). However, a further requirement of the molecular electronic wave function is that it must obey the Fermi-Dirac statistics, in particular that the electronic wave function must be anti-symmetric with respect to exchange of electron indices. The Hartree product given by Equation (3.12) does not satisfy the Fermi-Dirac statistics, being that the sign of \( \Psi^{HP} \) remains unchanged if two indices are exchanged. Adherence to the Fermi-Dirac statistics traditionally required detailed group algebra. This was greatly simplified by Slater, who circumvented group theoretical descriptions by introduction of the spin-orbital function directly into a determinant that would later bear his name [32].

Slater exploited the property of matrix algebra that, given a matrix, interchanging any two columns of the matrix will change the sign of the determinant of the matrix. Thus, Slater constructed a matrix in which the spin-orbitals are placed as the columns and the occupying electrons are placed as the rows of the matrix. The determinant of this matrix is the most general anti-symmetrized product wave function. Mathematically, one finds that,

\[
\Psi_{Slater} = (N!)^{-1} \begin{vmatrix}
\chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\
\chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N)
\end{vmatrix} = (N!)^{-1} \det \{ \chi_j(x_i) \}. \quad (3.17)
\]
At this point some discussion of the approximated one-electron potential in Equation (3.11) can be made. It is beyond the scope of this review to explicitly derive the form of the term $V_i^{HF}$, so it must suffice to say that the potential form can be obtained by employing Lagrange’s method of undetermined multipliers to the energy eigenvalue equation \[ \mathcal{H}_{el} \Psi^{Slater} = E \Psi^{Slater}. \] (3.18)

The resulting HF Hamiltonian (variously referred to as the Fockian and denoted $\mathcal{F}$) is a sum of $N$ Fock operators, which satisfy the eigenvalue equations of the form

\[
\left[ h_i^1 + \sum_{j \neq i}^N \mathcal{J}_j - \sum_{j \neq i}^N \mathcal{K}_j \right] \chi_i = \epsilon_i \chi_i. \tag{3.19}
\]

The term in brackets in the above equation is the Fock operator for orbital $i$. It can be seen that the approximated one-electron potential has been split into two components. The first is the coulomb operator, which defines the interaction of electrons with an average potential. The action of the coulomb operator is to provide an average repulsive potential felt by an electron at the position $x_1$ that arises from an electron in a second orbital. The coulomb operator has the inverse $r$ form of a coulomb interaction, weighted by the probability density of the orbital to be averaged, specifically,

\[
\mathcal{J}_i(x_1) \chi_j(x_1) = \left[ \int d\mathbf{x}_2 |\chi_i(\mathbf{x}_2)|^2 r_{ij}^{-1} \right] \chi_j(x_1). \tag{3.20}
\]

The coulomb operator arises as a consequence of the assumption that the electronic Hamiltonian is a sum of one-electron operators only. The second operator results from the anti-symmetrization of the wave function through the use of a Slater determinant. This operator, the exchange operator, results in the exchange of two electrons and produces a one-electron potential that is dependent upon the value of the orbital in question throughout all space \[30\]. The form of the exchange
operator is
\[ \mathcal{H}_i(x_1)\chi_j(x_1) = \left[ \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) r_{ij}^{-1} \chi_i(\mathbf{x}_2) \right] \chi_j(x_1). \] (3.21)

The effect of the coulomb operator is localized and has a classically intuitive interpretation, however, the action of the exchange operator is non-local and depends upon the location of these two orbitals in the spin-orbital space.

### 3.1.3 Solving the HF Equations: Basis Set Expansions

In Section 3.1.2, we introduced the Hartree-Fock integral-differential equations (now rewritten using Dirac notation),

\[ \mathcal{F} | \Psi^{Slater} \rangle = E | \Psi^{Slater} \rangle, \] (3.22)

by using Equations (3.18) - (3.21). Traditionally, one makes consistent use of Slater determinants for the molecular wave function, and superscripts on \( \Psi \) will consequently be dropped for the remainder of the chapter. The solution of these equations is still a non-trivial task. The first methods of solving these equations, specifically for small atomic systems, was through numerical integration [29].

A considerable breakthrough was introduced by Roothaan [33] in 1951. The computation routine of Roothaan involved expanding the molecular wave function in a basis of atomic spin-orbitals with the general form of a linear combination of spatial atomic orbital basis functions multiplied by the appropriate spin function. This expansion allowed the Hartree-Fock differential equations to be written as a set of algebraic matrix equations, which could be solved using available linear algebraic techniques.

The general form of the basis set expansion of the \( ith \) spatial component of the wave function takes the form
\[ \psi_i = \sum_{\mu=1}^{K} \phi_\mu \zeta_{\mu i}, \] (3.23)
where the basis set is composed of $K$ functions, $\{\phi_{\mu}|\mu = 1, 2, ..., K\}$. The term $c_{\mu i}$ represents the expansion coefficient for the $\mu$th basis function to form the $i$th spatial component of the wave function.

The size of the expansion ($K$) is in general not limited to a specific number. In fact, an infinite expansion would be desirable, as this would correspond to the full Hartree-Fock wave function. However, this is practically impossible due to computational limitations. The size of $K$ should ideally be large enough to offer the best descriptions of the molecular orbitals without becoming computationally inefficient. This, along with other specific criteria that must be considered will be addressed in the next section. At this point it will suffice to assume that some general function form and expansion size has been decided upon.

The Hartree-Fock equation for a given spatial component of the wave function can now be written as

$$\mathcal{F}|\psi_i\rangle = \epsilon_i|\psi_i\rangle,$$  \hspace{1cm} (3.24)

where $\epsilon_i$ is the orbital energy of the $i$th spatial orbital. The basis set expansion for $\psi_i$ can now be introduced. The result becomes

$$\mathcal{F} \sum_{\mu=1}^{K} |\phi_{\mu}\rangle c_{\mu i} = \epsilon_i \sum_{\mu=1}^{K} |\phi_{\mu}\rangle c_{\mu i}. \hspace{1cm} (3.25)$$

At this point, one can then multiply through on the left of the equation by an arbitrary basis component $\langle \phi_\nu |$ and integrate. The $i$th orbital energy is a number, and thus can be extracted from the integration, as can the expansion coefficients. Thus, the equation now becomes

$$\sum_{\mu=1}^{K} \langle \phi_\nu | \mathcal{F} |\phi_{\mu}\rangle c_{\mu i} = \sum_{\mu=1}^{K} \langle \phi_\nu | \phi_{\mu}\rangle c_{\mu i} \epsilon_i. \hspace{1cm} (3.26)$$

At this point, one must introduce two matrices with elements that are related to the terms in the above equation. The first is the Fock matrix, $\mathbf{F}$. The Fock matrix
The second matrix is the overlap matrix, \( S \). The elements of the overlap matrix are given as

\[
S_{\nu\mu} = \langle \phi_\nu | \phi_\mu \rangle
\]  

(3.28)

and arises from the fact that the basis functions are not necessarily orthogonal. The overlap matrix provides a measure of the linear dependence of the set of basis functions. Due to assumed normalization, the diagonal elements of the overlap matrix all have a magnitude of one. The off-diagonal elements will range in magnitude between zero and one. Elements approaching one will demonstrate a strong linear dependence between two basis functions, while a value approaching zero indicates a strong linear independence.

The HF equation can thusly be expressed using the newly defined matrix elements,

\[
\sum_{\mu=1}^{K} F_{\nu\mu} c_{\mu i} = \sum_{\mu=1}^{K} S_{\nu\mu} c_{\mu i} \epsilon_i.
\]  

(3.29)

It is clear at this point that the above equation is an element of one single matrix equation of the form

\[
FC = SC\epsilon,
\]  

(3.30)

where \( F \) and \( S \) are as defined above, \( C \) is the \( K \times K \) matrix of expansion coefficients, and \( \epsilon \) is a \( K \times K \) diagonal matrix with the orbital energies as the diagonal elements. Equation (3.30) is commonly referred to as the Roothaan-Hall equation \[34\]. A companion equation exists for unrestricted determinants, called the Pople-Nesbet equation \[30, 35\]. The Pople-Nesbet equations have individual matrix equations for each set of spin-orbitals, as each pair of spin-orbitals has a different spatial component in the unrestricted formalism.
As the overlap matrix and the Fock matrix are both Hermitian (and in many cases real and symmetric), relatively simple solution techniques are available for solving the Roothaan-Hall equations [36, 37]. The most common method involves diagonalization of the matrices by use of a unitary transformation. This method presents the eigenvalues (elements of $\mathbf{e}$) and eigenfunctions (elements of $\mathbf{C}$) for the matrix equation.

The rudiments of solving the Roothaan-Hall or Pople-Nesbet equations will not be discussed any further in this dissertation. Rather, in the next two sections specific interest will be placed on the general form and construction of basis sets for use with these matrix equations.

### 3.2 General Forms and Properties of Basis Sets

To this point, no mention has been made as to the functional form that the basis set should take. In general, any functional form is possible, but certain properties are desirable. Specifically, the wave function for the system must be single-valued, finite, continuous, and square-integrable [38]. It is thus desirable that one choose basis functions that possess these characteristics. A set of atomic orbitals (AOs) is an immediate choice for a given basis set, as AOs satisfy the above criteria as well as offer a chemical intuitiveness lacking in other choices.

#### 3.2.1 Slater-Type and Gaussian-Type Orbitals

A first choice of basis sets was a set of spatial orbitals with the same functional form as the hydrogenic orbitals,

$$
\psi_{\text{STO}} = \left[ \frac{(2\zeta)^{2n+1}}{(2n)!} \right]^{1/2} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi).
$$

Equation (3.31) is called a Slater-type orbital (STO) [29, 34]. The equation involves the terms $\zeta$, which is the orbital exponent; $n$ which is the principle quantum number; $l$, which is the azimuthal quantum number; and $m$, which is
the magnetic quantum number. The term $Y_{l}^{m}(\theta, \phi)$ is the spherical harmonic. As the functional form of hydrogenic orbitals are derived from specific linear combinations of STO basis functions, one may reasonably expect that they will be good approximations to orbitals in multi-electron atoms. In fact, STO functions have correct functional forms at small $r$ values and also at very large $r$ values. As can be seen from Equation (3.31), STO functions do not have any nodal structure, and therefore linear combinations must be constructed to properly mimic the nodal structure of atomic orbitals. However, basis sets built from relatively small linear combinations of STO basis functions have been quite successfully employed in quantum chemical calculations [29].

Despite the desirable functional form of the STOs, the principle drawback is numerical [34]. The large portion of computational time in the HF method is the calculation of the many-center two-electron integrals. Slater-type orbital basis functions do not admit simple analytical expression for such two-center integrals, and must therefore be numerically integrated [39]. This is a time consuming process and, as a result, for any system with more than a few atoms the accuracy obtained by using STO bases is outweighed by the severe decrease in computational efficiency.

This limitation was circumvented by Boys, who suggested using Gaussian-type functions instead of exponential functions [40]. The functional form of a Gaussian-type orbital (GTO) is [41]

$$\psi_{GTO} = \left[ \frac{(2/\pi)^{1/2}(4\alpha)^{2n+1}}{(2n-1)!!} \right]^{1/2} r^{n-1} e^{-\alpha r^{2}} Y_{l}^{m}(\theta, \phi), \quad (3.32)$$

where $n$, $l$, and $m$ are the same quantum numbers as given in Equation (3.31). The parameter $\alpha$ is a different orbital exponent specific to the GTO basis. Note that angularly, STO and GTO basis functions have the same functional form, the only difference lies in the radial factors.
The primary deficiency of the GTO basis is immediately clear. A GTO function does not provide the correct functional form as $r \to 0$ or at $r \to \infty$. In particular, an STO function will have $d\psi_{STO}/dr > 0$ at $r = 0$, whereas a GTO function will always have $d\psi_{GTO}/dr = 0$ at $r = 0$. Furthermore, the GTO basis function has a much faster drop-off in the tail of the orbital as $r \to \infty$ than does the STO function. This is a fairly severe limitation to the accuracy of GTO bases in computations, as the functional form of the STO basis sets leads to superior accuracy over GTO bases. The top panel in Figure 3.1 demonstrates the considerable difference between the radial part of the hydrogen 1s orbital represented as a single STO function and a single GTO function. This red curve is the hydrogenic 1s STO function and the blue line is a single GTO function in which the exponent has been optimized to provide the best least-squares fit to the STO [41].

One can improve the structure by building a linear combination of GTO basis functions (with optimized exponents) for each STO function employed. Both the set of exponents for each primitive Gaussian orbital and the set of contraction coefficients must be optimized to fit the Slater in question. The bottom panel in Figure 3.1 shows that a linear combination of six GTO functions (blue) provides a much better fit for the hydrogen 1s orbital as represented by a single STO function (red), but that it is still not particularly good at the cusp of the orbital. In general, a very large number of GTO functions with large exponents would be needed to correctly mimic the cusp of an STO function, but no matter how many terms where included in the linear combination, the derivative of the GTO function would still be zero at $r = 0$.

Despite this cusp deficiency, quite good accuracy can be obtained from a good sized linear combination of GTO basis functions per Slater. Yet, one must ask why a linear combination of six or more GTO functions is favorable over a single STO
Figure 3.1: Comparison of STO and GTO representations of the radial part of the hydrogen 1s orbital. Top: A single GTO function fit to a single STO function. Bottom: A linear combination of six GTO functions fit to a single STO function.

function, particularly when the accuracy of the STO basis is superior to the larger GTO basis. The answer lies in the fact that when a product of two GTOs is taken, the result is a third GTO [30]. This reduces a multi-center two-electron integral to a considerably simpler analytic form [39]. As a consequence, a calculation utilizing a larger GTO basis is much more efficient that a calculation using a smaller STO basis. This substantially greater computational speed has lead to the fact that most calculations of polyatomic systems have traditionally employed GTO basis sets [42].
Other basis sets have been employed in various studies, such as plane wave basis sets. However, these are still not as widely used as STO bases and, particularly, GTO bases. The remainder of this chapter will specifically focus on Slater and Gaussian basis sets.

### 3.2.2 The Structure of Basis Sets

Now that the general form of an orbital basis function has been chosen, either STO or GTO, the full basis set for an atom must be constructed. While there are (theoretically) no limitations on the construction of basis sets, practicality has restricted quantum chemists to certain accepted forms of contraction.

#### Minimal basis sets

Any atom must have at least enough orbitals available to completely contain the required number of electrons. Any basis set designed to completely represent only the ground state orbital structure of an atom is referred to a minimal basis set [30]. For example, a minimal basis set for a Mg atom would contain no less than 6 orbitals, the 1\(s\), 2\(s\), 2\(p_x\), 2\(p_y\), 2\(p_z\), and the 3\(s\) orbital. It would therefore be sufficient to build a minimal basis of 6 STO basis functions, three with \(n = 0\) and three different values of \(\zeta\) as well as three others with \(n = 1\) and a fourth value of \(\zeta\).

Furthermore, it would be possible to build a minimal basis set of six single, uncontracted GTO basis functions in the same manner. However, as the previous discussion indicated, the accuracy would be considerably less than the for the comparable STO basis. So, to remedy this, a specific number of Gaussian primitive functions (single GTO basis functions) are generally fit to each STO function in the minimal set. This describes the formalism to construct a minimal STO-NG basis set [43]. The title of this basis set indicates that \(N\) Gaussian primitives are optimized to fit a single STO function. While any number of primitives may be fit to a given STO function, in practice the STO-6G is the largest Gaussian minimal
basis that is employed. Without exception, the STO-3G is the most widely used minimal basis set.

Minimal basis sets are notoriously inaccurate basis sets. In general STO-NG basis sets offer qualitatively correct descriptions of fundamental chemical properties such as bonding and can be employed for initial guesses and for calculations involving very large molecules where more complete basis sets would be computationally inefficient. However, the small size of the STO-NG basis set is prohibitive to the use of minimal bases for calculations in which even moderate accuracy is required [30, 44].

As a final point concerning STO-NG minimal bases it should be noted that for certain atoms these bases are not truly minimal. Many times chemical bonding is not correctly mimicked using a truly minimal basis set. For this reason, the Group 1A and Group 2A metals, as well as the first two rows of transition metals, will include the low-lying $p$ orbitals even though they are unoccupied in the unbound atom [34]. The $s$ and $p$ exponents for a given principal energy level are identical. This is computationally more efficient than allowing for separate $s$ and $p$ exponents as each set of $s$ and $p$ orbitals will then have the same radial behavior and can, consequently, be integrated together [30].

**Double-zeta and split-valence basis sets**

One of the main limitations of the minimal basis set is the fact that there is no flexibility for the generated orbitals to change size under the influence of intramolecular surroundings. Each orbital has a single set of exponents that control the size and shape of the orbital, and while the amplitude of the orbital can be adjusted through the HF coefficients, the spatial size cannot be changed. To remedy this, one would desire to include more than a single linear combination of basis functions for a given orbital. This idea gives rise to the next level of basis sets, the double-zeta and the split valence basis sets. Much of this discussion
will be made in terms of STO bases. It should be remembered that these ideas can be translated directly to GTO bases by requiring that each STO function be constructed as a linear combination of GTO functions.

Specifically, the double-zeta functions allow for each orbital to be a composed of a linear combination of two STO basis functions, each with a different exponent. The larger exponent (a tighter function) is, in general, slightly larger than the optimal exponent for the single zeta function, while the smaller exponent (a more diffuse function) is slightly smaller \[30\]. Furthermore, as the double-zeta basis is more complete than a comparable single-zeta basis, a correctly optimized linear combination of double-zeta functions will be a better representation of the physical orbital than a single-zeta function. This results in an improvement in the ground state energy, as demonstrated by Clementi and Roetti in their seminal paper on double-zeta functions for atoms \[45\].

A simplification of the double-zeta basis can be made by realizing that, during a chemical process, the size and shape of core atomic orbitals will not change significantly. Therefore, under most any conditions, a single well-optimized STO function will provide a sufficient representation of a core orbital. One can then allow for the valence orbitals to be represented using a combination of two STO basis functions, as in the double-zeta basis. This is the formula for constructing split-valence basis sets \[34\].

Split-valence basis sets provide ground state energies that show improvements over minimal basis sets, but that are not as good as double-zeta bases. Again, this is due to the fact that a more complete description of core orbitals is obtained with the double-zeta functions. However, this energy difference is small when compared to the computational efficiency gained through using split-valence bases \[30\].

The most common split-valence basis sets that are employed in computational chemistry are the \(l:mnG\) basis sets. These are combinations of GTO functions such
that the core orbitals for the atom are represented as a contraction of \( l \) GTO basis functions. A given valence orbital is represented as a linear combination of two basis functions, one composed of \( m \) GTO primitives and the second composed of \( n \) GTO primitives [34]. The only exceptions occur with H and He, in which there are no core shells and only the valence shell structure is used (and as a consequence the 4:31G bases for H and He are identical to the 6:31G bases). The most common examples of split-valence bases are the 3:21G [46], 4:31G [47], and 6:31G [48] bases. This pattern can be extended to larger basis sets such as the 6:311G basis [44].

Double-zeta and split-valence basis sets improve the electronic representation in several ways. First, as mentioned above, the double-zeta bases allow for a better description of atomic orbitals by virtue of the increased completeness of the basis set. Also, the valence orbitals are now flexible enough to change size during a chemical process. In particular, this allows for better descriptions of bonding and anisotropic chemical processes, such as the anisotropy of the bonding \( p \)-orbitals when forming \( \sigma \) and \( \pi \) bonds in systems with bond orders greater than unity [34].

One last feature of split-valence bases is that, with proper optimization, the more diffuse valence functions can behave as virtual orbitals, a property not available in minimal basis sets. This feature will become increasingly important when one desires to investigate dynamical processes.

**Polarization basis sets**

Many physical processes require not only a change in the size of atomic orbitals over time, but also a change in the shape of the orbital. Examples include the behavior of the orbitals for an atom subject to an external electric field or the orbitals of an atom which has some non-zero momentum. Both of these processes result in a polarization of the atomic orbitals. This polarization causes a net increase of electron density in one area off-center from the nuclear center and a
corresponding net decrease in electron density in the region of space immediately
opposite the nuclear center.

While split-valence basis sets allow for the size of the orbitals to fluctuate,
they do not permit the shape of the orbital change. This cannot be accomplished
by merely changing the size of the orbital exponents. In order to change the shape
of atomic orbitals, the basis must flexible enough to allow combinations of basis
functions that represent occupied atomic orbitals with higher angular momentum
basis functions[30, 34, 44].

The most common methods of polarization involve the addition of basis
functions that mimic a d-orbital to the elements from Li to Ar. This level of
polarization is denoted using a single asterisk. The most common example is the
6:31G* basis [49], which is the basic split-valence 6:31G basis described above
with the addition of a single d-symmetry basis function [34] (or f-symmetry basis
function to transition metals) [44]. The second form includes the d-(f-)orbitals
for heavy atoms as well as an basis function with p-symmetry to H and He. This
level is denoted with two asterisks (such as 6:31G**) [49]. Again, this pattern can
be employed using larger split-valence bases, resulting in such combinations as
6:311G**, a basis that is commonly employed for correlated calculations [50].

The effect of including polarization functions has traditionally been observed
in structural properties, particularly in constrained systems where the electron
density is shifted away from the nuclear centers [34], and in systems subjected to
external electric fields [30]. In particularly, atoms which can be multiply bonded
will, in particular, require a greater degree of polarization. This is evident from the
valence-bond description of chemical bonding, in which the formation of “hybrid”
atomic orbitals (which are nothing more than polarized atomic orbitals) is the
underlying principle of chemical bond formation [51]. For this reason, it has long
been accepted that it is more important to include polarization basis sets on main
group elements rather than singly bonding species, such as Group 1 elements, as indicated by the strong statement of Szabo and Ostlund [30] that it “has been empirically determined that adding polarization functions to the heavy atoms is more important than adding polarization functions to hydrogen.” While this is generally true for structure calculations, it cannot be accepted when dynamical calculations are being performed. In particular, any atom that possesses non-zero momentum will experience a polarization of its electronic orbitals due to the motion of the atom. This effect will be present in all atoms, including H and He. For this reason, it is of crucial importance to include polarizing $p$-functions on H atoms for dynamical calculations.

**Diffuse basis sets**

The previously mentioned basis set structures do a good job of describing various chemical processes, however, all of them locate the electronic density relatively close to the nuclear centers. The split-valence structure allows for increasing the size of orbitals, but the exponents are always close in magnitude to the exponent in a comparable single-valence basis function. This limits the ability of the orbital constructed from a split-valence basis to expand beyond small fluctuations around the size of the orbital constructed from a single-valence basis. Additionally, the polarization functions allow for shifting of the electron density away from the nuclear center, say to a chemical bond. Again, this shift in the density is not large. As a consequence, systems with large electron densities that are located a significant distance from the nuclear center (such as anions and systems involving Rydberg states) are not properly modeled using minimal, split-valence, or polarization basis sets.

To properly describe such systems, diffuse basis sets must be employed [34, 44]. Diffuse basis sets are structured in a manner very similar to split-valence basis sets. A minimal (or split-valence or polarization) basis set in constructed and
additional basis functions are included to provide for the diffuse atomic orbitals. However, the exponents of these diffuse basis functions are much smaller than for the valence basis functions, resulting in an electron density that is located much further away from the nuclear center. In general, the diffuse functions are of the same angular momentum as the valence basis functions. This means that a carbon atom would incorporate one additional s- and one additional p-function. This diffuse structure is denoted using a + symbol [34]. If a single diffuse s-function is added to a hydrogen or helium atom, then this is denoted by two plus signs. Thus, one can now begin to employ a virtual alphabet soup of such combinations as 3:21+G*, 6:31++G*, or 6:311+G**.

**Even-tempered and universal even-tempered basis sets**

Further advances in the building of basis sets were made when it was realized that, as a basis set got larger, the orbital exponents within a given angular momentum converged to a geometric sequence. This geometric sequence takes the form

\[ \zeta_i = \zeta_0 \beta^i, \]  

where \( \zeta_i \) is the \( i \)th exponent in the sequence, \( \zeta_0 \) is the largest exponent, and \( \beta \) is a constant that is specific to the angular momentum. A basis set that is constructed using this type of method is called an even-tempered basis set [39, 42]. The general feature of an even-tempered basis set is that it limits the number of parameters that must be optimized. Furthermore, even-tempering ensures that a GTO expansion of an STO is well-spanned, with no regions in which the representation is particularly poor. There is in general a small energy price that must be paid, but this usually is on the order of several hundredths of a Hartree [42].

Furthermore, it has been postulated that, if enough even-tempered exponents are included in a contraction, then this set of exponents would eventually become
identical over an entire row of the periodic table. This leads to a universal even-
tempered basis set [39, 42].

**Other basis set structures**

In this section, a brief discussion has been made of the general structure of
basis sets, with details given about those basis sets most commonly employed in
quantum chemical calculations. This is only a very small sampling of the basis
sets available for computation, however, most of these basis sets include the basic
principles listed above. It is beyond the scope of this work to provide an in depth
discussion of the different types of basis sets used in calculations. The comparisons
made in the forthcoming sections will, in general, be related to the types of basis
sets reviewed in this section.

### 3.3 Method for Constructing Basis Sets Consistent with Dynamical
Calculations

The structure of a basis set is heavily dependent upon the types of physi-
cal properties that one desires to calculate. In some cases diffuse functions are
required, in others polarization functions are required. In most cases, some bal-
anced combination of all of the properties is needed. Because of this, many have
viewed basis set construction as an art (or black magic in some cases). Yet, no
matter what form the basis set takes, most have one trait in common: with very
few exceptions, basis sets must be optimized. Usually basis sets are optimized
with respect to the energy of the ground state of the system by means of the vari-
ational principle. However, the HF equations are non-linear, and therefore any
optimization process becomes computationally costly.

An additional feature that is common to most basis sets is that they are built
for use in stationary state calculations of the ground state of a given system. While
most of these basis sets do provide representations of unoccupied orbitals either due
to constructing a split-valence or diffuse basis set, these unoccupied orbitals bear little or no resemblance to the virtual orbitals in the system.

In this section a new method for the construction of basis sets will be introduced. This method has a simple physical underlying justification. The method does not require expensive and complex energy optimizations (and does not, in fact, require any optimizations at all). Finally, this method allows for the construction of physically meaningful virtual orbitals, a necessity for the computation of a wide variety of dynamical properties.

3.3.1 Basis Set Properties for Dynamical Calculations

In stationary state calculations minimal basis sets are rarely, if ever, sufficient for the description of the chemical species in question. As outlined in the previous section, a variety of extra basis functions must be included to improve the description. In this case any set of functions added to the minimal basis set generally demonstrates no physical resemblance to atomic orbitals in the system. Rather, they just act to provide a more complete spanning of the electronic Hilbert space, increasing the flexibility of the basis set. These extra basis functions serve to lower the ground state energy (due to an increase in the accuracy of the representation of the occupied atomic orbitals and in some cases by partially accounting for the correlation energy in the system) but they do little else.

For dynamical calculations, particularly charge transfer processes, the basis set must be flexible enough to allow for correct description of electronic transitions between atomic orbitals, either within a single atom or molecule or between the collision pair. One specific aspect of this requirement is the fact that virtual orbitals (atomic or molecular) must be available for occupation throughout the dynamical processes. To this point, little effort has been made by the computational community to construct atomic basis sets that properly describe virtual atomic orbitals, mainly due the fact that most basis sets are optimized with respect to the
total ground state energy of the system rather than optimized with respect to the individual atomic orbital energies. For this reason, and with very few exceptions, stock basis sets that are most commonly employed in computational chemistry are inadequate for use in dynamical calculations.

Methods for improving stock basis sets traditionally follow along the lines of increasing the size of the basis sets by the inclusion of more and more uncontracted diffuse primitives. This method will, in the limit of infinite expansion sizes, lead to correct virtual energy levels by virtue of the Hylleraas- Unsöld separation theorem [52]. However, this brute force method is extremely inefficient for basis set construction. As the number of basis function increases, so does computation time. While this is extremely limiting in the area of structure theory, it is virtually impossible in dynamical methods such and END, where a large number of calculations must be made per trajectory (with many trajectories required for a single collision energy). For this reason, a new method must be devised for building basis sets that include correct representations of virtual orbitals.

The construction of dynamically meaningful virtual orbitals is dependent most strongly upon two properties of the atomic orbitals, the energetics of the orbitals and the shapes of the orbitals. The energetics of the orbitals are the most obvious concern. If the orbital energies are not correct, then the energy required for electronic transitions within the basis set will not properly model the energy differences in nature. Too small of an energy gap will result in increased transfer probability while too large of a energy difference will have the opposite effect. In a single determinantal treatment of the electrons, the orbital energies should mimic the energetics of the system. Therefore, the correct energetic of the atomic orbitals should be a measure of the ability to correctly simulate dynamical transitions.

The shape of the orbital wave function is also important for dynamical calculations. The nodal structure of the wave function determines regions in which
electron density is zero or where it is non-zero. Again, a basis set must correctly model the electron density in an atom.

More discussion about these properties will be made in the next sections. However, at this point it will suffice to say that both of these properties can be addressed quite effectively through the use of STO basis sets. Specifically, the energetics of an orbital is largely dependent upon the structure of the tail of the orbital wave function. As was mentioned in the previous section, STO bases correctly describe the tail of hydrogenic orbitals and, likewise, reproduce the orbital tails in many-electron atoms quite well. Additionally, while single STO functions do not contain any nodal structure, linear combinations of STO functions can if carefully built. For this reason, it seems most reasonable to construct basis sets using STO functions, at least initially.

3.3.2 Physical Justification for the Basis Set Construction Method

As a part of the physical justification of the proposed method for basis set construction, one must first return to the radial factor of a Slater-type orbital basis function, given by the form

\[ R_{STO} = \left( \frac{(2\zeta)^{2n+1}}{(2n)!} \right)^{1/2} r^{n-1} e^{-\zeta r}. \]  

(3.34)

When one compares this form to the hydrogenic orbital functions, one finds that the orbital exponent is related directly to the nuclear charge of the hydrogenic atom in question, specifically

\[ \zeta = \frac{Z}{n}, \]  

(3.35)

where \( Z \) is the nuclear charge and \( n \) is the principal quantum number. In the case of a hydrogenic system, only one electron is associated with the system and therefore the electron will always feel the full nuclear charge (that is, there is no nuclear shielding due to the presence of other electrons).
This idea can be extended to the construction of a wave function for an orbital in any chosen atom. It should be noted, however, that for a given electron in an arbitrary orbital in a many-electron atom the nuclear charge felt by that electron will not be the full nuclear charge. Rather, the full nuclear charge will be shielded by electron density located between the orbital in question and the nucleus. This gives rise to the concept of an effective nuclear charge, \( Z_{\text{eff}} \). The orbital exponent now takes the form

\[
\zeta = \frac{Z_{\text{eff}}}{n}.
\]  
(3.36)

The effective nuclear charge will vary as a function of the principal quantum number, in general an orbital with a smaller principal quantum number will have a larger effective charge. Zener provided values for these effective charges based on variational calculations [53]. Slater [54] determined an empirical method for calculating the effective nuclear charge for any arbitrary orbital and presented the equation

\[
Z_{\text{eff}} = Z - s,
\]  
(3.37)

where \( Z \) in the full nuclear charge and \( s \) is a screening constant that is a function of the orbital and the number of electrons. For \( s\)- and \( p\)-orbitals, the screening constant was defined to be

\[
s = 0.35N_n + 0.85N_{n-1} + 1.00N_{n-2},
\]  
(3.38)

where \( N_n \) is the number of additional electrons in the same principal level, \( N_{n-1} \) is the number of electrons in the principal level immediately lower, and \( N_{n-2} \) is the number of all remaining electrons in lower principal levels [54]. Having defined the effective charge, Slater then suggests construction of atomic orbitals as single STO functions of the same form as Equation (3.31), with the exception that the orbital exponent takes the form of Equation (3.36) and the principal quantum number \( n \) is replaced by an effective quantum number, \( n^* \). The effective quantum
number deviates from the true quantum number only for \( n > 3 \) [54]. This, the form of the wave function consists of a single STO for each set of \( n \) and \( l \) quantum numbers, with the orbital exponent equal to the effective nuclear charge felt by the corresponding atomic orbital divided by the effective principal quantum number associated with the orbital.

Having discussed a specific method for the construction of basis sets for many-electron atoms, it is now time to consider some physical aspects of atomic orbitals in a bit more detail. One property that a basis set should properly model is the radial distribution of the electronic orbital, defined as [55]

\[
D_{nl}(r) = r^2 |R_{nl}(r)|^2.
\]

In the above equation, \( r \) is the radial distance from the nucleus, \( n \) is the principal quantum number, \( l \) is the azimuthal quantum number, and \( R_{nl} \) is the radial factor of the wave function for a given \( n \) and \( l \). The top panel of Figure 3.2 demonstrates the radial distribution functions for the first four \( s \)-orbitals in the hydrogen atom. The humps in the radial density function for a given orbital indicate regions in which the probability for the electron to exist is greatest. This feature demonstrates that the electron density corresponding to an orbital takes the form of concentric shells of electron density [29, 55]. From this it becomes clear that an atomic orbital with principal quantum number \( n \) will possess \( n \) regions of electron density, each becoming increasingly closer to the nucleus but with smaller probability. This fact is mirrored in the nuclear screening expression advanced by Slater and given in Equation (3.38). The shielding due to electrons in the next lowest principal level do not completely shield the nucleus, rather they have an only an 85% effective shielding due to the penetration of the higher principal levels.

This physical feature of atomic orbitals is not limited to \( s \)-orbitals, nor is it limited to the description of the hydrogen atomic orbitals. In Figure 3.2, the
Figure 3.2: Top: Plot of the radial distribution function for the 1s (—), 2s (− − −), 3s (⋯), and 4s (⋯⋯) orbitals of the hydrogen atom. Bottom: Plot of the radial distribution function for the 2p (—), 3p (− − −), and 4p (⋯⋯) orbitals of the hydrogen atom.

bottom panel demonstrates the radial density functions for the 2p-, 3p-, and 4p-orbitals of the hydrogen atom, where a similar shell structure is observed. Furthermore, Figure 3.3 shows the radial distribution functions for the occupied s- and p-orbitals in the Ar atom, in the top and bottom panel, respectively. In both plots, the orbitals wave functions that are plotted are the double-zeta wave functions of Clementi and Roetti [45]. Again, the shell structure is clearly evident.

At this point, the most significant physical attribute of these shells of electron density becomes apparent. In the case of s- and p-orbitals in the atoms of the first
Figure 3.3: Top: Plot of the radial distribution function for the 1s (—), 2s (−−−), and 3s (···) orbitals of the argon atom. The 1s-orbital is scaled by a factor of two-thirds. Bottom: Plot of the radial distribution function for the 2p (—) and 3p (−−−) orbitals of the argon atom.

Few rows of a periodic table, the radial location of the shells is largely independent of the principal quantum number associated with an orbital. In other words, all s-orbitals have a shell of electron density that has roughly the same radial location as the shell of electron density due to the 1s orbital. Likewise, all s-orbitals with principle quantum number $n$ have $n-1$ shells that have roughly the same radial location as the $n-1$ lower energy $s$-orbitals. This is also true for $p$-orbitals. The consequence is that any orbital of $s$ symmetry possesses a partial character of all of the lower energy $s$-orbitals. Further, each of these characteristic shells exists within
the same region of effective nuclear charge that is specific to that shell of electron density.

Now, relating the regions of effective nuclear charge back to the idea of the Slater orbital exponent, this now means that a given orbital can be constructed as a linear combination of all of the previous orbital basis functions, each with a specific orbital exponent that relates to the effective charge region experienced by the corresponding shell of electron density. Specifically, the orbital wave function can be written as

$$\psi_{n,l} = \sum_{i=1}^{n} c_i N_{n,i} e^{-\zeta_i r}, \quad (3.40)$$

where $N_{n,i}$ is the appropriate normalization factor for the STO in question, the $c_i$’s are the expansion coefficients, and the $\zeta_i$ is the orbital exponent (effective nuclear charge) for the $i$th shell. On the surface, this is nothing new. Relating the orbital exponent to an effective charge was proposed by Slater and the linear combination is nothing more than a restatement of the superposition principle [1] through which the HF method determines the HF eigenstates as a linear combination of the basis vectors [29]. However, this physical insight does serve as an important under-tone for the basis set construction proposed in this work.

### 3.3.3 Construction of the Basis Set

One begins construction of the basis set by defining a linear combination of STO functions, each with orbital exponents derived from the effective charge experienced by the orbital in question. The form of the effective charge may be determined in any number of ways, the simplest of which is to employ Slater’s formulation for the screening constant [54]. However, Slater’s screening constants are empirically modeled and may not be as accurate as those determined by other methods. Instead, one may consider the work of Clementi and Raimondi [56] as an extension of the earlier work of Slater and Zener. Clementi and Raimondi made
a study of the elements through Kr, representing each atomic orbital as a single
STO function (that is a minimal basis set) with variable orbital exponents. The
exponents where then optimized (with respect to the ground state energy) using an
SCF procedure.

At this point, the proposed method has not deviated from older methods of
basis set construction. By employing this method, one can construct a minimal
basis set for the ground state of the atom in question, however, no recourse is
available for construction of virtual orbitals. The optimization process could
be extended to determine the orbital coefficients for the virtual states, but this
would require calculations beyond the HF level to do so, as the transition energies
would be dependent upon electron correlation. The minimum level of theory that
could be employed would be configuration interaction. This would increase the
computational effort required to optimize the virtual orbital exponents.

To remedy this, a new approach to determining these virtual orbital exponents
is proposed in this work; a method that is extremely simplistic in its application,
yet has proven to be very powerful. The method begins through the investigation
of the behavior of Clementi’s shielded orbital exponents as a function of the
atomic number. Figure 3.4 demonstrates the functional behavior for the 1s orbital
exponents through Kr. As can be seen from the figure, the orbital exponents
exhibit a very linear dependence on the atomic number.

The top panel of Figure 3.5 shows the dependence of the 2s orbital exponents
on the atomic number. There are two data sets in this figure, the data of Clementi
and Raimondi [56], which are denoted using the plus symbols, and the data from
the present work, which are denoted using the open circles. Clementi’s data still
demonstrates a linear dependence of the exponent on the atomic number, however,
it becomes clear at this point that more than one linear region is observed. As
an example, the orbital exponents for the elements from Li through Ne have a
Figure 3.4: Plot of the 1s orbital exponent for the atoms through Kr as a function of atomic number. The data are from Clementi and Raimondi (+).

slightly different slope and intercept than for the remaining elements. Each block of elements will have a slightly different slope. The data points current to this work will be discussed at length later.

The data in the bottom panel of Figure 3.5 show the same relation for the 2p orbital exponents. Likewise, the plots in Figure 3.6 demonstrate the dependence for the 3s (top) and 3p (bottom) orbital exponents and those in Figure 3.7 present the data for the 4s (top) and 4p (bottom) orbitals. The most striking feature when comparing all of the previous plots is that, while the individual linear regions become more distinct from one another as the principal and azimuthal quantum numbers increase, the (local) linear dependence of the orbital exponent on the atomic number is still quite strong. It is this feature that defines the proposed method for virtual orbital construction.

Discussion must now be made with regards to the remaining sets of data points, those denoted with the open circles. These data points are new to this work and are derived from the data of Clementi and Raimondi. Specifically, these points are orbital exponents corresponding to virtual orbitals for the atoms in question.
Figure 3.5: Plot of the $2s$ and $2p$ orbital exponents for the atoms through Kr as a function of atomic number. Top: The $2s$ orbital exponents. Bottom: The $2p$ orbital exponents. The data are from Clementi and Raimondi (+) and from the present work (o).

These virtual orbital exponents are determined by first considering the hydrogen atom. As the hydrogen atom has only a single electron, there will never be any nuclear shielding for that atom. This the electron will always experience the same effective nuclear charge (of unit magnitude) no matter in which orbital the electron has probability for existing. This means that $Z_{\text{eff}} = 1$ always, and the orbital exponent for any orbital in the H atom is just equal to the reciprocal of the principal quantum number. At this point, one makes reference to the linear behavior of the occupied orbital exponents. The virtual orbital exponents are then
Figure 3.6: Plot of the $3s$ and $3p$ orbital exponents for the atoms through Kr as a function of atomic number. Top: The $3s$ orbital exponents. Bottom: The $3p$ orbital exponents. The data are from Clementi and Raimondi (+) and from the present work (o).

determined by making a linear interpolation between the H atom virtual orbital exponent and the exponent corresponding to the first available occupied orbital in that symmetry. For example, in the case of the $3p$ orbitals, the interpolation is made between the exponent corresponding to the H atom $3p$ orbital and the exponent that corresponds to the $3p$ orbital of Al (atomic number = 13).

This method for determining the exponents that correspond to virtual atomic orbitals relies on well-documented trends exhibited by a parameter that is related directly to a physical property, namely the trend in the regions of effective charge.
Figure 3.7: Plot of the 4s and 4p orbital exponents for the atoms through Kr as a function of atomic number. Top: The 4s orbital exponents. Bottom: The 4p orbital exponents. The data are from Clementi and Raimondi (+) and from the present work (○).

as demonstrated earlier in this section. However, it is important to note that a number of severe assumptions have been made. Perhaps the two strongest assumptions are that the virtual orbital exponents demonstrate the same linear behavior as do the occupied orbital exponents and the assumption that there is not a large change in the magnitude of the orbital exponent as one transitions from the occupied orbital exponents to the unoccupied orbital exponents. While neither of these assumptions can be tested without the construction of energy-optimized virtual orbital wave functions, the severity of the assumptions is tolerated in lieu
of the ease of application. And, in spite of these assumptions, the calculations using basis sets constructed from this starting point have yielded surprisingly good results for both stationary state and dynamical calculations, as will be demonstrated in the next section.

Once the interpolations have been accomplished, the next step is to construct the atomic orbital wave functions. This is begun with the wave function for the 1s orbital, which is represented by a single Slater-type orbital,

$$\phi_{1s} = N_{1s} (\zeta_{1s}) e^{-\zeta_{1s}r}.$$  \hspace{1cm} (3.41)

The expansion coefficient in just the normalization coefficient for an STO basis function with \( n = 1 \) and with orbital exponent \( \zeta_{1s} \). From this, the wave function of the 2s orbital can then be constructed as a linear combination of the 1s wave function (providing for the cusp) and a single STO basis function with \( n = 2 \) that is used to represent the tail portion of the orbital. The orbital wave function takes the form

$$\phi_{2s} = c_{1s} N_{1s} (\zeta_{1s}) e^{-\zeta_{1s}r} + c_{2s} N_{2s} (\zeta_{2s}) r e^{-\zeta_{2s}r}.$$  \hspace{1cm} (3.42)

Again, the terms \( N_{1s} \) and \( N_{2s} \) are the normalization coefficients for the specified STOs. In Equation (3.42), two expansion coefficients must be determined. This requires the simultaneous solution of a set of two equations. In this case the two equations are the normalization condition for the 2s orbital (\( \langle \phi_{2s} | \phi_{2s} \rangle = 1 \)) and the orthogonality of the 1s orbital with the 2s orbital (\( \langle \phi_{1s} | \phi_{2s} \rangle = 0 \)).

It becomes clear at this point that the above process can be iterated over as many s-orbitals as are required for an atomic basis set, be they occupied or virtual. Specifically, the \( ns \) orbital wave function is defined as

$$\phi_{ns} = \sum_{i=1}^{n} c_{is} N_{is} (\zeta_{is}) r^{i-1} e^{-\zeta_{is}r}.$$  \hspace{1cm} (3.43)
As before, the wave function has \( n \) undetermined coefficients and therefore requires the solution of a set of \( n \) simultaneous equations. These equations take the form the normalization of the \( ns \) wave function (\( \langle \phi_{ns} | \phi_{ns} \rangle = 1 \)) and the orthogonality of the \( ns \) wave function with the other wave functions (\( \langle \phi_{1s} | \phi_{ns} \rangle = \langle \phi_{2s} | \phi_{ns} \rangle = \ldots = \langle \phi_{(n-1)s} | \phi_{ns} \rangle = 0 \)). This forms a set of \( n \) simultaneous equations that can be used to determine a set of expansion coefficients. The construction of the \( p \)-orbital wave functions follows the same schema.

This proposed construction method is employed through a template designed for any commercial computational package, such as Maple, into which the orbital exponents are input. The program then calculates the expansion coefficients by solving the orthonormality conditions for each set of orbitals. The power of this method is that it does not require any expensive non-linear energy optimizations. Furthermore, it allows for a general construction of any atomic orbital, either occupied or virtual, provided that the orbital exponent is known or can be interpolated using the above mentioned method.

Wave functions have been built for the atoms from He through Ne. Table 3.2 presents the STO exponents and coefficients for He, Li, and Be. These exponents and coefficients were determined using the previously described method. Table 3.3 lists the wave function parameters for B, C, and N. Lastly, Table 3.4 contains the exponents and coefficients for O, F, and Ne.

As a final step, the STO wave functions must then be expanded in a basis GTO functions to allow for computations to be performed. There are two main methods by which this is accomplished. The first method is through use of a linear least-squares fitting program which will determine the best set of GTO exponents and expansion coefficients. The program that has been employed for some of the results reported in this work used a variation of the Amoeba program from Numerical Recipes [37]. In this method the GTO orbital exponents were
### Table 3.2: Slater Exponents and Coefficients for He, Li, and Be.

<table>
<thead>
<tr>
<th>Atom: Helium</th>
<th>Configuration: He : 1s²2s⁰2p⁰3s⁰3p⁰4s⁰4p⁰</th>
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<tbody>
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<td>s-Functions</td>
<td>p-Functions</td>
</tr>
<tr>
<td>Exponents</td>
<td>Exponents</td>
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<td>2s</td>
</tr>
<tr>
<td>1.6875</td>
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<td>Coefficients</td>
</tr>
<tr>
<td>1s</td>
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</tr>
<tr>
<td>2s</td>
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<tr>
<td>3s</td>
<td>0.22486</td>
</tr>
<tr>
<td>4s</td>
<td>0.17763</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom: Lithium</th>
<th>Configuration: Li : 1s²2s¹2p⁰3s⁰3p⁰4s⁰4p⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-Functions</td>
<td>p-Functions</td>
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<tr>
<td>Exponents</td>
<td>Exponents</td>
</tr>
<tr>
<td>1s</td>
<td>2s</td>
</tr>
<tr>
<td>2.6906</td>
<td>0.6396</td>
</tr>
<tr>
<td>Coefficients</td>
<td>Coefficients</td>
</tr>
<tr>
<td>1s</td>
<td>1.00000</td>
</tr>
<tr>
<td>2s</td>
<td>0.16487</td>
</tr>
<tr>
<td>3s</td>
<td>0.13471</td>
</tr>
<tr>
<td>4s</td>
<td>0.04890</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom: Beryllium</th>
<th>Configuration: Be : 1s²2s²2p⁰3s⁰3p⁰4s⁰4p⁰</th>
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</thead>
<tbody>
<tr>
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<td>p-Functions</td>
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<tr>
<td>Exponents</td>
<td>Exponents</td>
</tr>
<tr>
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<td>2s</td>
</tr>
<tr>
<td>3.6848</td>
<td>0.9560</td>
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<td>Coefficients</td>
<td>Coefficients</td>
</tr>
<tr>
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<tr>
<td>2s</td>
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<tr>
<td>3s</td>
<td>0.09188</td>
</tr>
<tr>
<td>4s</td>
<td>0.03755</td>
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Table 3.3: Slater Exponents and Coefficients for B, C, and N.

<table>
<thead>
<tr>
<th>Atom: Boron</th>
<th>Configuration: $B : 1s^22s^22p^13s^03p^04s^04p^0$</th>
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<td>p-Functions</td>
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<tr>
<td>Exponents</td>
<td>Exponents</td>
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<td>2s</td>
</tr>
<tr>
<td>Exponents</td>
<td>Exponents</td>
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<tr>
<td>2s</td>
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<td>3s</td>
<td>0.07096</td>
</tr>
<tr>
<td>4s</td>
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</tr>
<tr>
<td>Coefficients</td>
<td>Coefficients</td>
</tr>
<tr>
<td>1s</td>
<td>1.00000</td>
</tr>
<tr>
<td>2s</td>
<td>0.22393</td>
</tr>
<tr>
<td>3s</td>
<td>0.05798</td>
</tr>
<tr>
<td>4s</td>
<td>0.02788</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom: Carbon</th>
<th>Configuration: $C : 1s^22s^22p^23s^03p^04s^04p^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-Functions</td>
<td>p-Functions</td>
</tr>
<tr>
<td>Exponents</td>
<td>Exponents</td>
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<td>2s</td>
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<tr>
<td>Exponents</td>
<td>Exponents</td>
</tr>
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<td>0.2393</td>
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<td>3s</td>
<td>0.05798</td>
</tr>
<tr>
<td>4s</td>
<td>0.02788</td>
</tr>
<tr>
<td>Coefficients</td>
<td>Coefficients</td>
</tr>
<tr>
<td>1s</td>
<td>1.00000</td>
</tr>
<tr>
<td>2s</td>
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<tr>
<td>3s</td>
<td>0.05798</td>
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<tr>
<td>4s</td>
<td>0.02788</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom: Nitrogen</th>
<th>Configuration: $N : 1s^22s^22p^33s^03p^04s^04p^0$</th>
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<tbody>
<tr>
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<td>Exponents</td>
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</tr>
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<td>2s</td>
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<tr>
<td>Exponents</td>
<td>Exponents</td>
</tr>
<tr>
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<tr>
<td>2s</td>
<td>0.23080</td>
</tr>
<tr>
<td>3s</td>
<td>0.04925</td>
</tr>
<tr>
<td>4s</td>
<td>0.02866</td>
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<tr>
<td>Coefficients</td>
<td>Coefficients</td>
</tr>
<tr>
<td>1s</td>
<td>1.00000</td>
</tr>
<tr>
<td>2s</td>
<td>0.23080</td>
</tr>
<tr>
<td>3s</td>
<td>0.04925</td>
</tr>
<tr>
<td>4s</td>
<td>0.02866</td>
</tr>
</tbody>
</table>
Table 3.4: Slater Exponents and Coefficients for O, F, and Ne.

**Atom: Oxygen**

Configuration: \( O : 1s^22s^22p^43s^03p^04s^04p^0 \)

<table>
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<th>p-Functions</th>
</tr>
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<tr>
<td><strong>Exponents</strong></td>
<td><strong>Exponents</strong></td>
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<td>1s</td>
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<tr>
<td>7.6579</td>
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<table>
<thead>
<tr>
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<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s 1.00000 0.00000 0.00000 0.00000</td>
<td>( 2p 1.00000 0.00000 0.00000 )</td>
</tr>
<tr>
<td>2s 0.23710 -1.02772 0.00000 0.00000</td>
<td>( 3p 0.35976 -1.06274 0.00000 )</td>
</tr>
<tr>
<td>3s 0.04298 -0.19877 1.01854 0.00000</td>
<td>( 4p 0.20750 -0.75025 1.22490 )</td>
</tr>
<tr>
<td>4s 0.01173 -0.05606 0.46221 -1.27638</td>
<td>( )</td>
</tr>
</tbody>
</table>

**Atom: Fluorine**

Configuration: \( F : 1s^22s^22p^53s^03p^04s^04p^0 \)

<table>
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<th>p-Functions</th>
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<tr>
<td><strong>Exponents</strong></td>
<td><strong>Exponents</strong></td>
</tr>
<tr>
<td>1s</td>
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</tr>
<tr>
<td>8.6501</td>
<td>2.5638</td>
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<table>
<thead>
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<th>Coefficients</th>
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<tbody>
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<td>1s 1.00000 0.00000 0.00000 0.00000</td>
<td>( 2p 1.00000 0.00000 0.00000 )</td>
</tr>
<tr>
<td>2s 0.24136 -1.02871 0.00000 0.00000</td>
<td>( 3p 0.32735 -1.05222 0.00000 )</td>
</tr>
<tr>
<td>3s 0.03835 -0.17388 1.01419 0.00000</td>
<td>( 4p 0.18516 -0.71747 1.21094 )</td>
</tr>
<tr>
<td>4s 0.02018 -0.09298 0.71660 -1.37637</td>
<td>( )</td>
</tr>
</tbody>
</table>

**Atom: Neon**

Configuration: \( Ne : 1s^22s^22p^63s^03p^04s^04p^0 \)

<table>
<thead>
<tr>
<th>s-Functions</th>
<th>p-Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exponents</strong></td>
<td><strong>Exponents</strong></td>
</tr>
<tr>
<td>1s</td>
<td>2s</td>
</tr>
<tr>
<td>9.6421</td>
<td>2.8792</td>
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</table>

<table>
<thead>
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<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s 1.00000 0.00000 0.00000 0.00000</td>
<td>( 2p 1.00000 0.00000 0.00000 )</td>
</tr>
<tr>
<td>2s 0.24439 -1.02943 0.00000 0.00000</td>
<td>( 3p 0.30169 -1.04452 0.00000 )</td>
</tr>
<tr>
<td>3s 0.03483 -0.17388 1.01138 0.00000</td>
<td>( 4p 0.16788 -0.69204 1.20000 )</td>
</tr>
<tr>
<td>4s 0.02018 -0.09298 0.71660 -1.37637</td>
<td>( )</td>
</tr>
</tbody>
</table>
constrained to be even-tempered. Depending on the use of the basis set, any number of GTO functions (up to ten) were used for each STO fit.

While the first fitting method employs a fairly simple linear optimization to determine exponents and coefficients for GTO expansions of STO orbitals, the second method does not require any such optimizations. This method uses the results of Stewart [41]. Stewart performed least squares calculations to determine the best set of parameters that allows for the construction of an expansion of up to six GTO functions for a specified single STO function. As previously mentioned, this method does not require tedious optimizations, as they have already been performed. This allows for a simple template to be constructed in a numerical spreadsheet program. The orbital exponents are input into this spreadsheet template, along with the required parameters from Stewart’s paper, and the GTO orbital exponents and expansion coefficients are the resulting output.

While the method for basis set construction outlined in this section is very simplistic in its application, the physical underpinning of the construction is quite strong and maintained throughout the method. Furthermore, this formalism is easy to employ, with no costly or time-consuming optimizations required if engineered correctly. In the following section, results that have been obtained with basis sets constructed using this method are presented for comparison with several common stock basis sets that were built using energy optimization methods.

3.4 Comparative Results

This section will provide comparisons between basis sets constructed using the method proposed in the previous section and with some of the more commonly used stock basis sets, such as the 3-21G, the 6-31G, and the 6-31G* basis sets. The comparisons will be made such that a computation performed with, for example, a 6-31G basis set will be compared with a newly constructed basis set with the same size parameters (same number of expansions per orbital). Comparisons will be
made for several types of physical properties, specifically for the excitation energies within the specific atom, for charge transfer probabilities and cross sections, and for the vibrational and electronic properties of several diatomic and triatomic molecules. These first two comparisons are for properties that are important to dynamical processes. The third comparison relates properties that are traditionally calculated based on energy (such as diagonalization of the Hessian to obtain vibrational frequencies). This will offer comparison between energy optimized basis sets with the basis sets constructed from the current method (with no energy optimizations).

3.4.1 Atomic Energetics

In this section, the relative accuracy of electronic excitations within atoms will be compared. Six types of basis sets will be used in this comparison, including three stock basis sets (the 3-21G, 6-31G, and 6-31G** basis sets) and three comparable basis sets built using the previously proposed method (here called the 3-21B, 6-31B, and 6-31B** basis sets). The new basis sets have been constructed such that the same number of primitive Gaussians are used for each orbital contraction. This will help to ensure that meaningful comparisons can be made between the energy optimized stock basis sets and the newly constructed basis sets. The structure of the new, dynamically consistent basis sets can be found in the basis set library located in the Appendix.

The data in this section are comprised of excitation energies as calculated using the Gaussian 98 computational suite [57]. The excitation energies are calculated as the absolute energy difference between the two states in question. The absolute energies are calculated using the multi-configurational capabilities of Gaussian 98, as found within the CASSCF routine [44]. The complete active space is defined to be the set of valence shell electrons and the valence shell and all
Table 3.5: Atomic energies and electronic excitations in Helium

### Stock Basis Sets

Atomic HF Energy
(Experimental: -2.9031840 a.u.)

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Atomic HF Energy (a.u.)</th>
<th>Excitation Energies</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21G</td>
<td>-2.8505767</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-31G</td>
<td>-2.8701621</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-31G**</td>
<td>-2.8873650</td>
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<td></td>
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</table>

<table>
<thead>
<tr>
<th>Transition</th>
<th>Expt. Excitation (cm⁻¹)</th>
<th>3-21G Excitation (cm⁻¹)</th>
<th>% Error</th>
<th>6-31G Excitation (cm⁻¹)</th>
<th>% Error</th>
<th>6-31G** Excitation (cm⁻¹)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s²(1S) → 1s2s(3S)</td>
<td>159843.3</td>
<td>442932.5</td>
<td>177</td>
<td>322814.3</td>
<td>102</td>
<td>326589.9</td>
<td>104</td>
</tr>
<tr>
<td>1s²(1S) → 1s2s(1S)</td>
<td>166264.7</td>
<td>557807.8</td>
<td>235</td>
<td>421708.2</td>
<td>154</td>
<td>425452.4</td>
<td>156</td>
</tr>
<tr>
<td>1s²(1S) → 1s2p(3P)</td>
<td>169074.1</td>
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<td>N/A</td>
<td>483411.3</td>
<td>183</td>
<td>558949.8</td>
<td>227</td>
</tr>
<tr>
<td>1s²(1S) → 1s2p(1P)</td>
<td>171122.2</td>
<td>N/A</td>
<td>N/A</td>
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<td>-0.04</td>
<td>171592.9</td>
<td>0.28</td>
</tr>
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</table>

### Dynamically Consistent Basis Sets

Atomic HF Energy
(Experimental: -2.9031840 a.u.)

<table>
<thead>
<tr>
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<th>Excitation Energies</th>
<th>Error</th>
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</thead>
<tbody>
<tr>
<td>3-21B</td>
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</tr>
<tr>
<td>6-31B</td>
<td>-2.8118598</td>
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<td>6-31B**</td>
<td>-2.8119307</td>
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</table>

<table>
<thead>
<tr>
<th>Transition</th>
<th>Expt. Excitation (cm⁻¹)</th>
<th>3-21B Excitation (cm⁻¹)</th>
<th>% Error</th>
<th>6-31B Excitation (cm⁻¹)</th>
<th>% Error</th>
<th>6-31B** Excitation (cm⁻¹)</th>
<th>% Error</th>
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</thead>
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<td>159843.3</td>
<td>146507.5</td>
<td>-8.34</td>
<td>155196.7</td>
<td>-2.91</td>
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<td>-2.90</td>
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<tr>
<td>1s²(1S) → 1s2s(1S)</td>
<td>166264.7</td>
<td>155066.0</td>
<td>-6.74</td>
<td>162821.9</td>
<td>2.07</td>
<td>162778.0</td>
<td>-2.10</td>
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<td>1s²(1S) → 1s2p(3P)</td>
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<td>N/A</td>
<td>N/A</td>
<td>169004.0</td>
<td>-0.04</td>
<td>171592.9</td>
<td>0.28</td>
</tr>
<tr>
<td>1s²(1S) → 1s2p(1P)</td>
<td>171122.2</td>
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<td>N/A</td>
<td>171592.9</td>
<td>0.28</td>
<td>171592.9</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Table 3.6: Atomic energies and electronic excitations in Lithium

### Stock Basis Sets

**Atomic HF Energy**  
(Experimental: -7.8848995 a.u.)

<table>
<thead>
<tr>
<th></th>
<th>3-21G (a.u.)</th>
<th>6-31G (a.u.)</th>
<th>6-31G** (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic HF Energy</td>
<td>-7.3815132</td>
<td>-7.4312358</td>
<td>-7.4313723</td>
</tr>
</tbody>
</table>

**Excitation Energies**

<table>
<thead>
<tr>
<th>Transition</th>
<th>Expt. Excitation (cm⁻¹)</th>
<th>3-21G Excitation (cm⁻¹)</th>
<th>% Error</th>
<th>6-31G Excitation (cm⁻¹)</th>
<th>% Error</th>
<th>6-31G** Excitation (cm⁻¹)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s¹(2S) → 2p¹(2P)</td>
<td>14903.8</td>
<td>14620.3</td>
<td>-1.90</td>
<td>15626.9</td>
<td>4.85</td>
<td>15647.1</td>
<td>4.99</td>
</tr>
<tr>
<td>2s¹(2S) → 3s¹(2S)</td>
<td>27205.8</td>
<td>43415.8</td>
<td>59.6</td>
<td>46379.9</td>
<td>70.5</td>
<td>48098.6</td>
<td>76.8</td>
</tr>
<tr>
<td>2s¹(2S) → 3p¹(2P)</td>
<td>30925.9</td>
<td>43662.6</td>
<td>41.2</td>
<td>49549.6</td>
<td>60.2</td>
<td>46408.9</td>
<td>50.1</td>
</tr>
<tr>
<td>2s¹(2S) → 3d¹(2D)</td>
<td>31283.2</td>
<td>N/A</td>
<td></td>
<td>N/A</td>
<td></td>
<td>112671.0</td>
<td>260</td>
</tr>
</tbody>
</table>

### Dynamically Consistent Basis Sets

**Atomic HF Energy**  
(Experimental: -7.8848995 a.u.)

<table>
<thead>
<tr>
<th></th>
<th>3-21B (a.u.)</th>
<th>6-31B (a.u.)</th>
<th>6-31B** (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic HF Energy</td>
<td>-7.3252176</td>
<td>-7.4161167</td>
<td>-7.4161167</td>
</tr>
</tbody>
</table>

**Excitation Energies**

<table>
<thead>
<tr>
<th>Transition</th>
<th>Expt. Excitation (cm⁻¹)</th>
<th>3-21B Excitation (cm⁻¹)</th>
<th>% Error</th>
<th>6-31B Excitation (cm⁻¹)</th>
<th>% Error</th>
<th>6-31B** Excitation (cm⁻¹)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s¹(2S) → 2p¹(2P)</td>
<td>14903.8</td>
<td>14810.7</td>
<td>-0.62</td>
<td>15678.5</td>
<td>5.20</td>
<td>15678.5</td>
<td>5.20</td>
</tr>
<tr>
<td>2s¹(2S) → 3s¹(2S)</td>
<td>27205.8</td>
<td>26096.7</td>
<td>-4.08</td>
<td>26795.2</td>
<td>-1.51</td>
<td>26795.2</td>
<td>-1.51</td>
</tr>
<tr>
<td>2s¹(2S) → 3p¹(2P)</td>
<td>30925.9</td>
<td>43823.9</td>
<td>41.7</td>
<td>44431.2</td>
<td>43.7</td>
<td>44431.2</td>
<td>43.7</td>
</tr>
<tr>
<td>2s¹(2S) → 3d¹(2D)</td>
<td>31283.2</td>
<td>N/A</td>
<td></td>
<td>N/A</td>
<td></td>
<td>35503.5</td>
<td>13.5</td>
</tr>
</tbody>
</table>
virtual orbitals in the given basis set. By using the CASSCF methodology, essential correlation can be accounted for in the basis set comparisons.

The data in Table 3.5 demonstrates the excitations for the helium atom. The top part of the table relates the experimental ground state atomic energy and the excitation energies using the stock basis sets. The bottom half of the table shows the same values calculated in the newly constructed and dynamically consistent basis sets. It becomes clear immediately upon inspection of the data that the stock basis sets provide a much more accurate ground state atomic energy. However, this is to be expected, as the stock basis sets were constructed in such a way as to minimize the Hartree-Fock atomic energy and the dynamically consistent basis sets were not. It should be noted that, even in the worst case, the dynamically consistent basis sets are no more than 6.57 percent in error with the experimental energy, taken from Moore [58].

The most striking feature of the table is the excitation energy comparisons. The experimental excitation energies are taken from Bacher and Goudsmit [59]. The stock basis sets do not represent the orbital-to-orbital excitation energies well. One’s attention can first be directed to the percent errors of the calculated excitation energies (using stock basis sets) with respect to the experimental values. The smallest error is about 100 percent. Even more important is the fact that all of the excitations correspond to virtual orbitals that are bound states in the He atom. The excitation energies are all greater in magnitude than the ionization energy of the atom (about 197000 cm$^{-1}$) [59]. This fact is denoted by the red coloration of the excitation energy values.

By contrast, the dynamically consistent basis sets constructed in this work show a remarkable improvement in the excitation energetics. The percent errors are reduced from a minimum of 102 percent in the stock basis sets to a maximum
of 8.34 percent in the newly constructed basis sets. Moreover, all of the newly constructed orbitals represent bound states in the atom.

Table 3.6 relates the same data, though for the lithium atom. The experimental atomic energy value is calculated in this case by considering the correlation energy obtained by Eggarter and Eggarter using second-order perturbation methods \[60\], and the excitation energies are from Bacher and Goudsmit \[59\]. The atomic energies demonstrate the same pattern as the helium atom: the stock basis sets offer good representations of the atomic energy, while the newly constructed basis sets are not as good (though now the largest percent error is only 7.1 percent). The excitation energy data offers a considerably different comparison than in the case of helium. Particularly one finds that in this case the stock basis sets do allow for a good representation of the 2p virtual orbital excitation which are, in fact, better than the orbitals arising from the new basis sets. However, the 3s, 3p, and 3d orbitals are all unbound. The dynamically consistent basis sets all provide good 2p, 3s, and 3d virtual orbitals, yet perform very poorly in the description of the 3p orbitals. This can be attributed to either of the principal assumptions made in the interpolation method (c.f. Section 3.3.3).

### 3.4.2 Charge Transfer Results

From the preceding data, it becomes clear that a basis set can be constructed that has a relatively small size and physically meaningful excitations into virtual orbitals. While this is a physical characteristic that is very important in many dynamical properties, one must specifically investigate the behavior of the basis sets when calculating such dynamical properties. In this section, charge transfer probabilities are calculated using the 6-31G stock basis set and several basis sets constructed using the newly proposed methodology. The contraction schemes for each of the basis sets are given in the Appendix.
Three charge transfer systems will be investigated. The first is the near-resonant charge transfer in the H\(^+\)/Li collision system. In this process, the \(n = 2\) orbitals are in near-resonance with the \(2p\) orbitals in Li (with orbital energies of -0.125 a.u. and -0.130 a.u., respectively) \([61]\). Likewise, the \(n = 3\) orbitals of H are in near-resonance with the \(3p\) orbitals in Li (with orbital energies of -0.055 a.u. and 0.057 a.u., respectively) \([61]\). These near-resonances should result in a few regions of large probability for transfer, as the electron can be excited into one of the virtual orbitals in Li and then transfer over to the H atom. The second system is the resonant charge transfer in the Li\(^+\)/Li collision system. In this case, the orbitals in both collision species have the same energies, promoting strong resonances in the charge transfer process. Finally, the resonant transfer between He\(^+\) and He is investigated.

The minimal END formalism has been applied successfully to investigations of resonant charge transfer processes, particularly the collision of H\(^+\)/H \([62]\). The same methods are employed in this investigation. Specifically, the probability for electron transfer is calculated to be the difference in Mulliken population between the incident projectile and the fastest particle after collision, the differential cross section is calculated using the distinguishable or identical particle scattering amplitudes (as the case warrants), the scattering amplitude is calculated from the small angle Schiff Approximation, and the total cross section for resonant transfer is calculated using the semi-classical formula

\[
\sigma_{RT} = \int_{0}^{\infty} bP(b)db,
\]

where \(b\) is the impact parameter and \(P(b)\) is the transfer probability. All of the calculations in this section were performed using ENDyne, version 5 \([63]\).

The first comparison to be made is the transfer probability. Figure 3.8 demonstrates the near-resonant charge transfer probability in the H\(^+\)/Li collision
Figure 3.8: Comparison of the probability for near-resonant charge transfer between H$^+$ and Li at 10 keV collision energy. The following Li basis sets are used: 6-31G (red), 6-31B (blue), BJK01 (purple), BJK02 (black). The BJK01 basis set for H was used for each run.

system at 10 keV collision energy. The red line represents the transfer probability as calculated using the 6-31G basis set. The blue line shows the probability as calculated using the comparable 6-31B basis set. It becomes immediately obvious that the transfer probability is significantly dependent upon the basis set employed. As shown in the previous section, the 6-31B basis set for Li provides much more accurate excitations into the 2$p$, and 3$s$ orbitals than does the 6-31G basis set. At small impact parameter, more collisional energy is utilized for electronic excitation, therefore, the increase in transfer probability at small impact parameter that is accrued by changing from the 6-31G to the 6-31B basis set is due to the improved description of the virtual orbitals on the Li atom. Further improvement is made by altering the orbital exponent in the 3$p$ STO for the Li atom. This results in an improved representation of the 3$p$ virtual orbital. Furthermore, a larger number of contractions can also be utilized. The BJK01 (purple line) and BJK02 (black line) basis sets are a result of these modifications to the 6-31B basis set. The
Figure 3.9: Comparison of the probability for near-resonant charge transfer between H\(^+\) and Li at 1 keV collision energy. The following Li basis sets are used: 6-31G (red), 6-31B (blue), BJK01 (purple), BJK02 (black). The BJK01 basis set for H was used for each run.

BJK02 basis set provides the most accurate excitation energies (all less than 5 cm\(^{-1}\)). Due to this fact and the rapid convergence seen between the dynamically consistent basis sets, it can be inferred that the BJK02 basis set provides an excellent description of the near-resonant charge transfer between H\(^+\) and Li.

Figure 3.9 represents the transfer probability for the same reaction, though at a collision energy of 1000 eV. At this energy the higher virtual orbitals are less accessible energetically. Therefore, it can be expected that the stock basis sets will converge more strongly with the dynamically consistent basis set. This is what can be inferred from the figure. At very small impact parameter, the energy deposition from the projectile to the target is enough to allow for excitation to the lower lying states, but beyond about 3 atomic units of impact parameter the probabilities converge. However, as the description of excitation energies improves, the probability in the small impact parameter region is substantially improved.
Figure 3.10: Comparison of the differential cross section for near-resonant charge transfer between H$^+$ and Li at 10 keV collision energy. The following Li basis sets are used: 6-31G (red), 6-31B (blue), BJK01 (purple), BJK02 (black). The BJK01 basis set for H was used for each run.

Once the transfer probability distribution is determined, the differential cross section for transfer can be calculated. Figure 3.10 provides the differential cross sections for electron transfer at 10 keV collision energy. While all four basis sets provide for the same structure for the differential cross section, the newly constructed basis sets all show an increase in the magnitude over the stock basis set. Furthermore, the three newly constructed basis sets, all of varying contraction sizes, show a rapid convergence. Unfortunately, no experimentally measured differential cross sections are available for this system, which prohibits any comparison with experiment and only allows for discussion of convergence.

Finally, the total cross section for transfer can be evaluated. This property is calculated using Equation (3.44). Figure 3.11 shows the total cross section as calculated using the END formalism and compared to other theoretical as well as experimental values. The experimental data come from the work of Varghese et al. [64] and Aumayr et al. [65]. The theoretical data are from the work of Allan...
Figure 3.11: Comparison of the total cross section for near-resonant charge transfer between H\(^+\) and Li as a function of energy. The experimental data are: Varghese \textit{et al.} (+) and Aumayr \textit{et al.} (×). The theoretical data are: Allan \textit{et al} (—) and Fritsch and Lin (— - -). For the END data the following Li basis sets are used: 6-31G (□), 6-31B (○), BJK01 (△), BJK02 (◇). The BJK01 basis set for H was used for each run.

\textit{et al.} [66] and Fritsch and Lin [67]. The most striking feature of this figure is the fact that all but one of the basis sets provide data that are quite good in comparison with the experimental data. Furthermore, those basis sets that offer good comparison to experiment also show good precision amongst the cross section values. The 6-31B basis set appears to offer the best comparison with experiment. A point of consternation arises from the fact that data set that deviates most from the experimental data corresponds to the BJK02 basis set, in which the excitation energies are most accurate in comparison with the experimental values. Also of interest is the comparison of the BJK02 data with the data of Allan \textit{et al.} [66] which is represented by the two solid lines. Allan employed a molecular basis set of Slater orbital functions that had to be centered on either the projectile or the target. The lower line represents the cross section calculated when the molecular basis set was centered on the Li, while the upper line is the cross section when
the basis set was centered on the proton. The data corresponding to the BJK02 basis set matches the data with the molecular basis centered on the Li atom. While this feature is yet to be completely understood, it does suggest that the newly constructed atomic basis set can be employed in the construction of molecular basis sets with comparable results as Slater functions. Furthermore, the data reiterates the point that basis set construction is only one part of the panoply of factors contributing to dynamical calculations, and no particular dynamically consistent basis set will ever act as a silver bullet to correct for all of these features.

Figure 3.12: Comparison of the probability for resonant charge transfer between Li$^+$ and Li at 1 keV collision energy. The following Li basis sets are used: 6-31G (red), BJK02 (blue).

The next set of data demonstrate the charge transfer probability as a function of impact parameter for the resonant charge transfer in the Li$^+$ - Li collision system. Figure 3.12 demonstrates a similar trend to the previous collision system. The transfer probability for the 6-31G basis set converges with the transfer probability for the BJK02 basis set at larger impact parameters, but the BJK02 basis set shows an increase in transfer probability at smaller impact parameter, where the higher excited states will be energetically accessible. The same probabilities
are plotted in Figure 3.13, except that the collision energy is 10 keV. It can be seen that there is a region of impact parameters in which the transfer probability is greater for the stock basis set than for the dynamically consistent basis set. This may be a result of excitation energy into the $2p$ orbital in the 6-31G being larger in experimentally determined. This will result in an available energy level that can be accessed in the 6-31G basis that is not present in the BJK02 basis set.

![Graph showing transfer probability vs impact parameter](image)

Figure 3.13: Comparison of the probability for resonant charge transfer between Li$^+$ and Li at 10 keV collision energy. The following Li basis sets are used: 6-31G (red), BJK02 (blue).

Likewise, Figure 3.14 shows the features of the differential cross section at 1.0 keV collision energy. As before, the change in differential cross section is subtle, but the dynamically consistent basis set shows an increase in magnitude over the stock basis set. However, without experimental data to compare with, one can only speculate as to any possible improvement in the differential cross section.

Finally, Figure 3.15 provides a comparison of the calculated total cross sections for transfer with experimental and theoretical data. The experimental data are taken from Lorents et al. [68] and the theoretical data are from Sakabe and Izawa [69]. Immediately one can see that the total cross sections calculated using
Figure 3.14: Comparison of the differential cross section for resonant charge transfer between Li\(^+\) and Li at 1 keV collision energy. The following Li basis sets are used: 6-31G (red), BJK02 (blue).

the 6-31G basis set show the poorest comparison with experiment. The 6-31B demonstrates better agreement, but the BJK02 basis set shows the best agreement with experiment. It should be noted that Sakabe and Izawa calculated there cross section using a parameterized formula based on ionization potentials rather than through dynamical calculations. Furthermore, the BJK02 basis set shows the predicted oscillatory structure at higher collision energy.

The Li systems where chosen for comparisons because they are both pseudo-one-electron systems, in which the single valence electron is transfered and correlation effects are minimal. However, as demonstrated in the previous section, the 2\(p\) excitation energy for the stock basis set is relatively close to the experimentally observed value. As one wold reasonably expect the transition to the 2\(p\) orbital to predominate at most collision energies, it is not unreasonable to expect only a moderate change in the measured charge transfer in these systems. The final collision system, He\(^+\) on He, will allow for a much clearer demonstration of the difference
Figure 3.15: Comparison of the total cross section for resonant charge transfer between Li$^+$ and Li at as a function of collision energy. The experimental data are from Lorents et al. ($\times$). The theoretical data are from Sakabe and Izawa (—). For the END data the following Li basis sets are used: 6-31G (☐), 6-31B (○), BJK02 (△).

that can occur in charge transfer when energetically correct excitations are modeled in the basis set.

Figure 3.16 shows the resonant charge transfer probability as a function of impact parameter for the He$^+$ - He collision system at 5 keV. One immediately can see the highly oscillatory nature that is indicative of resonant charge transfer processes between atoms. It becomes clear that for impact parameters greater than about 1 a.u., the data for the three basis sets converge. This is the region in which the transfer occurs directly from the 1s orbital of the target into the 1s orbital of the projectile. At impact parameters less than about 1 remembered a.u., the 2s and 2p orbitals begin to take part, and the transfer probability changes significantly for the dynamically consistent basis sets.

This change is noted even more clearly Figure 3.17, which compares the differential cross section for resonant charge transfer as calculated using END to
the experimental values reported by Gao et al.\cite{70}. While the overall structure of the differential cross section calculated using the 6-31G** basis is reasonably good in comparison with experiment, one can see improvement in the data obtained when the dynamically consistent basis set are employed. There is a substantial phase shift that occurs between 0.1 and 1 degrees. Furthermore, the BJK01 basis set demonstrates a decrease in magnitude between the angle of 0.06 and 0.1 degrees that begins to converge with the experimental data. It must be remembered that the END calculations utilize a single determinantal representations of the electrons, and will never exactly reproduce the experimental results, however, it is evident that the energetically accessible virtual orbitals provided through the dynamically consistent bases are important to the correct description of the differential cross section.

In this section, it has been demonstrated that the dynamically consistent basis sets do result in increased charge transfer probabilities in regions of impact parameter and collision energy that allow virtual orbitals to be accessible to
Figure 3.17: Comparison of the differential cross section for resonant charge transfer between He$^+$ and He at 5 keV collision energy. The experimental data are from Gao et al. (●). For the END data the following He basis sets are used: 6-31G** (red), 6-31B** (blue), and BJK01 (purple).

excitations of the valence electrons. This effect, however, is most noticeable in systems where the stock basis sets provide a poor description of these virtual orbitals. While these dynamically consistent basis sets are not the only factor in improving dynamical calculations, they do play a role in improving result from such calculations.

3.4.3 Properties of Diatomic and Triatomic Molecules

One final collection of properties will be investigated. Many structure properties of molecules are based on ground state energy of the molecule in question. The most common of these properties is the calculation of vibrational normal modes of the molecule. This is accomplished by diagonalization of the Hessian matrix, the matrix of second derivatives of the energy with respect to the nuclear coordinates [44]. It is reasonable to expect that energy optimized basis sets would offer better vibrational analyses for molecules than basis sets that have not been subject
Table 3.7: Molecular properties of the nitrogen molecule.

N₂ Bond Length, r (Experimental: 1.0940 Å)

<table>
<thead>
<tr>
<th>Basis</th>
<th>r (Å)</th>
<th>% Err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21G</td>
<td>1.0829</td>
<td>-1.01</td>
</tr>
<tr>
<td>6-31G</td>
<td>1.0892</td>
<td>-0.44</td>
</tr>
<tr>
<td>6-31G**</td>
<td>1.0784</td>
<td>-1.43</td>
</tr>
</tbody>
</table>

Vibrational Frequency, ν (Experimental: 2359.61 cm⁻¹)

<table>
<thead>
<tr>
<th>Basis</th>
<th>ν (cm⁻¹)</th>
<th>% Err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21G</td>
<td>2611.84</td>
<td>10.7</td>
</tr>
<tr>
<td>6-31G</td>
<td>2660.99</td>
<td>12.8</td>
</tr>
<tr>
<td>6-31G**</td>
<td>2758.00</td>
<td>16.9</td>
</tr>
</tbody>
</table>

The first collection of data, given in Table 3.7, relates the bond length and normal mode frequency of the N₂ molecule as calculated using the various basis sets. The experimental values are taken from Herzberg [71]. Upon consideration of the bond lengths as calculated using the various basis sets, it becomes clear that the stock basis sets provide more accurate values (all in error by less than 1.5 percent). However, the values obtained using the dynamically consistent basis sets do not demonstrate significantly increased inaccuracy. All of the values provided show less than 9 percent error. Furthermore, comparison of the vibrational frequency shows very good results. The normal mode frequency calculated using the energy optimized basis sets demonstrates an consistent discrepancy of greater than ten percent, while the non-optimized basis sets are consistently in error by less
Table 3.8: Molecular properties of the carbon monoxide molecule.

<table>
<thead>
<tr>
<th>Basis</th>
<th>r (Å)</th>
<th>% Err.</th>
<th>Basis</th>
<th>r (Å)</th>
<th>% Err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21G</td>
<td>1.1285</td>
<td>0.03</td>
<td>3-21B</td>
<td>1.2271</td>
<td>8.77</td>
</tr>
<tr>
<td>6-31G</td>
<td>1.1307</td>
<td>0.22</td>
<td>6-31B</td>
<td>1.2132</td>
<td>7.53</td>
</tr>
<tr>
<td>6-31G**</td>
<td>1.1139</td>
<td>-1.27</td>
<td>6-31B**</td>
<td>1.2149</td>
<td>7.68</td>
</tr>
</tbody>
</table>

**Vibrational Frequency, ν (Experimental: 2170.21 cm⁻¹)**

<table>
<thead>
<tr>
<th>Basis</th>
<th>ν (cm⁻¹)</th>
<th>% Err.</th>
<th>Basis</th>
<th>ν (cm⁻¹)</th>
<th>% Err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21G</td>
<td>2315.30</td>
<td>6.69</td>
<td>3-21B</td>
<td>2055.77</td>
<td>-5.27</td>
</tr>
<tr>
<td>6-31G</td>
<td>2286.00</td>
<td>5.34</td>
<td>6-31B</td>
<td>2023.84</td>
<td>-6.74</td>
</tr>
<tr>
<td>6-31G**</td>
<td>2438.37</td>
<td>12.4</td>
<td>6-31B**</td>
<td>1986.84</td>
<td>-8.45</td>
</tr>
</tbody>
</table>

**Dipole Moment, μ (Experimental: 0.117 D)**

<table>
<thead>
<tr>
<th>Basis</th>
<th>μ (D)</th>
<th>% Err.</th>
<th>Basis</th>
<th>μ (D)</th>
<th>% Err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21G</td>
<td>0.3972</td>
<td>240</td>
<td>3-21B</td>
<td>0.5606</td>
<td>379</td>
</tr>
<tr>
<td>6-31G</td>
<td>0.5729</td>
<td>390</td>
<td>6-31B</td>
<td>0.4967</td>
<td>325</td>
</tr>
<tr>
<td>6-31G**</td>
<td>0.2642</td>
<td>126</td>
<td>6-31B**</td>
<td>0.4646</td>
<td>297</td>
</tr>
</tbody>
</table>

than 1.5 percent. However, it must be noted that a systematic error is introduced into vibrational calculations by virtue of correlation effects. This error is generally treated using well-accepted empirical multiplicative factors. The reported values do not account for these correlation effects. However, if one assumes that the newly constructed basis sets demonstrate comparable correlation effects, then the values computed using the dynamically consistent basis sets will be roughly 10% lower than the experimental frequency. This is reasonable, in light of the fact that the bond lengths are too long in comparison the experimental bond length. But, this 10% error is quite good in light of the simplicity of the proposed basis set construction method.

The second diatomic molecule submitted for investigation is carbon monoxide. The experimental values of the bond length and the normal mode frequency are taken from Herzberg [71], while the dipole moment is taken from Atkins [72]. Table 3.8 provides the bond lengths, normal mode frequencies, and dipole moments as calculated using the various basis sets. At this point, the trends are becoming
clear. The bond lengths are more accurate using the stock basis sets, though the dynamically consistent basis sets are not in error by more than 9%. Again, the frequencies calculated using the newly constructed basis sets are, upon initial investigation, more accurate than the values obtained using stock basis sets. However, when correlation effects are considered, the dynamically consistent basis sets lose some accuracy. The vibrational frequencies obtained by using the dynamically consistent basis sets can be reasonably expected to incur about 10% error. The final quantity to compare is the magnitude of the dipole moment. In the case of the dipole moment of CO, neither the stock basis sets nor the dynamically consistent basis sets perform well. The error in the stock basis sets is about 200% on average, while the error in the newly constructed basis sets is about 330%.

Furthermore, all of the basis sets provided dipole moments that are anti-parallel to the experimentally determined dipole moment. This is a well-known failure of the Hartree-Fock analysis of CO \cite{34}, but it demonstrates that, at this level of theory, the newly constructed basis sets perform comparably to the stock basis sets.

Finally, the calculated values for water are compared; these are given in Table 3.9. The experimental data are taken from the CRC Handbook \cite{73}. Again, the trends are confirmed. The bond lengths from the newly constructed basis sets are in error by about 7% and the vibrational frequencies show a comparable error of less than about 10%. The bond angle in water shows about a 5% error when the stock basis sets are employed. This decreases to about 3% when the dynamically consistent basis sets are used. This can possibly be attributed to the improved virtual orbital structure in the newly constructed basis sets and polarization effects. Finally, the dipole moment can be considered. Both the stock basis sets and the newly constructed basis sets demonstrate good comparison with experiment in the case of water. Of particular interest is the fact that the values calculated using the dynamically consistent basis sets are in error by about half in comparison
Table 3.9: Molecular properties of the water molecule.

O-H Bond Length, $r$ (Experimental: 0.9584 Å)

<table>
<thead>
<tr>
<th>Basis</th>
<th>$r$ (Å)</th>
<th>% Err.</th>
</tr>
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<tbody>
<tr>
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<td>0.9668</td>
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<td>6-31G</td>
<td>0.9497</td>
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</tr>
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<td>6-31G**</td>
<td>0.9428</td>
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<tbody>
<tr>
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<td>6-31B</td>
<td>1.0200</td>
<td>6.43</td>
</tr>
<tr>
<td>6-31B**</td>
<td>1.0185</td>
<td>6.27</td>
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H-O-H Angle, $\theta$ (Experimental: 104.45 °)

<table>
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<tbody>
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<td>6-31G</td>
<td>111.55</td>
<td>6.80</td>
</tr>
<tr>
<td>6-31G**</td>
<td>105.95</td>
<td>1.44</td>
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<table>
<thead>
<tr>
<th>Basis</th>
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<th>% Err.</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>6-31B</td>
<td>108.13</td>
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<td>6-31B**</td>
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Dipole Moment, $\mu$ (Experimental: 1.85 D)

<table>
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<tbody>
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<td>6-31G</td>
<td>2.501</td>
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<td>6-31G**</td>
<td>2.148</td>
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<table>
<thead>
<tr>
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<tbody>
<tr>
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<td>6-31B</td>
<td>2.172</td>
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1st Normal Mode, $\nu_1$ (Experimental: 1595 cm$^{-1}$)

<table>
<thead>
<tr>
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<tbody>
<tr>
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<tr>
<td>6-31G</td>
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</tr>
<tr>
<td>6-31G**</td>
<td>1769.02</td>
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<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>3-21B</td>
<td>1666.66</td>
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</tr>
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<td>6-31B</td>
<td>1606.26</td>
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<td>6-31B**</td>
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2nd Normal Mode, $\nu_2$ (Experimental: 3657 cm$^{-1}$)

<table>
<thead>
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<th>% Err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21G</td>
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</tr>
<tr>
<td>6-31G</td>
<td>3987.03</td>
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</tr>
<tr>
<td>6-31G**</td>
<td>4151.50</td>
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</table>

<table>
<thead>
<tr>
<th>Basis</th>
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<th>% Err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21B</td>
<td>3703.32</td>
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</tr>
<tr>
<td>6-31B</td>
<td>3668.15</td>
<td>0.44</td>
</tr>
<tr>
<td>6-31B**</td>
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3rd Normal Mode, $\nu_3$ (Experimental: 3756 cm$^{-1}$)

<table>
<thead>
<tr>
<th>Basis</th>
<th>$\nu_3$ cm$^{-1}$</th>
<th>% Err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21G</td>
<td>3943.74</td>
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</tr>
<tr>
<td>6-31G</td>
<td>4143.95</td>
<td>10.3</td>
</tr>
<tr>
<td>6-31G**</td>
<td>4268.43</td>
<td>13.6</td>
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</table>

<table>
<thead>
<tr>
<th>Basis</th>
<th>$\nu_3$ cm$^{-1}$</th>
<th>% Err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21B</td>
<td>3998.78</td>
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</tr>
<tr>
<td>6-31B</td>
<td>4034.29</td>
<td>7.41</td>
</tr>
<tr>
<td>6-31B**</td>
<td>4072.82</td>
<td>8.44</td>
</tr>
</tbody>
</table>
the values from the stock basis sets. The 6-31B** basis, in particular, provides a remarkably good dipole moment magnitude, which is likely a consequence of the improved polarization orbitals included in that basis set.

This chapter has demonstrated that a simple and computationally inexpensive method for construction of atomic basis sets can be achieved. This method focuses on the physical properties of occupied and virtual atomic orbitals, and as a consequence does not require expensive and tedious energy optimizations. These basis sets provide for physically meaningful electronic excitations within the atoms, marked improvement in charge transfer descriptions in comparison to stock basis sets, and are still capable of returning reasonable structural properties of ground state molecules. Furthermore, these properties can all be improved through minor modifications that may be made in the future.
In this chapter, the equations of motion for a multi-configurational formalism of Electron-Nuclear Dynamics are derived. The formalism is dubbed Vector Hartree-Fock (VHF). First, a Lagrangian for the system is introduced, with verification that the Schrödinger Equation is returned. Secondly, the new Lagrangian is parameterized in terms of the dynamical variables that describe the system. From this parameterized Lagrangian, the VHF equations of motion are derived.

4.1 Introduction of the Lagrangian and Verification of the Equations of Motion

In dynamics, a Lagrangian function introduced for a dynamical system is not unique. In fact, provided a given Lagrangian function returns the correct equations of motion, then that Lagrangian is a valid Lagrangian for the system in question [74]. With this in mind, the VHF equations of motion are more conveniently derived if one alters the form of the quantum mechanical Lagrangian as introduced in the first chapter.

Consider a state $|\zeta\rangle$ defined by a set of dynamical variables $\zeta = \{\zeta, \zeta^*\}$ with quantum mechanical Hamiltonian operator $\mathcal{H}$. A quantum mechanical Lagrangian can be constructed of the form

$$\mathcal{L}(\zeta, \zeta^*) = \langle \zeta | i \frac{\partial}{\partial t} - \mathcal{H} | \zeta \rangle.$$  \hspace{1cm} (4.1)

One can exploit the hermiticity of the time derivative to rewrite the Lagrangian as

$$\mathcal{L}(\zeta, \zeta^*) = \frac{i}{2} \langle \zeta | \frac{\partial}{\partial t} - \frac{\tilde{\partial}}{\partial \tilde{t}} | \zeta \rangle - \langle \zeta | \mathcal{H} | \zeta \rangle$$ \hspace{1cm} (4.2)
where the operators $\frac{\partial}{\partial t}$ and $\frac{\partial}{\partial t}$ act exclusively on the ket and the bra, respectively.

Hamilton’s Principle requires that variations in the action of the system vanish \[75],

$$\delta S = \int_{t_1}^{t_2} \delta L \, dt = 0. \quad (4.3)$$

The boundary conditions will be imposed such that $h(t_1) = h(t_2)$, If one assumes that the dynamical terms $\zeta$ and $\zeta^*$ are the only variable parameters, then by varying $\zeta^*$ one obtains $\langle \zeta(t_2)|\delta \zeta(t_2) \rangle - \langle \delta \zeta(t_1)|\zeta(t_1) \rangle = 0$ and by variation of $\zeta$ one obtains $\langle \zeta(t_2)|\zeta(t_2) \rangle - \langle \zeta(t_1)|\delta \zeta(t_1) \rangle = 0$. Furthermore, variation of the Lagrangian results in an expression

$$\delta L = \frac{i}{2} \left[ \langle \delta \zeta | \dot{\zeta} \rangle + \langle \zeta | \delta \dot{\zeta} \rangle - \langle \dot{\zeta} | \delta \zeta \rangle - \langle \dot{\zeta} | \delta \zeta \rangle \right] - \langle \delta \zeta | \mathcal{H} | \zeta \rangle - \langle \zeta | \mathcal{H} | \delta \zeta \rangle. \quad (4.4)$$

The above expression can be simplified by introducing the total time derivatives of $\langle \delta \zeta | \zeta \rangle$ and $\langle \zeta | \delta \zeta \rangle$,

$$\delta L = \frac{i}{2} \left[ \frac{d}{dt} \langle \zeta | \delta \zeta \rangle - \frac{d}{dt} \langle \delta \zeta | \zeta \rangle \right] + i \left[ \langle \delta \zeta | \dot{\zeta} \rangle - \langle \dot{\zeta} | \delta \zeta \rangle \right] - \langle \delta \zeta | \mathcal{H} | \zeta \rangle - \langle \zeta | \mathcal{H} | \delta \zeta \rangle. \quad (4.5)$$

Substitution of the above into Equation (4.3) and subsequent integration results in the expression

$$0 = \frac{i}{2} \left[ \langle \zeta | \delta \zeta \rangle |_{t_1}^{t_2} - \langle \delta \zeta | \zeta \rangle |_{t_1}^{t_2} \right] + \int_{t_1}^{t_2} i \left[ \langle \delta \zeta | \dot{\zeta} \rangle - \langle \dot{\zeta} | \delta \zeta \rangle \right] - \langle \delta \zeta | \mathcal{H} | \zeta \rangle - \langle \zeta | \mathcal{H} | \delta \zeta \rangle dt. \quad (4.6)$$

The first term on the right-hand side vanishes due to the constraints imposed by the boundary conditions, leaving

$$0 = \int_{t_1}^{t_2} i \langle \delta \zeta | \dot{\zeta} \rangle - \langle \delta \zeta | \mathcal{H} | \zeta \rangle + \text{complex conjugate} \, dt. \quad (4.7)$$

By the fact that the integral evaluates to zero and the fact that the parameters $\zeta$ and $\zeta^*$ are permitted to vary independently of each other, both terms in the
integrand must be identically zero. Considering only the first term, one obtains

\[ 0 = \langle \delta \zeta | \left\{ i \dot{\zeta} - \mathcal{H} | \zeta \rangle \right\}. \quad (4.8) \]

As no constraints on the variation of \( \zeta \) or \( \zeta^* \) were imposed, \( \langle \delta \zeta | \) is completely arbitrary, requiring that the bracketed term be identically zero. Thus,

\[ \mathcal{H} | \zeta \rangle = i \frac{\partial}{\partial t} | \zeta \rangle. \quad (4.9) \]

Furthermore, if the same analysis is performed on the complex conjugate term, the resulting equation takes the form

\[ \left( | \zeta \rangle \mathcal{H} \right) = -i \left( \langle \zeta | \frac{\partial}{\partial t} \right), \quad (4.10) \]

Equations (4.9) and (4.10) are the Schrödinger Equations for the system \( | \zeta \rangle \), verifying that the chosen Lagrangian does indeed return the correct dynamical equations.

### 4.2 Parameterization of the State Vector

The state vector will be assumed to take the form of a product wave function,

\[ | \psi \rangle = | R, P \rangle | z; R, P \rangle = | \phi \rangle | z \rangle. \quad (4.11) \]

The first factor is the nuclear component of the wave function,

\[ | \phi \rangle = \prod_{j,k} \sqrt{\frac{1}{b_k \sqrt{\pi}}} \exp \left[ -\frac{1}{2} \left( \frac{X_{jk} - R_{jk}}{b_k} \right)^2 + iP_{jk} (X_{jk} - R_{jk}) \right], \quad (4.12) \]

where \( X_{jk} \) is the \( k \)th Cartesian component of the \( j \)th nucleus, \( R_{jk} \) and \( P_{jk} \) are the corresponding average nuclear positions and momenta, and \( b \) is a non-dynamical width parameter. The nuclear wave packet will be treated in a “zero width” limit (i.e. classically), in the manner that \( b_k \to 0 \) (for all \( k \)) and \( \hbar \to 0 \), such that \( \frac{\hbar}{b_k} \to 1 \). The electronic factor \( | z \rangle \) is constructed from a collection of single
$N$-electron Thouless determinants that can be written as

$$D = \det\{\chi_i(x_j)\}$$  \hspace{1cm} (4.13)$$

and are expressed in terms of a set of dynamical spin-orbitals of the form

$$\chi_h = u_h + \sum_{p=N+1}^K u_p z_{ph},$$  \hspace{1cm} (4.14)$$

where $\{u_i\}$ is a set of basis functions of rank $K$, constructed from a set of Gaussian atomic orbitals that are centered on the average atomic positions. Furthermore, the complex-valued parameter $z_{ph}$ is the $p$th Thouless coefficient corresponding to the $h$th atomic orbital in the specified configuration. From this, it can be seen that the multi-configurational wave function now takes the form

$$\langle z \rangle = \sum_{\kappa} d_\kappa |D_\kappa\rangle,$$  \hspace{1cm} (4.15)$$

where $\kappa$ provides an index over included configurations. The expansion coefficients are permitted to be complex-valued. It is assumed in the current discussion that the spin orbitals within a given configuration are orthogonal, however, this restriction is not imposed on two spin orbitals from differing configurations.

Therefore, the normalization of the wave-function must be addressed, and is given the form

$$S = \sum_\kappa \sum_\lambda d_\kappa^* d_\lambda D_{\kappa\lambda}.$$  \hspace{1cm} (4.16)$$

In the above equation, the term $D_{\kappa\lambda}$ is the overlap integral between two different configurations, given the form

$$D_{\kappa\lambda} = \langle D_\kappa|D_\lambda\rangle = \det\{\Lambda_{\kappa\lambda}^*\},$$  \hspace{1cm} (4.17)$$
where the matrix $\Lambda_{\kappa\lambda}^\bullet$ is given as

$$\Lambda_{\kappa\lambda}^\bullet = J_\kappa^\dagger \left( \begin{array}{cc} I^\bullet & z^\dagger \\ \end{array} \right) \Delta \left( \begin{array}{c} I^\bullet \\ z \end{array} \right) J_\lambda.$$  

(4.18)

The previous equation utilizes a vector representation that corresponds to Equation (4.14) as well as the atomic overlap matrix, $\Delta$.

The electronic representation is constructed using a complete active space (CAS) formalism [76] which allows one to partition the electronic space. There is a total of $N$ electrons in a basis of $K$ spin orbitals. Of these, there are $K_1$ “core orbitals”, those spin orbitals that are occupied in every configuration. Secondly, there is an active space, which is defined as the set of spin orbitals that have some probability of being occupied that is between zero and unity. The rank of the active space is denoted by $K_2$. This requires that the virtual space (those orbitals that are never occupied) has a rank of $K - K_2$. All full matrices have dimension $K \times K$ and can be partitioned using the following construction

$$M = \begin{bmatrix} M^\bullet & M^> \\ M^< & M^\circ \end{bmatrix}. \quad (4.19)$$

The superscripts provide a mnemonic for remembering the structure of the matrices: the bullet ($\bullet$) represents the active block with dimensions $K_2 \times K_2$, the open circle ($\circ$) represents the virtual block with dimensions $(K - K_2) \times (K - K_2)$, the $>$ superscript points to the right and symbolizes the upper right block of the matrix with dimensions $K \times (K - K_2)$, and the $\vee$ superscript points down and symbolizes the $(K - K_2) \times K$ lower left block of the matrix. Furthermore, the symbols $I^\bullet$ and $I^\circ$ represent unit matrices with dimensions $K \times K$ and $(K - K_2) \times (K - K_2)$, respectively.
At this point, one can perform the prescribed matrix multiplication indicated in Equation (4.18), resulting the expanded form

$$\Lambda_{\kappa \lambda}^* = J^\dagger_\kappa (\Delta^\bullet + z^\dagger \Delta^\vee + \Delta^> z + z^\dagger \Delta^* z) J_\lambda.$$  \hspace{1cm} (4.20)

At this point, the $J$ matrices must be discussed. The matrix denoted as $J_\lambda$ is a matrix of ones and zeros with dimensions of $K_2 \times N$. The elements are defined such as to select the Thouless coefficients that correspond to a given configuration. The specific value of the element $(J_\lambda)_{hj}$ is a Kronecker delta

$$(J_\lambda)_{hj} = \delta_{hh},$$  \hspace{1cm} (4.21)

where $1 \leq h \leq K_2$ and where $h_j$ is a spin orbital in $D_\lambda$.

In this parameterization, the dynamical variables are \{R, P, z, z^*, d, d^*\}. Before the parameterized Lagrangian can be introduced, several comments concerning the properties of nuclear wave packets must be made. As the nuclear wave function is normalized at each time-step, the expectation value of an observable $\mathcal{O}$ is defined as $\langle \mathcal{O} \rangle = \langle \phi | \mathcal{O} | \phi \rangle$. From this, the average width of the normalized nuclear wave packet can be found,

$$\langle (X_{jk} - R_{jk}) \rangle = \frac{1}{b\sqrt{\pi}} \int_{-\infty}^{\infty} (X_{jk} - R_{jk}) e^{-\left(\frac{X_{jk} - R_{jk}}{b}\right)^2} dX$$

$$= 0,$$

(4.22)

due to the symmetry of the integrand. Secondly, the expectation value of the square of the average width of the wave packet can be found,

$$\langle (X_{jk} - R_{jk})^2 \rangle = \frac{1}{b\sqrt{\pi}} \int_{-\infty}^{\infty} (X_{jk} - R_{jk})^2 e^{-\left(\frac{X_{jk} - R_{jk}}{b}\right)^2} dX$$

$$= \frac{1}{b\sqrt{\pi}} \frac{b^3}{2}$$

$$= \frac{b^2}{2}.$$  \hspace{1cm} (4.23)
From this, the width (the root-mean-square value of the average width of the nuclear wave function, \( \Delta x = \sqrt{\langle (X_{jk} - R_{jk})^2 \rangle} \)) is \( \frac{b}{\sqrt{2}} \). Now one must consider expectation values involving the momentum operator, \( \hat{P} = -i\hbar \frac{\partial}{\partial X} \). Thus,

\[
\langle \hat{P} \rangle = \frac{i\hbar}{b\sqrt{\pi}} \int_{-\infty}^{\infty} \left\{ e^{-\frac{1}{2} \left( \frac{X_{jk} - R_{jk}}{b} \right)^2} - iP_{jk}(X_{jk} - R_{jk}) \right. \\
\times \left. \frac{\partial}{\partial X_{jk}} e^{\frac{i}{2} \left( \frac{X_{jk} - R_{jk}}{b} \right)^2 + iP_{jk}(X_{jk} - R_{jk})} dX \right\}
\]

\[
= - \frac{i\hbar}{b^3 \sqrt{\pi}} \langle \phi | X_{jk} - R_{jk} + iP_{jk} | \phi \rangle
\]

\[
= - \frac{i\hbar}{b^3 \sqrt{\pi}} \langle (X_{jk} - R_{jk}) + iP_{jk} | \phi \rangle \langle \phi | \phi \rangle (4.24)
\]

\[
= \frac{P_{jk} b \sqrt{\pi}}{b^3 \sqrt{\pi}} \langle \phi | \phi \rangle
\]

\[
= \frac{P_{jk} \hbar}{b^2} \langle \phi | \phi \rangle
\]

in our limit \( b \to 0, \hbar \to 0, \hbar/b^2 \to 1 \) and with normalized nuclear wave functions. Furthermore,

\[
\langle \hat{P}^2 \rangle = - \frac{1}{b\sqrt{\pi}} \int_{-\infty}^{\infty} \left\{ e^{-\frac{1}{2} \left( \frac{X_{jk} - R_{jk}}{b} \right)^2} - iP_{jk}(X_{jk} - R_{jk}) \right. \\
\times \left. \frac{\partial^2}{\partial X_{jk}^2} e^{\frac{i}{2} \left( \frac{X_{jk} - R_{jk}}{b} \right)^2 + iP_{jk}(X_{jk} - R_{jk})} dX \right\}
\]

\[
= - \left\{ - \left[ P_{jk}^2 + \frac{1}{b^2} \right] \langle \phi | \phi \rangle + \frac{1}{b^4} \langle (X_{jk} - R_{jk})^2 \rangle \right\}
\]

\[
= P_{jk}^2 + \frac{1}{2b^2}
\]

again with the limits mentioned above. Likewise, it is very simple to show that \( \langle P_{jk} \rangle = P_{jk} \langle \phi | \phi \rangle \). Finally, realizing that the numerical value of \( \langle \phi | \phi \rangle \) is 1, then

\[
\langle \hat{P}^2 - P_{jk}^2 \rangle = \langle \hat{P}^2 \rangle - \langle P_{jk}^2 \rangle
\]

\[
= \frac{1}{2b^2} (4.26)
\]
from which it immediately follows that \( \Delta P = \sqrt{\langle \hat{P}^2 - \hat{P}_{jk}^2 \rangle} = \frac{1}{\sqrt{2b}}. \) The result that can now be concluded is that the minimum uncertainty in the nuclear Gaussian wave packet is \( \Delta X \Delta P = \frac{1}{2} \) in atomic units.

Additionally, two specific expectation values of derivatives must be evaluated. Firstly, in atomic units,

\[
\left\langle \frac{\partial}{\partial R_{jk}} \right\rangle = -i \langle \hat{P}_{jk} \rangle
\]

\[
\left\langle \frac{\partial}{\partial X_{jk}} \right\rangle = -i P_{jk} \langle \phi | \phi \rangle. \tag{4.27}
\]

Secondly,

\[
\left\langle \frac{\partial}{\partial P_{jk}} \right\rangle = \langle (X_{jk} - R_{jk}) \rangle
\]

\[
= 0, \tag{4.28}
\]

as previously demonstrated.

One final comment must be made concerning the expectation value of the Hamiltonian operator, \( \langle \psi | \mathcal{H} | \psi \rangle \). The total energy of the system can be expressed as

\[
E = - \sum_{jk} p_{jk}^2 \frac{2M_k}{2M_k} - \frac{\langle \psi | \mathcal{H}_el | \psi \rangle}{\langle \psi | \psi \rangle}, \tag{4.29}
\]

where \( \mathcal{H}_el \) is the separable electronic component of the Hamiltonian operator.

Using the previously derived properties of Gaussian wave packets, it is easy to show that the kinetic energy term in the Equation (4.29) can be rewritten as

\[
- \sum_{jk} p_{jk}^2 \frac{2M_k}{2M_k} \]

\[
= \frac{\langle \psi | T | \psi \rangle}{\langle \psi | \psi \rangle}, \tag{4.30}
\]

where \( T \) is the average kinetic energy operator, \( T = - \sum_{jk} p_{jk}^2 \frac{2M_k}{2M_k} \). Now, substitution of Equation (4.30) in to Equation (4.29) and recognizing that \( \mathcal{H} = T + \mathcal{H}_el \), then
it becomes evident that

$$E = \frac{\langle \psi | \mathcal{H} | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (4.31)$$

Therefore, it can easily be seen that

$$\langle \psi | \mathcal{H} | \psi \rangle = \langle \mathcal{H} \rangle = ES; \quad (4.32)$$

which is the energy of the system weighted by the electronic normalization.

Furthermore, from the earlier explored properties of the nuclear wave function

$$\langle \langle \hat{\mathcal{P}}^2 \rangle = \mathbf{P}^2_{jk} \text{ in the narrow wave packet limit} \rangle$$

and the normalization condition, it can be seen that

$$\langle \mathcal{H} \rangle = \langle z | \mathcal{H} | z \rangle. \quad (4.33)$$

One important feature of the electronic norm is that if the electronic configurations are normalized at time $t = 0$, then they will remain normalized throughout the dynamics. Therefore, if special care is taken that the electronic configurations are normalized initially, then the expectation value of the Hamiltonian is equal to the energy of the system at all time-steps. As a result, any derivative of the normalized expectation value of the Hamiltonian with respect to a given dynamical variable is a force expression. This is of special importance when the matrix form of the equations of motion is investigated later.

Now, from the previous section, one can separate the Lagrangian in the form

$$\mathcal{L} = \frac{i}{2} \left[ \langle \phi | \frac{\partial}{\partial t} | \phi \rangle - \langle \phi | \frac{\partial}{\partial t} | \phi \rangle \right] \langle z | z \rangle + \frac{i}{2} \left[ \langle z | \frac{\partial}{\partial t} | z \rangle - \langle z | \frac{\partial}{\partial t} | z \rangle \right] \langle \phi | \phi \rangle - \langle \mathcal{H} \rangle. \quad (4.34)$$
Expansion of the time derivative with respect to the dynamical variables allows the Lagrangian to be expressed as

\[ \mathcal{L} = \frac{i}{2} \sum_{jk} \left\{ \left( \langle \phi | \frac{\partial}{\partial R_{jk}} | \phi \rangle - \langle \phi | \frac{\partial}{\partial R'_{jk}} | \phi \rangle \right) \dot{R}_{jk} \langle z | \phi \rangle + \left( \langle \phi | \frac{\partial}{\partial P_{jk}} | \phi \rangle - \langle \phi | \frac{\partial}{\partial P'_{jk}} | \phi \rangle \right) \dot{P}_{jk} \langle z | \phi \rangle + \left( \langle z | \frac{\partial}{\partial R_{jk}} | z \rangle - \langle z | \frac{\partial}{\partial R'_{jk}} | z \rangle \right) \ddot{R}_{jk} \langle \phi | \phi \rangle + \langle z | \frac{\partial}{\partial P_{jk}} | z \rangle - \langle z | \frac{\partial}{\partial P'_{jk}} | z \rangle \ddot{P}_{jk} \langle \phi | \phi \rangle \right\} \]  

\[ + \frac{i}{2} \sum_{\kappa} \left\{ \sum_{ph} \left( \langle z | \frac{\partial}{\partial z_{ph}} | z \rangle z_{ph} - \langle z | \frac{\partial}{\partial z'_{ph}} | z \rangle z_{ph}^* \right) + \langle z | \frac{\partial}{\partial d_{\kappa}} | z \rangle d_{\kappa} - \langle z | \frac{\partial}{\partial d'_{\kappa}} | z \rangle d_{\kappa}^* \right\} \langle \phi | \phi \rangle - \langle \mathcal{H} \rangle, \]  

\[ (4.35) \]

where it is understood that the bra is a function of \( R', P', z^*, d^* \) and the ket is a function of \( R, P, z, d, \) in the limit where \( R', P' \to R, P. \) From this point forward, the dependence of \( z \) and \( z^* \) on \( \kappa \) will not be explicitly indicated, such that \( z_{ph}^\kappa = z_{ph} \) and \( z_{ph}^{\kappa*} = z_{ph}^* \).

Now, introduction of Equations (4.27) and (4.28) into the above form of the Lagrangian allows one to write

\[ \mathcal{L} = \sum_{jk} \left\{ \left( P_{jk} \langle z | \phi \rangle + \frac{1}{2} \left( \langle z | \frac{\partial}{\partial R_{jk}} | z \rangle - \langle z | \frac{\partial}{\partial R'_{jk}} | z \rangle \right) \right) \dot{R}_{jk} \right\} \]  

\[ + \frac{i}{2} \left\{ \langle z | \frac{\partial}{\partial P_{jk}} | z \rangle - \langle z | \frac{\partial}{\partial P'_{jk}} | z \rangle \right\} \langle \phi | \phi \rangle \]  

\[ + \frac{i}{2} \sum_{\kappa} \left\{ \sum_{ph} \left( \langle z | \frac{\partial}{\partial z_{ph}} | z \rangle \dot{z}_{ph} - \langle z | \frac{\partial}{\partial z'_{ph}} | z \rangle \dot{z}_{ph}^* \right) + \langle z | \frac{\partial}{\partial d_{\kappa}} | z \rangle \ddot{d}_{\kappa} - \langle z | \frac{\partial}{\partial d'_{\kappa}} | z \rangle \ddot{d}_{\kappa}^* \right\} \langle \phi | \phi \rangle - \langle \mathcal{H} \rangle. \]  

\[ (4.36) \]

Before the final form of the parameterized Lagrangian can be introduced, the derivative expressions must be rewritten to properly reflect the dependence on the
chosen dynamical variables. Recalling the fact that $\langle z \rangle = \langle R', P', z^*, d^* \rangle$ and that $|z\rangle = |R, P, z, d\rangle$, then it is trivial to show that

$$\frac{\partial}{\partial R} \langle z | z \rangle = \langle z | \frac{\partial}{\partial R} | z \rangle$$

$$\frac{\partial}{\partial P} \langle z | z \rangle = \langle z | \frac{\partial}{\partial P} | z \rangle$$

$$\frac{\partial}{\partial z} \langle z | z \rangle = \langle z | \frac{\partial}{\partial z} | z \rangle$$

$$\frac{\partial}{\partial d} \langle z | z \rangle = \langle z | \frac{\partial}{\partial d} | z \rangle$$

Now, by recalling that the multi-configurational electronic overlap is $S = \langle z | z \rangle$, and introducing the above identities, the parameterized Lagrangian now takes the form

$$\mathcal{L} = \left\{ \sum_{jk} \left[ SP_{jk} \dot{R}_{jk} + \frac{i}{2} \left( \frac{\partial S}{\partial R_{jk}} - \frac{\partial S}{\partial R'_{jk}} \right) \dot{R}_{jk} + \frac{i}{2} \left( \frac{\partial S}{\partial P_{jk}} - \frac{\partial S}{\partial P'_{jk}} \right) \dot{P}_{jk} \right] \right\} \langle \phi | \phi \rangle - \langle \mathcal{H} \rangle. \tag{4.37}$$

4.3 The VHF Equations of Motion

It has been demonstrated that the proper physical description of the system can be achieved by imposing Hamilton’s Principle upon the quantum mechanical Lagrangian. The derivation of the equations of motion can be facilitated by employing a mathematical equivalent the Hamilton’s Principle, the Euler-Lagrange equations [75],

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}} = \frac{\partial \mathcal{L}}{\partial q} \tag{4.38}$$

where $q$ is an element of the set of dynamical variables. By solving the above equation for each dynamical variable, a set of coupled differential equations of motion will be obtained. The dynamics of the system can then be calculated as solutions to this coupled set of equations of motion.
4.3.1 Derivation of the Equations of Motion

As the derivation of the equations of motion for each dynamical variable is a lengthy and tedious undertaking, a detailed derivation with respect to only one variable will be used to demonstrate the process. Let \( q = R \), indicating that

\[
\frac{\partial \mathcal{L}}{\partial R_{il}} = SP_{il} + \frac{i}{2} \left[ \frac{\partial S}{\partial R_{il}} - \frac{\partial S}{\partial R'_{il}} \right].
\] (4.39)

Again, it is necessary to introduce the full expansion of the time derivative with respect to the dynamical variables, such that

\[
\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial R_{il}} = \sum_{jk} P_{il} \left( \frac{\partial S}{\partial R_{jk}} + \frac{\partial S}{\partial R'_{jk}} \right) \dot{R}_{jk}
\]

\[
+ \frac{i}{2} \left( \frac{\partial^2 S}{\partial R_{jk} \partial R_{il}} + \frac{\partial^2 S}{\partial R'_{jk} \partial R_{il}} - \frac{\partial^2 S}{\partial R_{jk} \partial R'_{il}} - \frac{\partial^2 S}{\partial R'_{jk} \partial R'_{il}} \right) \dot{R}_{jk}
\]

\[
+ S \delta_{ij,lk} \dot{P}_{jk} + P_{il} \left( \frac{\partial S}{\partial P_{jk}} + \frac{\partial S}{\partial P'_{jk}} \right) \dot{P}_{jk}
\]

\[
+ \frac{i}{2} \left( \frac{\partial^2 S}{\partial P_{jk} \partial R_{il}} + \frac{\partial^2 S}{\partial P'_{jk} \partial R_{il}} - \frac{\partial^2 S}{\partial P_{jk} \partial R'_{il}} - \frac{\partial^2 S}{\partial P'_{jk} \partial R'_{il}} \right) \dot{P}_{jk}
\] (4.40)

\[
+ \frac{i}{2} \sum_{\kappa} \left[ \left( \frac{\partial^2 S}{\partial d_{\kappa} \partial R_{il}} - \frac{\partial^2 S}{\partial d_{\kappa} \partial R'_{il}} \right) \dot{d}_{\kappa} + \left( \frac{\partial^2 S}{\partial d^*_{\kappa} \partial R_{il}} - \frac{\partial^2 S}{\partial d^*_{\kappa} \partial R'_{il}} \right) \dot{d}^*_{\kappa} \right]
\]

\[
+ \sum_{ph} \left[ \left( \frac{\partial^2 S}{\partial z_{ph} \partial R_{il}} - \frac{\partial^2 S}{\partial z_{ph} \partial R'_{il}} \right) \dot{z}_{ph} + \left( \frac{\partial^2 S}{\partial z^*_{ph} \partial R_{il}} - \frac{\partial^2 S}{\partial z^*_{ph} \partial R'_{il}} \right) \dot{z}^*_{ph} \right]
\].
Likewise, one finds that

$$
\frac{\partial \mathcal{L}}{\partial R_{il}} = \sum_{jk} \left\{ \left( \frac{\partial S}{\partial R_{il}} + \frac{\partial S}{\partial R'_{il}} \right) P_{jk} \dot{R}_{jk} 
+ \frac{i}{2} \left( \frac{\partial^2 S}{\partial R_{il} \partial R_{jk}} + \frac{\partial^2 S}{\partial R'_{il} \partial R_{jk}} - \frac{\partial^2 S}{\partial R_{il} \partial R'_{jk}} - \frac{\partial^2 S}{\partial R'_{il} \partial R'_{jk}} \right) \dot{R}_{jk} 
+ i \left( \frac{\partial^2 S}{\partial R_{il} \partial P_{jk}} + \frac{\partial^2 S}{\partial R'_{il} \partial P_{jk}} - \frac{\partial^2 S}{\partial R_{il} \partial P'_{jk}} - \frac{\partial^2 S}{\partial R'_{il} \partial P'_{jk}} \right) \dot{P}_{jk} \right\}
+ \frac{i}{2} \sum_{\kappa} \left\{ \left( \frac{\partial^2 S}{\partial R_{il} \partial d_{\kappa}} + \frac{\partial^2 S}{\partial R'_{il} \partial d_{\kappa}} \right) \dot{d}_{\kappa} - \left( \frac{\partial^2 S}{\partial R_{il} \partial d^*_{\kappa}} + \frac{\partial^2 S}{\partial R'_{il} \partial d^*_{\kappa}} \right) \dot{d}^*_{\kappa} \right\}
+ \sum_{ph} \left[ \left( \frac{\partial^2 S}{\partial R_{il} \partial z^*_{ph}} + \frac{\partial^2 S}{\partial R'_{il} \partial z^*_{ph}} \right) \dot{z}^*_{ph} \right]
+ \frac{\partial \langle \mathcal{H} \rangle}{\partial R_{il}}. \tag{4.41}
$$

When the previous two equations are substituted into the Euler-Lagrange equations, one finds that

$$
\frac{\partial \langle \mathcal{H} \rangle}{\partial R_{il}} = \sum_{jk} \left\{ \left( \frac{\partial S}{\partial R_{il}} + \frac{\partial S}{\partial R'_{il}} \right) P_{jk} - P_{il} \left( \frac{\partial S}{\partial R_{jk}} + \frac{\partial S}{\partial R'_{jk}} \right) \dot{R}_{jk} 
+ i \left( \frac{\partial^2 S}{\partial R'_{il} \partial R_{jk}} - \frac{\partial^2 S}{\partial R_{il} \partial R'_{jk}} \right) \dot{R}_{jk} 
+ i \left( \frac{\partial^2 S}{\partial R'_{il} \partial P_{jk}} - \frac{\partial^2 S}{\partial R_{il} \partial P'_{jk}} \right) \dot{P}_{jk} \right\}
+ \sum_{\kappa} \left\{ \left( P_{il} \frac{\partial S}{\partial d_{\kappa}} + i \frac{\partial^2 S}{\partial R'_{il} \partial d_{\kappa}} \right) \dot{d}_{\kappa} + \left( P_{il} \frac{\partial S}{\partial d^*_{\kappa}} - i \frac{\partial^2 S}{\partial R_{il} \partial d^*_{\kappa}} \right) \dot{d}^*_{\kappa} \right\}
+ \sum_{ph} \left[ \left( P_{il} \frac{\partial S}{\partial z_{ph}} + i \frac{\partial^2 S}{\partial R'_{il} \partial z_{ph}} \right) \dot{z}_{ph} + \left( P_{il} \frac{\partial S}{\partial z^*_{ph}} - i \frac{\partial^2 S}{\partial R_{il} \partial z^*_{ph}} \right) \dot{z}^*_{ph} \right]. \tag{4.42}
$$
The two terms containing the second derivatives of the overlap found under the summation over \( j \) and \( k \) each represent the difference of a complex number and its complex conjugate. In general, for a complex number \( c = a + ib \) one finds that \( c - c^* = (a + ib) - (a - ib) = 2ib = 2i\text{Im}(c) \). Likewise, the single derivative terms under the \( j \) and \( k \) summation represent the sum of a complex number and its complex conjugate. Following the previous example, \( c + c^* = (a + ib) + (a - ib) = 2a = 2\text{Re}(c) \).

These identities can be used to further simplify the above equation, yielding

\[
\frac{\partial \langle \mathcal{H} \rangle}{\partial R_{il}} = \sum_{jk} \left\{ \left[ 2\text{Re} \left( \frac{\partial S}{\partial R_{il}} \right) P_{jk} - P_{il} 2\text{Re} \left( \frac{\partial S}{\partial R_{jk}} \right) - 2\text{Im} \left( \frac{\partial^2 S}{\partial R_{il} \partial R_{jk}} \right) \hat{R}_{jk} \right] - \left[ S\delta_{ij,kl} - P_{il} 2\text{Re} \left( \frac{\partial S}{\partial P_{jk}} \right) - 2\text{Im} \left( \frac{\partial^2 S}{\partial R_{il} \partial P_{jk}} \right) \hat{P}_{jk} \right] \right. \\
+ \sum_{\kappa} \left\{ \left[ \left( P_{il} \frac{\partial S}{\partial d_{\kappa}} + i \frac{\partial^2 S}{\partial P_{il} \partial d_{\kappa}} \right) \hat{d}_{\kappa} + \left( P_{il} \frac{\partial S}{\partial d_{\kappa}^*} - i \frac{\partial^2 S}{\partial R_{il} \partial d_{\kappa}^*} \right) \hat{d}_{\kappa}^* \right] \\
+ \sum_{ph} \left[ \left( P_{il} \frac{\partial S}{\partial z_{ph}} + i \frac{\partial^2 S}{\partial P_{il} \partial z_{ph}} \right) \hat{z}_{ph} + \left( P_{il} \frac{\partial S}{\partial z_{ph}^*} - i \frac{\partial^2 S}{\partial R_{il} \partial z_{ph}^*} \right) \hat{z}_{ph}^* \right] \right\} \right\},
\]

which is the final form of the equation of motion for \( q = R \). The above equation of motion can be rewritten as a vector equation by collecting the nuclear Cartesian components (summation of \( j \)) and by combining the \( z \) parameters and expansion coefficients \( d \) into a separate rectangular matrices, \( z \) and \( d \). By introducing the coupling matrices

\[
(C_{zz})_{\alpha\beta} = \frac{\partial^2 S}{\partial z_{\alpha} \partial z_{\beta}}, \quad (C_{zX})_{\beta} = \frac{\partial^2 S}{\partial z_{\beta} \partial X}, \\
(C_{dd})_{\alpha\beta} = \frac{\partial^2 S}{\partial d_{\alpha} \partial d_{\beta}}, \quad (C_{dX})_{\beta} = \frac{\partial^2 S}{\partial d_{\beta} \partial X}, \\
(C_{zd})_{\alpha\beta} = \frac{\partial^2 S}{\partial z_{\alpha} \partial d_{\beta}}, \quad (C_{z})_{\beta} = \frac{\partial S}{\partial z_{\beta}}, \\
C_X = 2\text{Re} \left( \frac{\partial S}{\partial X} \right), \quad C_{XY} = -2\text{Im} \left( \frac{\partial^2 S}{\partial X \partial Y} \right) \bigg|_{X' \to X, \ Y' \to Y}.
\]
where \(X, Y \in \{R, P\}\), Equation (4.43) can be written in the vector form

\[
\nabla_{R_i}(\mathcal{H}) = \sum_k \left\{ [C_{R_k} P_k - P_k C_{R_k} + C_{R_k R_k}] \dot{R}_k + \left[ S1 - P_k C_{P_k} + C_{R_k R_k} \right] \ddot{P}_k \right\} \\
+ \left[ P_k C_z + i C^T_{z R_k} \right] \dot{z} + \left[ P_k C_Z - i C^T_{z R_k} \right] \dot{Z}^* + \left[ P_k C_d + i C^T_{d R_k} \right] \dot{d} \\
+ \left[ P_k C_d - i C^T_{d R_k} \right] \dot{d}^*.
\]

(4.44)

The term \(1\) in the above vector equation is the unit matrix of appropriate dimension.

Following the same derivation schema as just shown the remaining five equations of motion can be derived. When \(q = P\) one obtains,

\[
\nabla_{P_i}(\mathcal{H}) = \sum_k \left\{ \left[ S1 + C_{P_k} P_k + C_{P_k R_k} \right] \dot{R}_k + C_{P_k R_k} \dot{P}_k \right\} \\
+ i C^T_{z P_k} \dot{z} - i C^T_{z P_k} \dot{Z}^* + i C^T_{d P_k} \dot{d} - i C^T_{d P_k} \dot{d}^*.
\]

(4.45)

When \(q = z\), one obtains

\[
\frac{\partial \langle \mathcal{H} \rangle}{\partial z} = \sum_k \left\{ \left[ C^*_z P_k - i C^*_z R_k \right] \dot{R}_k - i C^*_z \dot{P}_k \right\} - i C^*_z \dot{z}^* - i C^*_z \dot{d}^*. \]

(4.46)

When \(q = z^*\), one obtains

\[
\frac{\partial \langle \mathcal{H} \rangle}{\partial z^*} = \sum_k \left\{ \left[ C_z P_k + i C_{z R_k} \right] \dot{R}_k + i C_{z P_k} \dot{P}_k \right\} + i C_{z z} \dot{z} + i C_{z d} \dot{d}. \]

(4.47)

When \(q = d\), one obtains

\[
\frac{\partial \langle \mathcal{H} \rangle}{\partial d} = \sum_k \left\{ \left[ C^*_d - i C^*_d R_k \right] \dot{R}_k - i C^*_d \dot{P}_k \right\} - i C^*_d \dot{z}^* - i C^*_d \dot{d}^*. \]

(4.48)

Finally, when \(q = d^*\), one obtains

\[
\frac{\partial \langle \mathcal{H} \rangle}{\partial d^*} = \sum_k \left\{ \left[ C_d P_k + i C_{d R_k} \right] \dot{R}_k + i C_{d P_k} \dot{P}_k \right\} + i C^T_{d d} \dot{z} + i C_{d d} \dot{d}. \]

(4.49)

By combining Equations (4.44) - (4.49) the VHF equations of motion can now be represented as one grand matrix equation of the form given in Equation (4.50), found on the following page.
\[
\begin{bmatrix}
  iC_{z\z} & 0 & C_z P + iC_{zR} & iC_{zP} & iC_{zd} & 0 \\
  0 & -iC_{z\z}^* & C_z^* P - iC_{zR}^* & -iC_{zP}^* & 0 & -iC_{zd}^* \\
  PC_z^* + iC_{zR}^T & PC_z - iC_{zR}^T & C_{RP} - PC_R + C_{RR} & S1 - PC_P + C_{RP} & PC_d^* + iC_{dR}^T & PC_d - iC_{dR}^T \\
  iC_{zP}^T & -iC_{zP}^T & S1 + C_{P} P + C_{PR} & C_{PP} & iC_{dP}^T & -iC_{dP}^T \\
  iC_{zd}^T & 0 & C_d P + iC_{dR} & iC_{dP} & iC_{dd} & 0 \\
  0 & -iC_{zd}^T & C_d^* - iC_{dR}^* & -iC_{dP}^* & 0 & -iC_{dd}^* 
\end{bmatrix}
\]
\[
\begin{bmatrix}
  \dot{z} \\
  \dot{z}^* \\
  \dot{\mathbf{R}} \\
  \dot{\mathbf{P}} \\
  \dot{d} \\
  \dot{d}^* 
\end{bmatrix} = \begin{bmatrix}
  \frac{\partial \mathcal{H}}{\partial z^*} \\
  \frac{\partial \mathcal{H}}{\partial z} \\
  \frac{\partial \mathcal{H}}{\partial \mathbf{R}} \\
  \frac{\partial \mathcal{H}}{\partial \mathbf{P}} \\
  \frac{\partial \mathcal{H}}{\partial d^*} \\
  \frac{\partial \mathcal{H}}{\partial d} 
\end{bmatrix}
\quad \text{(4.50)}
Some very striking similarities between the END equations of motion and Hamilton’s equations of motion are immediately obtained. First, if one represents the matrix in Equation (4.50) as $C$, and represents the left- and right-hand side vectors as $\dot{\zeta}$ and $\frac{\partial E}{\partial \zeta}$, respectively, and if $C^{-1}$ is assumed to exist, then Equation (4.50) can be inverted to the form

$$\dot{\zeta} = C^{-1} \frac{\partial E}{\partial \zeta}$$

(4.51)

which is analogous to the symplectic form of Hamilton’s equations [74]. Furthermore, a generalized Poisson bracket for any two differentiable functions of the dynamical variables can be introduced in this symplectic form,

$$\{f(\zeta), g(\zeta)\} = \left[ \frac{\partial f}{\partial \zeta} \right]^T C^{-1} \left[ \frac{\partial g}{\partial \zeta^*} \right].$$

(4.52)

From this and the general symplectic form of the equations of motion, it is easy to verify that the time-evolution of the dynamical variable can be expressed using the generalized Poisson bracket,

$$\dot{\zeta} = \{\zeta, E\},$$

(4.53)

indicating that the dynamics are governed by Hamilton-like equations.

4.3.2 Evaluating the Equations of Motion

The END equations of motion given in Equation (4.50) contain 34 different sub-blocks that each depend directly upon various derivatives of the electronic overlap and the expectation value of the Hamiltonian operator. In this section, these derivatives will be explicitly evaluated. First, one must recall that the electronic state vector takes the form

$$|\zeta\rangle = \sum_{\kappa} d_\kappa |D_\kappa\rangle.$$  

(4.54)
Thus, the electronic overlap has the form

\[ S = \sum_{\kappa \lambda} d^*_\kappa d_\lambda D_{\kappa \lambda}, \]  

(4.55)

where

\[ D_{\kappa \lambda} = \det \left\{ J^\dagger_\kappa \left( I^* \cdot z^\dagger \right) \Delta \left( I^* \atop z \right) J_\lambda \right\} \]

= \det \left\{ J^\dagger_\kappa \left( \Delta^* + z^\dagger \Delta^\top + \Delta^\top z + z^\dagger \Delta^\circ z \right) J_\lambda \right\} \]

(4.56)

= \det \left\{ A^\star_{\kappa \lambda} \right\},

where \( \Delta \) is the overlap of the atomic basis.

It will be helpful to introduce some auxiliary expressions that will allow for simplification of the derivative expressions. First, the one-electron density matrix (the one-density) can be introduced. The one-density can be partitioned according to configurations. The building blocks of the one-density are the matrices \( \Gamma_{\kappa \lambda} \) of the form

\[ \Gamma_{\kappa \lambda} = \left( \begin{array}{c} I^* \\ z \end{array} \right) J_\lambda A^{\star -1}_{\kappa \lambda} J^\dagger_\kappa \left( \begin{array}{c} I^* \\ z^\dagger \end{array} \right), \]  

(4.57)

from which the one-density can be constructed. The one-density has the form

\[ \Gamma = \frac{1}{S} \sum_{\kappa \lambda} d^*_\kappa d_\lambda D_{\kappa \lambda} \Gamma_{\kappa \lambda}. \]  

(4.58)

The derivatives of the electronic overlap with respect to the nuclear coordinates and momenta will contain terms that have the general form

\[ A_{\kappa \lambda, k} = \text{Tr} \left( \Gamma_{\kappa \lambda} \nabla^0_X \Delta \right) \]  

(4.59)

\[ B_{\kappa \lambda, kl} = \text{Tr} \left( \Gamma_{\kappa \lambda} \nabla^0_X \nabla^0_X \Delta \right) \]  

(4.60)

\[ F_{\kappa \lambda, kl} = \text{Tr} \left( \Gamma_{\kappa \lambda} \nabla^0_X \Delta \nabla^0_X \Delta \right) \]  

(4.61)
The derivatives of the overlap with respect to electronic degrees of freedom will
generate expressions that utilize the following expressions

\[ Q^\kappa_\gamma = [\Delta^\gamma + \Delta^\gamma \mathbf{J}] J_\kappa \]

\[ Q^\gamma_\kappa = Q^\gamma_\kappa \mathbf{J}^\dagger \left[ \Delta^\gamma + z^\dagger \Delta^\gamma \right] \]

\[ P^\gamma_{\kappa\lambda} = Q^\gamma_{\lambda} \Lambda_{\kappa\lambda}^{\ast -1} \]

\[ P^\kappa_{\kappa\lambda} = \Lambda_{\kappa\lambda}^{\ast -1} Q^\kappa_\gamma \]

\[ R^\kappa_{\kappa\lambda} = \Delta^\kappa - Q^\kappa_{\lambda} \Lambda_{\kappa\lambda}^{\ast -1} Q^\kappa_\gamma \]

\[ V_{\kappa\lambda} = \left( \begin{array}{c} 0 \end{array} \right) - Q^\gamma_{\lambda} \Lambda_{\kappa\lambda}^{\ast -1} J^\dagger \left( \begin{array}{c} \mathbf{I} \end{array} \right) \left( \begin{array}{c} \mathbf{z} \end{array} \right) \]

\[ W_{\kappa\lambda} = \left( \begin{array}{c} \mathbf{I} \\mathbf{z} \end{array} \right) J_{\lambda} \Lambda_{\kappa\lambda}^{\ast -1} \]

\[ U^\gamma_{\kappa\lambda} = V_{\kappa\lambda} \nabla_{\kappa\lambda}^\dagger W_{\kappa\lambda} \]

As with the application of the Euler-Lagrange equations, the derivations of the
individual terms for the symplectic form are tedious. For this reason, any repetition
will be avoided. One can begin with the first derivatives of the electronic overlap.
Specifically, if one takes the derivative with respect to \( z_{ph}^\ast \), one finds that

\[ (C_z)_{ph} = \frac{\partial S}{\partial z_{ph}^\ast} \]

\[ = \sum_{\kappa\lambda} d^\ast_{\kappa} d_{\lambda} \frac{\partial \det \{ \Lambda_{\kappa\lambda}^\ast \}}{\partial z_{ph}^\ast} \]
Now, the determinant of any non-singular $N \times N$ matrix, $M$, can be expressed using the Laplace expansion [77],

$$\det \{M\} = \frac{1}{N} \sum_{i,j} M_{ij} \text{ad}_{ji}(M),$$

(4.71)

where $\text{ad}_{ji}(M)$ is the $j,i$th element of the adjoint matrix. Thus,

$$(C_z)_{ph} = \sum_{\kappa\lambda} d_{\kappa}^* d_{\lambda} \frac{1}{K_2} \sum_{f,g} \frac{\partial (\mathbf{A}_{\kappa\lambda}^*)_{fg}}{\partial z_{ph}^*} \text{ad}_{gf}(\mathbf{A}_{\kappa\lambda}^*).$$

(4.72)

In the above equation, the derivative of the adjoint is not required. This is because the adjoint is the transpose of the minors of the matrix in question. Since the minor of a given matrix is the determinant of the sub-matrix generated when the $i$th column and the $j$th row are removed, $\text{ad}_{ji}(\mathbf{A}_{\kappa\lambda})$ does not depend on $(\mathbf{A}_{\kappa\lambda})_{ij}$. At this point, one can consider only the derivative,

$$\frac{\partial (\mathbf{A}_{\kappa\lambda}^*)_{fg}}{\partial z_{ph}^*} = \frac{\partial}{\partial z_{ph}^*} (J_{\kappa}^\dagger [\Delta^\dagger + z^\dagger \Delta^\dagger + \Delta^\dagger z + z^\dagger \Delta^\dagger z] J_{\lambda})_{fg}$$

$$= \frac{\partial}{\partial z_{ph}^*} \left[ (J_{\kappa}^\dagger \Delta^\dagger J_{\lambda})_{fg} + \sum_{r} (J_{\kappa}^\dagger z)_{rf} (\Delta^\dagger J_{\lambda})_{rg} \right. + \sum_{s} (J_{\kappa}^\dagger \Delta^\dagger J_{\lambda})_{fs} (zJ_{\lambda})_{sg} + \sum_{r} (J_{\kappa}^\dagger z)_{rf} (\Delta^\dagger zJ_{\lambda})_{rg} \right] + \sum_{r} (J_{\kappa}^\dagger \Delta^\dagger J_{\lambda})_{fg} (\Delta^\dagger zJ_{\lambda})_{rg}.$$

(4.73)

At this point, it must be recognized that the derivative of the first and third term inside the brackets will be zero. Furthermore, as the $J_{\kappa}^\dagger$ selects the Thouless coefficients for the $\kappa$ configuration, it is only only meaningful to differentiate with respect to that configuration. Therefore, the $\kappa$ configuration is implied and the $J_{\kappa}$ matrix is now redundant. Thus,

$$\frac{\partial (\mathbf{A}_{\kappa\lambda}^*)_{fg}}{\partial z_{ph}^*} = \left[ \sum_{r} (\Delta^\dagger J_{\lambda})_{rg} \delta_{rp} \delta_{fh} + \sum_{r} (\Delta^\dagger zJ_{\lambda})_{rg} \delta_{rp} \delta_{fh} \right]$$

(4.74)

$$= ([\Delta^\dagger + \Delta^\dagger z] J_{\lambda})_{pg} \delta_{fh}.$$
Thus,

\[
\begin{align*}
(C_z)_{ph} &= \sum_{\kappa\lambda} d_\kappa^* d_\lambda \frac{1}{K^2} \sum_{f,g} (\Delta^f + \Delta^g z J_\lambda)_{pg} \text{ad}_{gf}(\Lambda_{\kappa\lambda}^*) \delta_{fh}.
\end{align*}
\] (4.75)

Now, employing the inverse of Equation (4.71), one finds that

\[
\text{ad}_{ij}(\Lambda_{\kappa\lambda}^*) = K_2 D_{\kappa\lambda} (\Lambda_{\kappa\lambda}^{*-1})_{ij},
\] (4.76)

and therefore,

\[
\begin{align*}
(C_z)_{ph} &= \sum_{\kappa\lambda} d_\kappa^* d_\lambda D_{\kappa\lambda} \sum_{f,g} (\Delta^f + \Delta^g z J_\lambda)_{pg} (\Lambda_{\kappa\lambda}^{*-1})_{gf} \delta_{fh} \\
&= \sum_{\kappa\lambda} d_\kappa^* d_\lambda D_{\kappa\lambda} (P_{\kappa\lambda}^\vee)_{ph}.
\end{align*}
\] (4.77)

Repeating the process with $z_{ph}$ results in the expression

\[
(C^*)_{ph} = \sum_{\kappa\lambda} d_\kappa^* d_\lambda D_{\kappa\lambda} (P_{\kappa\lambda}^\geq)_{hp},
\] (4.78)

which is the Hermitian conjugate of the derivative with respect to $z^*$, as would be expected from the symplectic structure.

As the determinant does not depend upon $d$ or $d^*$, the derivatives of the overlap with respect to the configuration expansion coefficients are trivial:

\[
\begin{align*}
(C_d)_\nu &= \frac{\partial}{\partial d_\nu} \sum_{\kappa\lambda} d_\kappa^* d_\lambda D_{\kappa\lambda} \\
&= \sum_\lambda d_\lambda D_{\nu\lambda},
\end{align*}
\] (4.79)

and

\[
\begin{align*}
(C_d^*)_\nu &= \frac{\partial}{\partial d_\nu} \sum_{\kappa\lambda} d_\kappa^* d_\lambda D_{\kappa\lambda} \\
&= \sum_\kappa d_\kappa^* D_{\kappa\nu}.
\end{align*}
\] (4.80)

The dependence of the determinant upon the nuclear degrees of freedom arises in the overlap of the atomic basis only. However, it is important that one be specific
as to whether the derivative is being taken with respect to the primed (bra) or unprimed (ket) nuclear degrees of freedom, as the derivatives are taken before the limits of \( R' \to R \) and \( P' \to P \) are imposed. To specify which derivative is being taken, the nuclear symbol will be superscripted with either a bra or a ket. The derivative with respect to the nuclear degrees of freedom (symbolized as \( X \) or \( Y \)) involves application of the chain rule to the determinant

\[
\nabla_X^\dagger D_{\kappa\lambda} = \sum_{f,g} \frac{\partial \det \{ \Lambda_{\kappa\lambda}^\bullet \} \partial (\Lambda_{\kappa\lambda}^\bullet)_{fg}}{\partial (\Lambda_{\kappa\lambda}^\bullet)_{fg}} \frac{\partial (\Lambda_{\kappa\lambda}^\bullet)_{fg}}{\partial X_k} \\
= \sum_{f,g} \frac{1}{K^2} \sum_{h,i} \frac{\partial (\Lambda_{\kappa\lambda}^\bullet)_{hi}}{\partial (\Lambda_{\kappa\lambda}^\bullet)_{fg}} \text{ad}_{ih} (\Lambda_{\kappa\lambda}^\bullet) \frac{\partial (\Lambda_{\kappa\lambda}^\bullet)_{fg}}{\partial X_k} \\
= \sum_{f,g} \frac{1}{K^2} \text{ad}_{gf} (\Lambda_{\kappa\lambda}^\bullet) \frac{\partial (\Lambda_{\kappa\lambda}^\bullet)_{fg}}{\partial X_k} \\
= D_{\kappa\lambda} \sum_{f,g} (\Lambda_{\kappa\lambda}^\bullet^{-1})_{gf} \left[ J^\dagger \left( \begin{array}{c} I^\bullet \\ z^\dagger \end{array} \right) \nabla_X^\dagger \Delta \left( \begin{array}{c} I^\bullet \\ z \end{array} \right) \right]_{fg} \\
= D_{\kappa\lambda} \text{Tr} \left[ \Lambda_{\kappa\lambda}^\bullet^{-1} J^\dagger \left( \begin{array}{c} I^\bullet \\ z^\dagger \end{array} \right) \nabla_X^\dagger \Delta \left( \begin{array}{c} I^\bullet \\ z \end{array} \right) \right] \right] \\
= D_{\kappa\lambda} A_{\kappa\lambda,k}.
\]

Thus, it becomes clear that

\[
(C_X)_k = \nabla_X^\dagger \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} D_{\kappa\lambda} \\
= \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} D_{\kappa\lambda} A_{\kappa\lambda,k},
\]

(4.82)

and

\[
(C_X)_k = \nabla_X^\dagger \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} D_{\kappa\lambda} \\
= \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} D_{\kappa\lambda} A_{\kappa\lambda,k},
\]

(4.83)

where proper attention is given to which derivative is being taken.
At this juncture, the second derivatives of the electronic overlap can be evaluated by direct differentiation of the first derivative terms. The process is very similar to that for the first derivative evaluation, however, in most cases derivatives of the inverse of $\Lambda_{\kappa\lambda}^*$ are required. Again, the chain rule can be applied, resulting in the general form

$$
\frac{\partial (\Lambda_{\kappa\lambda}^{\bullet-1})}{\partial \zeta} = - \sum_{ij} (\Lambda_{\kappa\lambda}^{\bullet-1})_{fi} \frac{\partial (\Lambda_{\kappa\lambda}^{\bullet})_{ij}}{\partial \zeta} (\Lambda_{\kappa\lambda}^{\bullet-1})_{jg},
$$

(4.84)

for the selected dynamical degrees of freedom. The evaluation of the derivatives of $\Lambda_{\kappa\lambda}^{\bullet-1}$ will not be repeated here, as they depend upon expression that have previously been derived. The derivative of $\Lambda_{\kappa\lambda}^{\bullet-1}$ have the form

$$
\frac{\partial (\Lambda_{\kappa\lambda}^{\bullet-1})}{\partial z_{ph}} = - (\Lambda_{\kappa\lambda}^{\bullet-1})_{fh} ([\Delta^\gamma + \Delta^\alpha z] J_{\lambda} \Lambda_{\kappa\lambda}^{\bullet-1})_{pg}
$$

(4.85)

and

$$
\frac{\partial (\Lambda_{\kappa\lambda}^{\bullet-1})}{\partial z_{ph}} = - (\Lambda_{\kappa\lambda}^{\bullet-1})_{fh} (\mathbf{P}^{\gamma\lambda}_{\kappa\lambda})_{pg}
$$

(4.86)

for the electronic gradients and

$$
\nabla_{X_k}^{\perp} (\Lambda_{\kappa\lambda}^{\bullet-1})_{fg} = - \left( \Lambda_{\kappa\lambda}^{\bullet-1} J_{\kappa}^\dagger \left( \mathbf{I}^* \ z^\dagger \right) \nabla_{X_k}^{\perp} \Delta \left( \mathbf{I}^* \ z \right) J_{\lambda} \Lambda_{\kappa\lambda}^{\bullet-1} \right)_{fg}
$$

(4.87)

$$
= - (W_{\kappa\lambda}^{\dagger} \nabla_{X_k}^{\perp} W_{\kappa\lambda})_{fg}
$$

and

$$
\nabla_{X_k}^{\perp} (\Lambda_{\kappa\lambda}^{\bullet-1})_{fg} = - \left( \Lambda_{\kappa\lambda}^{\bullet-1} J_{\kappa}^\dagger \left( \mathbf{I}^* \ z^\dagger \right) \nabla_{X_k}^{\perp} \Delta \left( \mathbf{I}^* \ z \right) J_{\lambda} \Lambda_{\kappa\lambda}^{\bullet-1} \right)_{fg}
$$

(4.88)

$$
= - (W_{\kappa\lambda}^{\dagger} \nabla_{X_k}^{\perp} W_{\kappa\lambda})_{fg}
$$
for the nuclear gradients. The derivatives of $\mathbf{A}^{-1}_{\kappa\lambda}$ with respect to the expansion coefficients are all zero.

Using these terms, the second derivatives can now be evaluated. The derivatives with respect to the electronic parameters will be considered first:

\[
(C_{zz})_{qq;ph} = \frac{\partial}{\partial z_{qg}^*} \frac{\partial S}{\partial z_{ph}} \\
= \frac{\partial}{\partial z_{qg}^*} \sum_{\kappa\lambda} d_{\kappa}^* d_{\lambda} D_{\kappa\lambda} \left( \mathbf{A}^{-1}_{\kappa\lambda} \mathbf{J}_{\kappa}^* \left( \mathbf{\Delta}^+ + z^+ \mathbf{\Delta}^o \right) \right)_{hp} \\
= \sum_{\kappa\lambda} d_{\kappa}^* d_{\lambda} D_{\kappa\lambda} \left\{ \left[ (\mathbf{\Delta}^+ + \mathbf{\Delta}^o \mathbf{z}) \mathbf{J}_{\kappa} \mathbf{A}^{-1}_{\kappa\lambda} \right]_{qq} \left[ \mathbf{A}^{-1}_{\kappa\lambda} \mathbf{J}_{\kappa}^* \left( \mathbf{\Delta}^+ + z^+ \mathbf{\Delta}^o \right) \right]_{hp} \\
+ \left[ \mathbf{A}^{-1}_{\kappa\lambda} \right]_{hg} \left[ \mathbf{\Delta}^o - (\mathbf{\Delta}^+ + \mathbf{\Delta}^o \mathbf{z}) \mathbf{J}_{\kappa} \mathbf{A}^{-1}_{\kappa\lambda} \mathbf{J}_{\kappa}^* \left( \mathbf{\Delta}^+ + z^+ \mathbf{\Delta}^o \right) \right]_{qp} \right\} \\
= \sum_{\kappa\lambda} d_{\kappa}^* d_{\lambda} D_{\kappa\lambda} \left\{ (\mathbf{P}^{V}_{\kappa\lambda})_{qg}(\mathbf{P}^{V}_{\kappa\lambda})_{hp} + (\mathbf{A}^{-1}_{\kappa\lambda})_{hg}(\mathbf{R}^{o}_{\kappa\lambda})_{qp} \right\}
\]

and therefore,

\[
(C^*_z)_{qq;ph} = \sum_{\kappa\lambda} d_{\kappa}^* d_{\lambda} D_{\kappa\lambda} \left\{ (\mathbf{P}^{V}_{\kappa\lambda})_{qg}(\mathbf{P}^{V}_{\kappa\lambda})_{ph} + (\mathbf{R}^{o}_{\kappa\lambda})_{pq}(\mathbf{A}^{-1}_{\kappa\lambda})_{gh} \right\}; \quad (4.90)
\]

also

\[
(C_{dd})_{\nu} = \frac{\partial}{\partial d_{\nu}^*} \frac{\partial S}{\partial d_{\mu}} \\
= D_{\nu\mu} \\
\]

and therefore,

\[
(C^*_{dd})_{\nu} = \frac{\partial}{\partial d_{\nu}} \frac{\partial S}{\partial d_{\mu}^*} \\
= D_{\mu\nu}. \quad (4.92)
\]

The derivatives that couple the electronic parameters with the expansion coefficients are performed in the same manner, but the transpose and the Hermitian
conjugate must also be evaluated, such that

\[
(C_{zd})_{qg,\nu} = \frac{\partial}{\partial z_{qg}^*} \frac{\partial S}{\partial d_{\nu}} = \frac{\partial}{\partial z_{qg}^*} \sum_{\kappa} d_{\kappa}^* D_{\kappa\nu} = \sum_{\kappa} d_{\kappa}^* D_{\kappa\nu} (P_{\kappa\nu}^\nu)_{qg} \tag{4.93}
\]

and

\[
(C_{zd}^*)_{qg,\nu} = \frac{\partial}{\partial z_{qg}} \frac{\partial S}{\partial d_{\nu}^*} = \frac{\partial}{\partial z_{qg}} \sum_{\lambda} d_{\lambda} D_{\nu\lambda} = \sum_{\lambda} d_{\lambda} D_{\nu\lambda} (P_{\nu\lambda}^{\nu\lambda})_{qg} \tag{4.94}
\]

and

\[
(C_{zd}^T)_{\mu,ph} = \frac{\partial}{\partial d_{\mu}} \frac{\partial S}{\partial z_{ph}^*} = \frac{\partial}{\partial d_{\mu}} \sum_{\kappa\lambda} d_{\kappa}^* d_{\lambda} D_{\kappa\lambda} (P_{\kappa\lambda}^{\nu\lambda})_{ph} = \sum_{\kappa\lambda} d_{\kappa}^* D_{\kappa\mu} (P_{\kappa\mu}^{\nu\lambda})_{ph} \tag{4.95}
\]

and finally,

\[
(C_{zd}^\dagger)_{\mu,ph} = \frac{\partial}{\partial d_{\mu}^*} \frac{\partial S}{\partial z_{ph}} = \frac{\partial}{\partial d_{\mu}^*} \sum_{\lambda} d_{\kappa}^* d_{\lambda} D_{\kappa\lambda} (P_{\kappa\lambda}^{\nu\lambda})_{ph} = \sum_{\lambda} d_{\lambda} D_{\mu\lambda} (P_{\mu\lambda}^{\nu\lambda})_{ph} \tag{4.96}
\]

It should be noted that the transpose and Hermitian conjugate terms are identical to the two previous derivatives. However, the transpose and Hermitian conjugate terms are maintained in order to emphasize the symplectic structure of the equations of motion.
Using the same procedure, the derivatives that couple the electronic and nuclear degrees of freedom can be evaluated. Firstly,

\[
(C_{zX})_{qq} = \frac{\partial}{\partial z_q} \nabla_{X_k} S
\]

\[
= \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} \left\{ \frac{\partial D_{\kappa\lambda}}{\partial z_{qg}} \text{Tr} \left[ \Lambda^{-1}_{\kappa\lambda} J^\dagger_{\kappa} \left( \mathbf{I}^* \mathbf{z}^\dagger \right) \Delta \left( \mathbf{I}^* \mathbf{z} \right) J_{\lambda} \right] \right. \\
+ D_{\kappa\lambda} \frac{\partial}{\partial z_{qg}} \sum_{f,g} (\Lambda^{-1}_{\kappa\lambda})_{gf} \left[ J^\dagger_{\kappa} \left( \mathbf{I}^* \mathbf{z}^\dagger \right) \Delta \left( \mathbf{I}^* \mathbf{z} \right) J_{\lambda} \right]_{fg} \right\}
\]

\[
= \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} D_{\kappa\lambda} \left\{ \left[ (\Delta^\nu + \Delta^\zeta) J_{\lambda} \Lambda^{-1}_{\kappa\lambda} \right]_{qg} \right. \\
\times \text{Tr} \left[ \Lambda^{-1}_{\kappa\lambda} J^\dagger_{\kappa} \left( \mathbf{I}^* \mathbf{z}^\dagger \right) \Delta \left( \mathbf{I}^* \mathbf{z} \right) J_{\lambda} \right] \\
+ \left\{ \left( \begin{array}{c} 0 \\ \mathbf{I}^\nu \\ \mathbf{I}^\zeta \end{array} \right) - (\Delta^\nu + \Delta^\zeta) J_{\lambda} \Lambda^{-1}_{\kappa\lambda} J^\dagger_{\kappa} \left( \mathbf{I}^* \mathbf{z}^\dagger \right) \right\} \\
\times \nabla_{X_k} \Delta \left( \mathbf{I}^* \mathbf{z} \right) J_{\lambda} \Lambda^{-1}_{\kappa\lambda} \right\} \\
\right.
\]

\[
= \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} D_{\kappa\lambda} \left\{ (\mathbf{P}^\nu_{\kappa\lambda})_{qg} A_{\kappa\lambda,k} + (\mathbf{U}^\nu_{\kappa\lambda})_{qg} \right\} \\
\]

And, by appropriately transposing and conjugating, one finds

\[
(C_{zX})_{ph} = \frac{\partial}{\partial z_{ph}} \nabla_{X_k} S
\]

\[
= \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} \left\{ (\mathbf{P}^\nu_{\kappa\lambda})_{qg} A_{\kappa\lambda,k} + (\mathbf{U}^\nu_{\kappa\lambda})_{qg} \right\} \\
\]

\[
= \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} \left\{ A_{\kappa\lambda,l} (\mathbf{P}^\nu_{\kappa\lambda})_{ph} + (\mathbf{U}^\nu_{\kappa\lambda})_{ph} \right\} \\
\]

\[
= \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} D_{\kappa\lambda} \left\{ A_{\kappa\lambda,l} (\mathbf{P}^\nu_{\kappa\lambda})_{ph} + (\mathbf{U}^\nu_{\kappa\lambda})_{ph} \right\} \\
\]
and, lastly,
\[
\left( \mathbf{C}_{dX}^l \right)_{t,ph} = \nabla_{X_k}^{(l)} \frac{\partial S}{\partial z_{ph}} \\
= \sum_{\kappa,\lambda} d^*_\kappa d_\lambda D_{\kappa,\lambda} \left\{ A_{\kappa,\lambda,k} \left( \mathbf{P}_{k,\lambda}^* \right)_{hp} + \left( \mathbf{U}_{k,\lambda}^* \right)_{hp} \right\}.
\]

(4.100)

Now the second derivative terms involving the nuclear degrees of freedom and the expansion coefficients can be evaluated. The symmetries of the derivatives become more obvious, but each term will be kept explicit to preserve the symplectic structure. Specifically,
\[
\left( \mathbf{C}_{dX}^\mu \right)_{\mu,k} = \frac{\partial}{\partial d^*_\mu} \nabla_{X_k}^{(l)} S \\
= \frac{\partial}{\partial d^*_\mu} \sum_{\kappa,\lambda} d^*_\kappa d_\lambda D_{\kappa,\lambda} \text{Tr} \left[ A_{\kappa,\lambda}^{-1} \mathbf{J}^l_{\kappa,\lambda} \left( \mathbf{I}^* \ z^l \right) \nabla_{X_k}^{(l)} \Delta \left( \mathbf{I}^* \ z^l \right) \mathbf{J}_\lambda \right] \\
= \sum_{\lambda} d_\lambda D_{\mu,\lambda} A_{\mu,\lambda,k},
\]

(4.101)

and
\[
\left( \mathbf{C}_{dX}^*_{\mu,k} \right)_{\mu,k} = \frac{\partial}{\partial d^*_\mu} \nabla_{X_k}^{(l)} S \\
= \sum_{\kappa} d^*_\kappa D_{\kappa,\mu} A_{\kappa,\mu,k},
\]

(4.102)

and
\[
\left( \mathbf{C}_{dX}^{\nu,l} \right)_{\nu,l} = \nabla_{X_i}^{(l)} \frac{\partial S}{\partial d^*_\nu} \\
= \sum_{\lambda} d_\lambda D_{\nu,\lambda} A_{\nu,\lambda,l},
\]

(4.103)

and finally,
\[
\left( \mathbf{C}_{dX}^l \right)_{\nu,l} = \nabla_{X_i}^{(l)} \frac{\partial S}{\partial d^*_\nu} \\
= \sum_{\kappa} d^*_\kappa D_{\kappa,\nu} A_{\kappa,\nu,l}.
\]

(4.104)
The final components of the symplectic form are the second derivatives with respect to the nuclear parameters only. These four expressions can be generalized by a single term,

$$(C_{XY})_{i,k} = \nabla_{X_i}^{(l)} \nabla_{Y_k}^{(l)} S$$

$$= \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} D_{\kappa\lambda} \left\{ \text{Tr} \left[ \Lambda^{-1}_{\kappa\lambda} J^\dagger_{\kappa} \left( I^* \ z^\dagger \right) \Delta \left( I^* \ z \right) J_{\lambda} \right] \right. \right.$$  

$$\times \text{Tr} \left[ \Lambda^{-1}_{\kappa\lambda} J^\dagger_{\kappa} \left( I^* \ z^\dagger \right) \Delta \left( I^* \ z \right) J_{\lambda} \right]$$

$$+ \text{Tr} \left[ \Lambda^{-1}_{\kappa\lambda} J^\dagger_{\kappa} \left( I^* \ z^\dagger \right) \Delta \left( I^* \ z \right) J_{\lambda} \Lambda^{-1}_{\kappa\lambda} \right]$$

$$- \left( I^* \ z^\dagger \right) \Delta \left( I^* \ z \right) J_{\lambda} \Lambda^{-1}_{\kappa\lambda}$$

$$\times J^\dagger_{\kappa} \left( I^* \ z^\dagger \right) \Delta \left( I^* \ z \right) J_{\lambda} \} \right\}$$

$$(4.105)$$

$$= \sum_{\kappa\lambda} d^*_{\kappa} d_{\lambda} D_{\kappa\lambda} \left\{ A_{\kappa\lambda,i} A_{\kappa\lambda,k} + B_{\kappa\lambda,ik} - F_{\kappa\lambda,ik} \right\} .$$

Having completed the evaluation of the left-hand side of the VHF equation of motion, one can now investigate the derivatives found on the right-hand side. These terms are the derivatives of the expectation value of the Hamiltonian operator with respect to the dynamical variables, and are analogous to the dynamical forces experienced by the system. In an orthonormal basis of spin orbitals, \( \{ \psi_i \} \), the full ab initio molecular Hamiltonian can be written in second quantization in the form \[6\]

$$\mathcal{H} = \sum_{k=1}^{N_{\text{at}}} \left\{ \frac{P_k^2}{2M_k} + \sum_{l=k+1}^{N_{\text{at}}} \frac{Z_k Z_l}{|R_k - R_l|} \right\} + \sum_{i,j=1}^{K} h_{ij} b_i^\dagger b_j + \frac{1}{4} \sum_{i,j,k,l=1}^{K} V_{ijkl} b_i^\dagger b_j^\dagger b_k b_l . \quad (4.106)$$
In the above expression, \( Z_k \) is the atomic number of the \( k \)th nucleus, \( h \) is the Hermitian one-electron integral matrix with elements
\[
h_{ij} = \int \psi_i^*(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 - \sum_{k=1}^{N_{\text{at}}} \frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|} \right) \psi_j(\mathbf{r}) d^3r,
\]
and \( V \) represents the anti-symmetrized two-electron integrals
\[
V_{ijkl} = \langle ij|kl \rangle - \langle ij|lk \rangle,
\]
where
\[
\langle ij|kl \rangle = \int \frac{\psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \psi_k(\mathbf{r}_1) \psi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}.
\]
From this, it becomes clear that the molecular Hamiltonian can be partitioned in to a zero-electron component,
\[
\mathcal{H}^{(0)} = \sum_{k=1}^{N_{\text{at}}} \left\{ \frac{P_k^2}{2M_k} + \sum_{l=k+1}^{N_{\text{at}}} \frac{Z_l Z_k}{|\mathbf{R}_k - \mathbf{R}_l|} \right\},
\]
a one-electron component,
\[
\mathcal{H}^{(1)} = \sum_{i,j=1}^{K} h_{ij} b_i^\dagger b_j,
\]
and a two-electron component,
\[
\mathcal{H}^{(2)} = \frac{1}{4} \sum_{i,j,k,l=1}^{K} V_{ijkl} b_i^\dagger b_j^\dagger b_k b_l.
\]
Thus, the expectation value of the Hamiltonian becomes
\[
\langle \mathcal{H} \rangle = \sum_{\kappa \lambda} d_{\kappa}^* d_{\lambda} \langle D_\kappa | \mathcal{H} | D_\lambda \rangle = \sum_{\kappa \lambda} d_{\kappa}^* d_{\lambda} \left[ \mathcal{H}_{\kappa \lambda}^{(0)} + \mathcal{H}_{\kappa \lambda}^{(1)} + \mathcal{H}_{\kappa \lambda}^{(2)} \right],
\]
where \( \mathcal{H}_{\kappa \lambda}^{(0)} = \langle D_\kappa | \mathcal{H}^{(0)} | D_\lambda \rangle \) and so forth. From this, it can be seen that the derivatives of the expectation value of the Hamiltonian operator with respect to the
expansion coefficients are trivial to evaluate. Particularly,

\[ \frac{\partial \langle \mathcal{H} \rangle}{\partial d \nu} = \sum \lambda d \lambda [ \mathcal{H}^{(0)}_{\nu \lambda} + \mathcal{H}^{(1)}_{\nu \lambda} + \mathcal{H}^{(2)}_{\nu \lambda}] \]  

(4.114)

and

\[ \frac{\partial \langle \mathcal{H} \rangle}{\partial d \nu} = \sum \kappa d \kappa [ \mathcal{H}^{(0)}_{\kappa \nu} + \mathcal{H}^{(1)}_{\kappa \nu} + \mathcal{H}^{(2)}_{\kappa \nu}] . \]  

(4.115)

To evaluate the remaining derivatives it is convenient to rewrite the one- and two-electron components of the expectation value in terms of the blocks of the one- and two-density matrices. The blocks of the one-density were introduced previously, and the blocks of the two-density can be constructed as [6]

\[ \left( \Gamma^{(2)}_{\kappa \lambda} \right)_{\ i j, k l} = (\Gamma_{\kappa \lambda})_{k i} (\Gamma_{\kappa \lambda})_{l j} - (\Gamma_{\kappa \lambda})_{k j} (\Gamma_{\kappa \lambda})_{l i} . \]  

(4.116)

The one- and two-electron components of the expectation value now become [3]

\[ \mathcal{H}^{(1)}_{\kappa \lambda} = \text{Tr} [h \Gamma_{\kappa \lambda}] \]  

(4.117)

and

\[ \mathcal{H}^{(1)}_{\kappa \lambda} = \frac{1}{4} \text{Tr} \left[ V \Gamma^{(2)}_{\kappa \lambda} \right] . \]  

(4.118)

Furthermore, as the zero-electron component does not operate on the elements of the electronic space, one can write

\[ \mathcal{H}^{(0)}_{\kappa \lambda} = \mathcal{H}^{(0)} \Delta_{\kappa \lambda}. \]  

(4.119)

At this point, it becomes clear that the dependence of the expectation value of the Hamiltonian on the Thouless coefficients and the nuclear parameters occurs ultimately in the blocks of the one-density. It becomes necessary, then, to evaluate differentiate the one-density with respect to the electronic parameters and the nuclear parameters.

Investigation of the one-density block given in Equation (4.57) clearly indicates that there is no dependence upon the expansion coefficients and, as a consequence,
the derivatives with respect to \(d\) and \(d^*\) are both zero. The derivatives of the one-density block can be taken with respect to the Thouless coefficients, with the results that

\[
\frac{\partial (\Gamma_{\kappa\lambda})_{ij}}{\partial z_{ph}^*} = \sum_r \left[ \left( \begin{array}{c} \mathbf{I}^* \\ \mathbf{z} \end{array} \right) \mathbf{J}_\lambda \right] \frac{\partial}{\partial z_{ph}^*} \left[ \Lambda_{\kappa\lambda}^{-1} J^\dagger_\kappa \left( \begin{array}{c} \mathbf{I}^* \\ \mathbf{z}^\dagger \end{array} \right) \right]_{rj}
\]

\[
= \left[ \left( \begin{array}{c} \mathbf{I}^* \\ \mathbf{z} \end{array} \right) \mathbf{J}_\lambda \Lambda_{\kappa\lambda}^{-1} \right]_{ijh}
\times \left[ \left( \begin{array}{cc} 0 & \mathbf{I}^\circ \end{array} \right) - (\Delta^\vee + \Delta^\circ \mathbf{z}) \mathbf{J}_\lambda \Lambda_{\kappa\lambda}^{-1} J^\dagger_\kappa \left( \begin{array}{c} \mathbf{I}^\circ \\ \mathbf{z}^\dagger \end{array} \right) \right]_{pj}
\]

\[
= \left[ \mathbf{W}_{\kappa\lambda} \right]_{ijh} \left[ \mathbf{V}_{\kappa\lambda} \right]_{pj}
\]

and

\[
\frac{\partial (\Gamma_{\kappa\lambda})_{ij}}{\partial z_{ph}} = \sum_r \frac{\partial}{\partial z_{ph}^*} \left[ \left( \begin{array}{c} \mathbf{I}^* \\ \mathbf{z} \end{array} \right) \mathbf{J}_\lambda \Lambda_{\kappa\lambda}^{-1} \right]_{ir}
\times \left[ \left( \begin{array}{c} \mathbf{I}^\circ \\ \mathbf{z}^\dagger \end{array} \right) \mathbf{J}_\kappa \right]_{rj}
\]

\[
= \left[ \mathbf{V}_{\kappa\lambda}^\dagger \right]_{jp} \left[ \mathbf{W}_{\kappa\lambda}^\dagger \right]_{hi}.
\]

The derivatives with respect to the nuclear coordinates can be similarly evaluated with the result that

\[
\nabla_{X_k} (\Gamma_{\kappa\lambda})_{ij} = \sum_{rs} \left[ \left( \begin{array}{c} \mathbf{I}^* \\ \mathbf{z} \end{array} \right) \mathbf{J}_\lambda \right] \nabla_{X_k} \left( \Lambda_{\kappa\lambda}^{-1} \right)_{rs} \left[ \left( \begin{array}{c} \mathbf{I}^* \\ \mathbf{z}^\dagger \end{array} \right) \mathbf{J}_\kappa \right]_{sij}
\]

\[
= - \left[ \left( \begin{array}{c} \mathbf{I}^* \\ \mathbf{z} \end{array} \right) \mathbf{J}_\lambda \Lambda_{\kappa\lambda}^{-1} J^\dagger_\kappa \left( \begin{array}{c} \mathbf{I}^* \\ \mathbf{z}^\dagger \end{array} \right) \nabla_{X_k} \Delta \right]
\times \left[ \left( \begin{array}{c} \mathbf{I}^* \\ \mathbf{z} \end{array} \right) \mathbf{J}_\lambda \Lambda_{\kappa\lambda}^{-1} J^\dagger_\kappa \left( \begin{array}{c} \mathbf{I}^* \\ \mathbf{z}^\dagger \end{array} \right) \right]_{ij}
\]

\[
= - \left[ \Gamma_{\kappa\lambda} \nabla_{X_k} \Delta \Gamma_{\kappa\lambda} \right]_{ij}.
\]
The previous expressions for the derivatives of the one-density block can now be employed in the evaluation of the expectation value of the Hamiltonian. Starting with the electronic degrees of freedom, one finds that

\[
\frac{\partial \mathcal{H}^{(0)}_{\kappa\lambda}}{\partial z^{*}_{ph}} = \mathcal{H}^{(0)} \frac{\partial D_{\kappa\lambda}}{\partial z^{*}_{ph}} = \mathcal{H}^{(0)} \Delta_{\kappa\lambda} \left( \left[ \Delta^\upsilon + \Delta^\circ z \right] J_\lambda \Lambda_{\kappa\lambda}^{-1} \right)_{ph} = \mathcal{H}^{(0)}_{\kappa\lambda} (P_{\kappa\lambda}^{\upsilon})_{ph}
\]

and

\[
\frac{\partial \mathcal{H}^{(1)}_{\kappa\lambda}}{\partial z^{*}_{ph}} = \sum_{ij} h_{ij} \frac{\partial (\Gamma_{\kappa\lambda})_{ji}}{\partial z^{*}_{ph}} = \sum_{ij} h_{ij} [W_{\kappa\lambda}]_{jh} [V_{\kappa\lambda}]_{pi} = \sum_{ij} [V_{\kappa\lambda}]_{pi} h_{ij} [W_{\kappa\lambda}]_{jh} = [V_{\kappa\lambda} h W_{\kappa\lambda}]_{ph}.
\]

To evaluate the derivative of the two-electron component, one must recall that (assuming that ETFs are not included) real-valued basis functions are employed in END. Therefore, the two-electron integral term \((V)\) will be hermitian with respect to the exchange of any sets of electronic indices. However, any terms involving the one-density or its derivatives are still anti-symmetric, requiring bookkeeping for the
signs. Thus,

\[
\frac{\partial \mathcal{H}^{(2)}}{\partial z_{\text{ph}}^*} = \frac{1}{4} \sum_{ijkl} V_{ik;jl} \frac{\partial}{\partial z_{\text{ph}}^*} \left[ (\Gamma_{\kappa\lambda})_{ji} (\Gamma_{\kappa\lambda})_{lk} - (\Gamma_{\kappa\lambda})_{jk} (\Gamma_{\kappa\lambda})_{il} \right]
\]

\[= \frac{1}{4} \sum_{ijkl} V_{ik;jl} \left[ [W_{\kappa\lambda}]_{jh} [V_{\kappa\lambda}]_{pi} (\Gamma_{\kappa\lambda})_{lk} + (\Gamma_{\kappa\lambda})_{ji} [W_{\kappa\lambda}]_{lh} [V_{\kappa\lambda}]_{pk} \\
- [W_{\kappa\lambda}]_{jh} [V_{\kappa\lambda}]_{pk} (\Gamma_{\kappa\lambda})_{li} - (\Gamma_{\kappa\lambda})_{jk} [W_{\kappa\lambda}]_{lh} [V_{\kappa\lambda}]_{pi} \right] \] (4.125)

\[= \frac{1}{2} \sum_{ijkl} V_{ik;jl} \left[ [W_{\kappa\lambda}]_{jh} [V_{\kappa\lambda}]_{pi} (\Gamma_{\kappa\lambda})_{lk} - (\Gamma_{\kappa\lambda})_{jk} [W_{\kappa\lambda}]_{lh} [V_{\kappa\lambda}]_{pi} \right]
\]

\[= \sum_{ijkl} V_{ik;jl} [W_{\kappa\lambda}]_{jh} [V_{\kappa\lambda}]_{pi} (\Gamma_{\kappa\lambda})_{lk} \]

where the \(i\) and \(k\) indices were exchanged in the second and third terms in the second step and the \(l\) and \(j\) indices were exchanged in the third step. Now,

\[
\frac{\partial \mathcal{H}^{(2)}}{\partial z_{\text{ph}}^*} = \sum_{ij} [V_{\kappa\lambda}]_{pi} \sum_{lk} V_{ik;jl} (\Gamma_{\kappa\lambda})_{lk} [W_{\kappa\lambda}]_{jh}
\]

\[= \sum_{ij} [V_{\kappa\lambda}]_{pi} [\text{Tr} (V\Gamma_{\kappa\lambda})_{b}]_{ij} [W_{\kappa\lambda}]_{jh} \] (4.126)

\[= [V_{\kappa\lambda} \text{Tr} (V\Gamma_{\kappa\lambda})_{b} W_{\kappa\lambda}]_{\text{ph}}, \]

where the partial trace has has been utilized,

\[\text{Tr} (V\Gamma_{\kappa\lambda})_{b} = \sum_{lk} V_{ik;jl} (\Gamma_{\kappa\lambda})_{lk}. \] (4.127)

Now, the individual contributions can be summed to yield the derivative of the expectation value of the Hamiltonian with respect to the Thouless parameters,

\[
\frac{\partial \langle \mathcal{H} \rangle}{\partial z_{\text{ph}}^*} = \sum_{\kappa\lambda} d^*_\kappa d_\lambda \left\{ \frac{\partial \mathcal{H}_{\kappa\lambda}^{(0)}}{\partial z_{\text{ph}}^*} + \frac{\partial \mathcal{H}_{\kappa\lambda}^{(1)}}{\partial z_{\text{ph}}^*} + \frac{\partial \mathcal{H}_{\kappa\lambda}^{(2)}}{\partial z_{\text{ph}}^*} \right\}
\]

\[= \sum_{\kappa\lambda} d^*_\kappa d_\lambda \left\{ \mathcal{H}_{\kappa\lambda}^{(0)} (P_{\kappa\lambda})_{\text{ph}} \right. \]

\[+ [V_{\kappa\lambda} h W_{\kappa\lambda}]_{\text{ph}} + [V_{\kappa\lambda} \text{Tr} (V\Gamma_{\kappa\lambda})_{b} W_{\kappa\lambda}]_{\text{ph}} \right\} \]

\[= \sum_{\kappa\lambda} d^*_\kappa d_\lambda \left\{ \mathcal{H}_{\kappa\lambda}^{(0)} P_{\kappa\lambda} + V_{\kappa\lambda} (h + \text{Tr} (V\Gamma_{\kappa\lambda})_{b}) W_{\kappa\lambda} \right\}_{\text{ph}}. \] (4.128)
It should be noted that the term \( h + \text{Tr} \left( V \tau_\alpha \right) \) has the same form as the Fock matrix except that it is evaluated over two different configurations. In the case of a single determinantal reference, this expression reduces to the Fock matrix.

At this point, the derivatives with respect to the nuclear parameters must be evaluated. The zero-electron component of the Hamiltonian contains explicit dependence upon both the nuclear positions and momenta. Therefore, the derivative with respect to each part must be evaluated separately. Both derivatives are simple, and differentiation results in the forms

\[
\nabla_{R_k} \mathcal{H}_{\alpha\lambda}^{(0)} = \nabla_{R_k} D_{\alpha\lambda} \sum_{k=1}^{N_{\text{at}}} \left\{ \frac{P_k^2}{2M_k} + \sum_{l=k+1}^{N_{\text{at}}} \frac{Z_k Z_l}{|R_k - R_l|} \right\}
\]

\[
+ D_{\alpha\lambda} \nabla_{R_k} \sum_{k=1}^{N_{\text{at}}} \left\{ \frac{P_k^2}{2M_k} + \sum_{l=k+1}^{N_{\text{at}}} \frac{Z_k Z_l}{|R_k - R_l|} \right\}
\]

\[
= D_{\alpha\lambda} \mathcal{H}_{\alpha\lambda,k} + D_{\alpha\lambda} \sum_{l(\neq k)=1}^{N_{\text{at}}} \frac{Z_k Z_l e^2 (R_k - R_l)}{|R_k - R_l|^3}
\]

\[
= \mathcal{H}_{\alpha\lambda}^{(0)} A_{\alpha\lambda,k} + D_{\alpha\lambda} \sum_{l(\neq k)=1}^{N_{\text{at}}} \frac{Z_k Z_l e^2 (R_k - R_l)}{|R_k - R_l|^3}
\]

and likewise,

\[
\nabla_{P_k} \mathcal{H}_{\alpha\lambda}^{(0)} = \nabla_{P_k} D_{\alpha\lambda} \sum_{k=1}^{N_{\text{at}}} \left\{ \frac{P_k^2}{2M_k} + \sum_{l=k+1}^{N_{\text{at}}} \frac{Z_k Z_l}{|R_k - R_l|} \right\}
\]

\[
+ D_{\alpha\lambda} \nabla_{R_k} \sum_{k=1}^{N_{\text{at}}} \left\{ \frac{P_k^2}{2M_k} + \sum_{l=k+1}^{N_{\text{at}}} \frac{Z_k Z_l}{|R_k - R_l|} \right\}
\]

\[
= D_{\alpha\lambda} \mathcal{H}_{\alpha\lambda,k} + D_{\alpha\lambda} \sum_{l(\neq k)=1}^{N_{\text{at}}} \frac{Z_k Z_l e^2 (R_k - R_l)}{|R_k - R_l|^3} + D_{\alpha\lambda} \frac{P_k}{M_k}
\]

\[
= \mathcal{H}_{\alpha\lambda}^{(0)} A_{\alpha\lambda,k} + D_{\alpha\lambda} \frac{P_k}{M_k}
\]
The derivatives of the one- and two-electron components will have the same general structure. For the one-electron component,

\[ \nabla X_k \mathcal{H}^{(1)}_{\kappa\lambda} = \sum_{ij} \left[ \nabla X_k h_{ij} (\Gamma_{\kappa\lambda})_{ji} + h_{ij} \nabla X_k (\Gamma_{\kappa\lambda})_{ji} \right] \]

\[ = \sum_{ij} \left[ \nabla X_k h_{ij} (\Gamma_{\kappa\lambda})_{ji} - h_{ij} [\Gamma_{\kappa\lambda} \nabla X_k \Delta \Gamma_{\kappa\lambda}]_{ji} \right] \]

\[ = \text{Tr} (\nabla X_k h_{ij} \Gamma_{\kappa\lambda}) - \text{Tr} (h_{ij} \Gamma_{\kappa\lambda} \nabla X_k \Delta \Gamma_{\kappa\lambda}) \]

\[ = \text{Tr} (\nabla X_k h_{ij} \Gamma_{\kappa\lambda}) - \text{Tr} (\nabla X_k \Delta \Gamma_{\kappa\lambda} h_{ij} \Gamma_{\kappa\lambda}) . \]

In the same manner, differentiation of the two-electron component (with careful reordering of the electronic indices) results in the form

\[ \nabla X_k \mathcal{H}^{(2)}_{\kappa\lambda} = \frac{1}{4} \sum_{ijkl} \left\{ \nabla X_k V_{ik;jl} \left[ (\Gamma_{\kappa\lambda})_{ji} (\Gamma_{\kappa\lambda})_{lk} - (\Gamma_{\kappa\lambda})_{jk} (\Gamma_{\kappa\lambda})_{li} \right] \right\} \]

\[ + \frac{1}{2} \sum_{ijkl} \left\{ \nabla X_k V_{ik;jl} \left[ (\Gamma_{\kappa\lambda})_{ji} (\Gamma_{\kappa\lambda})_{lk} \right] \right\} \]

\[ = \frac{1}{2} \sum_{ijkl} \left\{ \nabla X_k V_{ik;jl} \left[ (\Gamma_{\kappa\lambda})_{ji} (\Gamma_{\kappa\lambda})_{lk} \right] \right\} \]

\[ = \frac{1}{2} \text{Tr} \left( \text{Tr} (\nabla X_k V \Gamma_{\kappa\lambda})_a \Gamma_{\kappa\lambda} \right)_b \]

\[ + \frac{1}{2} \sum_{ijkl} V_{ik;jl} \nabla X_k \left[ (\Gamma_{\kappa\lambda})_{ji} (\Gamma_{\kappa\lambda})_{lk} \right] . \]
Now the derivative in the second term must be evaluated,

\[ \nabla_{X_k} \mathcal{H}_{\kappa \lambda}^{(2)} = \frac{1}{2} \text{Tr} \left( \text{Tr} (\nabla_{X_k} V \Gamma_{\kappa \lambda})_a \Gamma_{\kappa \lambda})_b \right) \]

\[ + \frac{1}{2} \sum_{ijkl} V_{ijkl} \left[ \nabla_{X_k} (\Gamma_{\kappa \lambda})_{ji} (\Gamma_{\kappa \lambda})_{lk} + (\Gamma_{\kappa \lambda})_{ji} \nabla_{X_k} (\Gamma_{\kappa \lambda})_{lk} \right] \]

\[ = \frac{1}{2} \text{Tr} \left( \text{Tr} (\nabla_{X_k} V \Gamma_{\kappa \lambda})_a \Gamma_{\kappa \lambda})_b \right) \]

\[ - \frac{1}{2} \sum_{ijkl} V_{ijkl} \left[ (\Gamma_{\kappa \lambda} \nabla_{X_k} \Delta \Gamma_{\kappa \lambda})_{ji} (\Gamma_{\kappa \lambda})_{lk} \right] \]

\[ + (\Gamma_{\kappa \lambda})_{ji} (\Gamma_{\kappa \lambda} \nabla_{X_k} \Delta \Gamma_{\kappa \lambda})_{lk} \]  

(4.133)

\[ = \frac{1}{2} \text{Tr} \left( \text{Tr} (\nabla_{X_k} V \Gamma_{\kappa \lambda})_a \Gamma_{\kappa \lambda})_b \right) \]

\[ - \sum_{ijkl} V_{ijkl} \left[ (\Gamma_{\kappa \lambda} \nabla_{X_k} \Delta \Gamma_{\kappa \lambda})_{ji} (\Gamma_{\kappa \lambda})_{lk} \right] \]

\[ = \frac{1}{2} \text{Tr} \left( \text{Tr} (\nabla_{X_k} V \Gamma_{\kappa \lambda})_a \Gamma_{\kappa \lambda})_b \right) - \text{Tr} \left( \text{Tr} (V \Gamma_{\kappa \lambda} \nabla_{X_k} \Delta \Gamma_{\kappa \lambda})_a \Gamma_{\kappa \lambda})_b \right) \]

\[ = \frac{1}{2} \text{Tr} \left( \text{Tr} (\nabla_{X_k} V \Gamma_{\kappa \lambda})_a \Gamma_{\kappa \lambda})_b \right) - \text{Tr} \left( \text{Tr} (\nabla_{X_k} \Delta \Gamma_{\kappa \lambda} V \Gamma_{\kappa \lambda})_a \Gamma_{\kappa \lambda})_b \right) \]

In the above derivation, the double partial trace was used, in which

\[ \text{Tr} (\text{Tr} (V \Gamma_{\kappa \lambda})_a \Gamma_{\kappa \lambda})_b) = \sum_{lk} [\text{Tr} (V \Gamma_{\kappa \lambda})_a]_{lk} (\Gamma_{\kappa \lambda})_{lk} \]

\[ = \sum_{ijkl} V_{ijkl} (\Gamma_{\kappa \lambda})_{ji} (\Gamma_{\kappa \lambda})_{lk} . \]  

(4.134)

Now the derivatives of the expectation value of the Hamiltonian can be written in full form, first for the nuclear positions

\[ \nabla_{R_k} \langle \mathcal{H} \rangle = \sum_{\kappa \lambda} d^\ast_{\kappa \lambda} d_{\kappa \lambda} \left\{ \nabla_{R_k} \mathcal{H}^{(0)}_{\kappa \lambda} + \nabla_{R_k} \mathcal{H}^{(1)}_{\kappa \lambda} + \nabla_{R_k} \mathcal{H}^{(2)}_{\kappa \lambda} \right\} \]

\[ = \sum_{\kappa \lambda} d^\ast_{\kappa \lambda} d_{\kappa \lambda} D_{\kappa \lambda} \left\{ \left[ \mathcal{H}^{(0)} A_{\kappa \lambda, k} - \sum_{l \neq k} \frac{Z_k Z_l e^2 (R_k - R_l)}{|R_k - R_l|^3} \right] \right\} \]

\[ + \text{Tr} (\nabla_{R_k} h \Gamma_{\kappa \lambda}) - \text{Tr} (\nabla_{R_k} \Delta \Gamma_{\kappa \lambda} h \Gamma_{\kappa \lambda}) \]

\[ + \frac{1}{2} \text{Tr} \left( \text{Tr} (\nabla_{R_k} V \Gamma_{\kappa \lambda})_a \Gamma_{\kappa \lambda})_b \right) - \text{Tr} \left( \text{Tr} (\nabla_{R_k} \Delta \Gamma_{\kappa \lambda} V \Gamma_{\kappa \lambda})_a \Gamma_{\kappa \lambda})_b \right) \]  

(4.135)
and secondly for the nuclear momenta

\[ \nabla_{P_k} (\mathcal{H}) = \sum_{\kappa\lambda} d^{\kappa}_{\alpha} d^{\lambda}_{\beta} \left\{ \nabla_{P_k} \mathcal{H}^{(0)}_{\kappa\lambda} + \nabla_{P_k} \mathcal{H}^{(1)}_{\kappa\lambda} + \nabla_{P_k} \mathcal{H}^{(2)}_{\kappa\lambda} \right\} \]

\[ = \sum_{\kappa\lambda} d^{\kappa}_{\alpha} d^{\lambda}_{\beta} \left\{ \left[ \mathcal{H}^{(0)}_{\alpha\beta} A_{\kappa\lambda} - \frac{P_k}{M_k} \right] + \text{Tr} (\nabla_{P_k} h \Gamma_{\kappa\lambda}) \right. \]

\[ - \text{Tr} (\nabla_{P_k} \Delta \Gamma_{\kappa\lambda} h \Gamma_{\kappa\lambda}) + \frac{1}{2} \text{Tr} \left( \text{Tr} (\nabla_{P_k} V \Gamma_{\kappa\lambda}) a \Gamma_{\kappa\lambda} \right) \]

\[ - \left. \text{Tr} \left( \text{Tr} (\nabla_{P_k} \Delta \Gamma_{\kappa\lambda} V \Gamma_{\kappa\lambda}) a \Gamma_{\kappa\lambda} \right) \right) \]  

(4.136)

4.4 Implementation of the Vector Hartree-Fock Method

As the equations of motion have been fully disclosed, a method for the implementation of the Vector Hartree-Fock method must be proposed. Some work has already been made toward this implementation, through a combination of altering the current structure of the code and inclusion of new calculation subroutines as needed. It is desirable to implement the VHF code in such a way as to parallel the current code as much as possible, thus eliminating the need for massive structural reorganization of the existing framework.

The current implementation of the minimal END formalism is through the program endyne, version 5 [63]. As was previously mentioned, the electronic wave function is treated as a single determinant in this version. Figure 4.1 provides a general schematic of the computer code structure that is employed to perform calculations in ENDyne, version 5. The top level indicates that the kernel of ENDyne, version 5 is called using the module endkerndrv.f90. Inside the kernel, once the conditions are such that evolution of the dynamics is chosen, the subroutine dynevo is called. Inside of dynevo, the subroutine runkern is called. The subroutine runkern contains the various subroutines that will compute the symplectic form, the forces, and other properties that are desired by the user.

Of the subroutines called by runkern, two are of particular interest for the dynamical evolution of the state. The first, runforce allows for the calculation
of the force vector and the individual terms in the symplectic form. In particular, \texttt{runforce} will call subroutines from the module \texttt{endthouless.f90} in order to calculate expressions that depend explicitly upon the Thouless parameters. To calculate the elements of the molecular Hamiltonian, \texttt{runforce} calls subroutines found in the module \texttt{endmolecule.f90}. Finally, subroutines from the module \texttt{endkernwork} are called which results in the calculation of the nuclear symplectic form and the force vector.

Once the force vector and the symplectic form are evaluated and stored, the subroutine \texttt{runspeed} is called by \texttt{runkern}. Inside \texttt{runspeed}, the symplectic form is inverted using standard LAPACK \cite{LAPACK} routines. From the inverted symplectic and the force vector, \texttt{runspeed} calculates the velocity vector which is passed back to the differential equation solver to determine the dynamics of the system for the given time-step.
It is important to realize, that this is a very generalized schematic of only a small part of the current ENDeyne computer code, specifically the part that relates to the dynamical evolution of the electronic state. The details of these calculations (that is to say, the explicit form of the individual expressions found in the symplectic form) can be found in the review by Deumens et al. [10].

Figure 4.2: Structural flow chart for Vector Hartree-Fock END electronic calculations.

Figure 4.2 provides a proposed schematic flow chart for dynamical evolution in the VHF method. It is clear that the overall structure of the dynamical calculations is very similar to that for minimal END. While some structural changes may be required within the various subroutines, the most substantial alteration
occurs when the `runwork` subroutine is called by `runforce`. As was demonstrated in the derivations of the previous sections, the equations of motion are conveniently calculated by considering only two configurations at a time. To accomplish this, `runkern` will call the subroutine `runconfigloop` if a multi-configurational reference is provided in the input deck. Once inside `runconfigloop`, the program will cycle through all possible combinations of configurations. For each set of configurations, \(\kappa\) and \(\lambda\), `runconfigloop` will call the subroutine `runconfigpair`.

The subroutine `runconfigpair` has a similar structure to `runkern` in the current version of ENDyne, but the structure of many of the subroutines and the order in which they are called must be altered. This is principally due to the fact that a number of the terms that are used in the current implementation (such as the END phase) are meaningless in the VHF implementation and the fact that the summation over all configurations must be done through `runconfigloop` rather than inside `runconfigpair`. In the current implementation, the summations over the single configuration can be tallied as each expression is evaluated, however, in the VHF method, the expressions are evaluated in blocks that correspond to a given pair of configurations. It is only after these evaluations are made for a given pair of configurations that the sum can be incremented.

The same trio of modules will be accessed from within `runconfigpair` as are accessed from `runkern` in the current version, with several alterations made to each. The most substantial alterations (as could be expected) will occur in `endthouless.f90`, where those expressions that are explicitly dependent upon the Thouless parameters are evaluated. In particular, the current method for construction of the derivatives with respect to the dynamical parameters involves transformation of the Thouless coefficients from the occupied subspace to the virtual subspace, as outlined in the review by Deumens et al. [10]. This transformation is not necessary and is imposed for aesthetic reasons, as it simplifies the
equations into a more compact form. The virtual space in the single determinantal reference is the set of spin orbitals that are not occupied at a given time. However, in a CAS reference the set of unoccupied spin orbitals will be a union of the $K - K_2$ spin orbitals that are never occupied in any of the configurations and the spin orbitals in the active space that are not occupied at a given time. As the unoccupied orbitals in each configuration are always different from the other configurations, there is no meaningful way to make this transformation from the occupied subspace to the unoccupied subspace. This necessitates a restructuring of the subroutines contained in `endhouless.f90`. While this is only one of the changes that must occur, it is by far one of the most significant.

One final aspect to the new implementation is that it must be consistent with the current implementation when a single determinant reference is chosen in the input deck. To accomplish this with minimal code changes, a number of the current expressions will be evaluated only in case of the single determinant.

The following pseudo-code provides a proposed structure for the `runconfigpair` subroutine. While the details of the subroutines are not included, the result of each is indicated. The subroutines will be located in the appropriate modules, either `endhouless.f90`, `endmolecule.f90`, or `endkernwork.f90`. 


subroutine runconfigpair
  !
  ! Description of routine
  !
  ! Compute one- and two-electron integrals and build
  ! the one-density blocks and auxiliary blocks from
  ! the configurations kappa and lambda as well as
  ! contributions to the energies, gradients, symplectic
  ! form.
  ! Declare variables
  !
  ! Build quantities using the overlap matrix Delta and its
  ! derivatives wrt P and R.
  !
  ! Calculates the blocks of the one-density
  call densth
  if single determinant
    ! Compute a set of virtual orbitals, v, that
    ! orthonormal with the occupied orbitals, z.
    call coefvth
    ! Calculate the intermediate expressions needed for
    ! the construction of the symplectic form for a
    ! single configuration.
    call auxvth
  else (if multi-determinant)
    ! Calculate the intermediate expressions needed for
    ! the construction of the symplectic form for
    ! multiple configurations.
    call auxth
    ! Calculate the contribution to the MC electronic
    ! overlap for the current configurations.
  end if
  ! Calculate the electronic components of the symplectic
  ! form.
  call elespformth
  ! Calculate the intermediate expressions needed for
  ! the construction of the nuclear symplectic form.
  call auxdr
  ! Calculate the nuclear components of the symplectic
  ! form.
  call nucspform
  ! Calculates the coupled components of the symplectic
  ! form.
call cplspformth
! Increment the total electronic overlap by adding the
! contribution of the current pair of configurations.
!
! Build quantities using the 2-electron integrals and
! the derivative integrals.
!
! Loop through electronic indices for the two given
! configurations to calculate the two-electron integrals.
call teloop
!
! Build quantities using the one-electron integrals, the
! derivative integrals and the auxiliary quantities from
! before.
!
! Calculate the one-electron energy.
call oeegy
! Calculate the sum of the electronic kinetic and potential
! energies (in the form of the Fock matrix).
call oefock
! Calculate the gradient of the energy with respect to
! nuclear parameters (done in two parts).
call oeograd
call gradfin
! Calculate the gradient of the energy with respect to
! the Thouless coefficients.
call gradth
!
! Return the needed expressions
return
end
CHAPTER 5
CONCLUSION

For several years, it has been clear that the electronic representations in END must be improved. The stock basis sets that had been employed did not provide for proper dynamical descriptions and the single determinant wave function was inadequate in describing more complex spin states. In this work, improvements to both the construction of basis sets and the form of the wave function are proposed.

The method of constructing dynamically consistent basis sets has a number of advantages over traditional methods of basis set construction. Specifically, the new dynamically consistent method employs simple, physically intuitive principles in the construction. The proposed method is computationally inexpensive, as no non-linear energy optimizations are required. The basis sets constructed from the proposed method are very general, as they are not constructed with particular properties in mind. Finally, the basis sets derived from the proposed construction method provide good descriptions of electronic excitations in atoms and demonstrate improvement in charge transfer cross sections while still allowing for good descriptions of commonly evaluated structural properties such as magnitudes of dipole moments and vibrational frequencies.

The Vector Hartree-Fock method has been advanced as a route of implementing multi-configurational representations of electrons in the END formalism. The Vector Hartree-Fock method utilizes a non-orthonormal complete active space representation of the electrons, which is consistent with the generalized theory of vector coherent states. The Vector Hartree-Fock equations of motion arise from the
application of the Time-Dependent Variational Principle on the quantum mechanical action and have been completely derived. The structure of the equations of motion permit a symplectic form, guaranteeing that the evolution of the nuclei can be calculated using Hamilton’s equations and that the evolution of the electronic degrees of freedom can be calculated using Hamilton-like equations. Finally, a suggested implementation is given that preserves as much of the current ENDyne computer code as possible.

The implementation of these new electronic representations, either individually or in congress, will allow for increased flexibility from the ENDyne computational suite. Most importantly, the proposed improvements to the electronic representations will permit better descriptions of energy barriers, allowing for increased accuracy in chemical reactions that occur at lower energies. This will provide a complement to the current implementation of ENDyne that has demonstrated remarkable accuracy at higher reaction energies.
This Appendix provides a library of the dynamically consistent basis sets discussed in this dissertation. The library structure employed in this work is the ACESII basis sets library structure. The stock basis sets are available in any quantum chemistry basis set library and will not be repeated here.

H:3-21B
Built to same standards as 3-21G

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0
2
3

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0.871741 0.000000
2.286437 0.000000
0.000000 1.000000

H:6-31B
Built to same standards as 6-31G

1
0
2
4

2.227661 0.405771 0.109818 0.014150
0.547081 0.000000
2.897688 0.000000
1.576183 0.000000
0.000000 1.000000
H:BJK01
Constructed from scratch

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0.0515950  0.0000000  0.0000000
0.1960018  0.0000000  0.0000000
0.5082867  0.0000000  0.0000000
0.3753349  0.1425000  0.0000000
0.0000000  -1.0000000  0.1000000
0.0000000  0.0000000  -1.0000000

0.5623620  0.1023930  0.0276610  0.00691525

0.0509264  0.0000000
0.4163883  0.0000000
0.6755409  0.1000000
0.0000000  1.0000000

0.0150000

1.0000000
H: 6-31B**
Built to same standards as 6-31G**

2
0 1
2 1
4 1

2.227661 0.405771 0.109818 0.014150

0.5470819 0.0000000
1.8976888 0.0000000
1.5761883 0.0000000
0.0000000 1.0000000

0.015482
1.0000000

HE: 3-21B
Built to same standards as 3-21G

1
0
2
3

2.425687 0.431771 0.032862

1.5247658 0.0000000
2.4066857 0.0000000
0.0000000 1.0000000
HE:6-31B
Built to same standards as 6-31G

1
0
2
4

6.343612 1.155497 0.312723 0.032862

0.5470819 0.0000000
1.8976888 0.0000000
1.5761883 0.0000000
0.0000000 1.0000000

HE:6-31B**
Built to same standards as 6-31G**

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2 1
4 1

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1.5761883 0.0000000
0.0000000 1.0000000

0.080818

1.0000000
HE:633B
Built from scratch

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LI:3-21B

Built to same standards as 3-21G

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0  1
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6  3

16.126766  2.937511  0.795005  0.052866  0.020080
0.009968

0.5470819  0.0000000  0.0000000
1.8976888  0.0000000  0.0000000
1.5761883  0.0000000  0.0000000
0.0000000  2.6483533  0.0000000
0.0000000  1.0124187  0.0000000
0.0000000  0.0000000  1.0000000

0.316384  0.078252  0.023133

1.8512504  0.0000000
2.7478869  0.0000000
0.0000000  1.0000000
LI:6-31B
Built to same standards as 6-31G

2
  0  1
  3  2
 10  4

56.034549  10.366392  2.827920  1.079960  0.518147
  0.271519  2.518400  0.615480  0.050150  0.009502

0.1437761  0.0000000  0.0000000
0.6068918  0.0000000  0.0000000
1.5266054  0.0000000  0.0000000
1.3194583  0.0000000  0.0000000
0.4352521  0.0000000  0.0000000
0.0399570  0.0000000  0.0000000
0.0000000  0.5263900  0.0000000
0.0000000  0.3533601  0.0000000
0.0000000 -3.6409892  0.0000000
0.0000000  0.0000000  1.0000000

1.597154  0.295474  0.080313  0.016313

0.1085890  0.0000000
0.8613239  0.0000000
1.3740381  0.0000000
0.0000000  1.0000000
LI:6-31B**
Built to same standards as 6-31G**

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| 56.034549 | 10.366392 | 2.827920 | 1.079960 | 0.518147 |
| 0.271519 | 2.518400 | 0.615480 | 0.050150 | 0.009502 |

0.1437761 0.0000000 0.0000000
0.6068918 0.0000000 0.0000000
1.5266054 0.0000000 0.0000000
1.3194583 0.0000000 0.0000000
0.4352521 0.0000000 0.0000000
0.0399570 0.0000000 0.0000000
0.0000000 0.5263900 0.0000000
0.0000000 0.3533601 0.0000000
0.0000000 -3.6409892 0.0000000
0.0000000 0.0000000 1.0000000

1.597154 0.295474 0.080313 0.016313

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1.0000000
LI: BJK01

Modified from 6-31B

2

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3 2
9 4

921.300000 138.700000 31.940000 9.353000 3.158000
1.157000 0.444600 0.076660 0.010250

0.0013670 0.0000000 0.0000000
0.0104250 0.0000000 0.0000000
0.0498590 0.0000000 0.0000000
0.1607010 0.0000000 0.0000000
0.3446040 0.0000000 0.0000000
0.4251970 0.0000000 0.0000000
0.1694680 -0.2223110 0.0000000
0.0000000 1.1164770 0.0000000
0.0000000 0.0000000 1.0000000

1.488000 0.266700 0.0738501 0.0117250

0.0387700 0.0000000
0.2362570 0.0000000
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0.0000000 1.0000000
LI:BJK02
Modified from BJK01

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| 196.918997 | 29.537856 | 8.245056 | 4.135330 | 1.838264 |
| 0.789296   | 0.371748  | 0.083903  | 0.624800  | 0.097215  |
| 0.037250   | 0.061045  | 0.015458  | 0.008525  |

| 1.615800   | 0.401248  | 0.121326  | 0.045016  | 0.020500  |
| 0.009850   | 0.005102  |

| 0.0327336  | 0.000000  |
| 0.2021071  | 0.000000  |
| 0.8964778  | 0.000000  |
| 0.9642687  | 0.000000  |
| 0.2252693  | -0.8998926 |
| 0.0000000  | -1.3680179 |
| 0.0000000  | -0.6532625 |
C:3-21B
Built to same standards as 3-21G

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0  1
3  2
6  7

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<tr>
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<tr>
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C:6-31B
Built to same standards as 6-31G

2
0 1
3 2
10 4

743.444586 136.309751 38.134556 13.100249 5.087210
2.095194 6.677585 0.405486 0.155672 0.018102

0.0324841 0.0000000 0.0000000
0.1749819 0.0000000 0.0000000
0.5974527 0.0000000 0.0000000
1.3136109 0.0000000 0.0000000
1.4764240 0.0000000 0.0000000
0.4620223 0.0000000 0.0000000
0.0000000 0.2124986 0.0000000
0.0000000 -2.1129015 0.0000000
0.0000000 -1.6242009 0.0000000
0.0000000 0.0000000 1.0000000

2.259772 0.579963 0.196906 0.052516

0.6647319 0.0000000
2.3175110 0.0000000
1.7286327 0.0000000
0.0000000 1.0000000
C:6-31B**
Built to same standards as 6-31G**

2
0 1 2
3 2 1
10 4 1

743.444586 136.309751 38.134556 13.100249 5.087210
2.095194 6.677585 0.405486 0.155672 0.018102

0.0324841 0.000000 0.000000
0.1749819 0.000000 0.000000
0.5974527 0.000000 0.000000
1.3136109 0.000000 0.000000
1.4764240 0.000000 0.000000
0.4620223 0.000000 0.000000
0.0000000 0.2124986 0.0000000
0.0000000 -2.1129015 0.0000000
0.0000000 -1.6242009 0.0000000
0.0000000 0.0000000 1.0000000

2.259772 0.579963 0.196906 0.052516

0.6647319 0.000000
2.3175110 0.000000
1.7286327 0.000000
0.0000000 1.0000000

0.096212

1.0000000
N:3-21B
Built to same standards as 3-21G

2
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3 2
6 7

98.960609 18.025798 4.878485 0.478223 0.181648
0.021345

0.5470819 0.0000000 0.0000000
1.8976888 0.0000000 0.0000000
1.5761883 0.0000000 0.0000000
0.0000000 2.6483533 0.0000000
0.0000000 1.0124187 0.0000000
0.0000000 0.0000000 1.0000000

1.588988 0.393007 0.064966

1.8512501 0.0000000
2.7478869 0.0000000
0.0000000 1.0000000
N: 6-31B
Built to same standards as 6-31G

2
  0  1
  3  2
 10  4

1026.318860  188.174439  52.644427  18.084782  7.022850
  2.892397  9.553445  0.580118  0.222716  0.021345

0.0324841  0.0000000  0.0000000
0.1749819  0.0000000  0.0000000
0.5974527  0.0000000  0.0000000
1.3136109  0.0000000  0.0000000
1.4764240  0.0000000  0.0000000
0.4620223  0.0000000  0.0000000
0.0000000  0.2124986  0.0000000
0.0000000 -2.1129015  0.0000000
0.0000000 -1.6242009  0.0000000
0.0000000  0.0000000  1.0000000

3.378097  0.866978  0.294351  0.294351

0.6647319  0.0000000
2.3175110  0.0000000
1.7286327  0.0000000
0.0000000  1.0000000
N:6-31B**
Built to same standards as 6-31G**

2
0 1 2
3 2 1
10 4 1

1026.318860 188.174439 52.644427 18.084782 7.022850
2.892397 9.553445 0.580118 0.222716 0.021345

0.0324841 0.0000000 0.0000000
0.1749819 0.0000000 0.0000000
0.5974527 0.0000000 0.0000000
1.3136109 0.0000000 0.0000000
1.4764240 0.0000000 0.0000000
0.4620223 0.0000000 0.0000000
0.0000000 0.2124986 0.0000000
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0.0000000 0.0000000 1.0000000

3.378097 0.866978 0.294351 0.294351

0.6647319 0.0000000
2.3175110 0.0000000
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0.0000000 1.0000000

0.116370

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0:3-21B
Built to same standards as 3-21G

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  6  7

130.637663  23.795813  6.440076  0.651776  0.247570
  0.024862
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1.8976888  0.0000000  0.0000000
1.5761883  0.0000000  0.0000000
0.0000000  2.6483533  0.0000000
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0.0000000  0.0000000  1.0000000

2.143685  0.530201  0.078722

1.8512501  0.0000000
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Built to same standards as 6-31G

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| 1354.841066 | 248.408626 | 69.495782 | 23.873677 | 9.270847 |
| 3.818247    | 13.020494  | 0.790649  | 0.303542  | 0.024862 |

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0.1749819 0.0000000 0.0000000
0.5974527 0.0000000 0.0000000
1.3136109 0.0000000 0.0000000
1.4764240 0.0000000 0.0000000
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0.0000000 0.2124986 0.0000000
0.0000000 -2.1129015 0.0000000
0.0000000 -1.6242009 0.0000000
0.0000000 0.0000000 1.0000000

4.557349 1.169629 0.397106 0.078722

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1.7286327 0.0000000
0.0000000 1.0000000
0:6-31B**
Built to same standards as 6-31G**

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REFERENCES


BIOGRAPHICAL SKETCH

Benjamin J. (Ben) Killian was born in Lake City, FL, on May 12, 1976, to Jane C. and James W. Killian. His first scientific interest was for dinosaurs and was fostered by a visit to the Smithsonian Natural History Museum in Washington, D.C., at the age of five. From that point onward he has been interested in physical sciences.

Ben graduated from Columbia High School, located in Lake City, in 1994. He then attended Lake City Community College for two years, where he was named the Math and Science Student of Year in 1996. He earned his A.A. degree with a physical science emphasis in 1996.

That same year he transferred to the University of Florida, where he majored in chemistry. In 1998 he graduated with his Bachelor of Science degree in chemistry, with American Chemical Society certification.

In 1999, Ben was accepted as a graduate student in the Chemistry Department at UF. Two years later, he was accepted to candidacy and began his doctoral work in Electron-Nuclear Dynamics with Yngve Öhrn and Erik Deumens. As a graduate student, Ben spent a large portion of his time as a teaching assistant, for which he was twice recognized with a UF Chemistry Department Teaching Award. In 2005, Ben was awarded a second place Stasch Award for Publication Excellence.

In May of 2001, Ben married his loving wife Donna, who has since been an increasingly strong supporter of his work.