MODERN ELECTRONIC STRUCTURE THEORY:
THE SEARCH FOR CHEMICAL ACCURACY

by

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The following individuals read and discussed the thesis submitted by student Jonathan Prince, and they evaluated the student’s presentation and response to questions during the final oral examination. They found that the student passed the final oral examination.

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The final reading approval of the thesis was granted by Clifford LeMaster, Ph.D., Chair of the Supervisory Committee. The thesis was approved by the Graduate College.
DEDICATION

This work is dedicated to Richard Prince,

for showing me what it means to live on

your own terms. Rest easy, big guy.
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ABSTRACT

Electronic structure theory has progressed significantly within the last few decades, venturing far from the early days of the Hartree-Fock self-consistent field method. Modern electronic structure theory focuses on compound methods, which operate under the idea that we can take a lower level of theory computation (typically, a result from Hartree-Fock, Configuration Interaction, Coupled Cluster or Moller-Plesset perturbation theory) and add in higher level of the theory corrections such as extrapolations to the infinite basis set limit, as well as, relativistic effects.

Using the Gaussian-n, Complete Basis Set and Weizmann compound methods, we were able to provide theoretical evidence to justify the claim that the mechanism for the isomerization process of perfluoro-2-azapropene was through either a nitrogen inversion or rotational mechanism. Following the previous study was the realization that what is predicted to be the most accurate compound method (the Weizmann method) doesn’t yield the most accurate result, led us to ask the question “Is there a compound method available that’s both computationally feasible on a workstation computer, as well as, able to produce the best results regardless of the molecule or process being studied?”.

What we found was that the Weizmann-2 method is computationally feasible on a workstation computer, as well as, claims to produce chemically accurate results (results within 1 kcal mole$^{-1}$) from their experimental values for all molecules and processes. However, the Weizmann-2 method has only been tested against thermochemical data with little to no work being done with any kinetic parameter. These realizations sparked
our interest to verify the validity of this claim by testing the accuracy of the Weizmann-2 method against a kinetic parameter such as a barrier height. The results of the Weizmann-2 investigation were then used to develop a modification to the Weizmann-2 method which was able to produce chemically accurate barrier heights for all of the well-behaved molecules studied.
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CHAPTER 1: INTRODUCTION AND MOTIVATION

I.)   \textit{Introduction to Compound Methods.}

Electronic structure theory is fundamentally grounded in quantum mechanics and arguably pure mathematics. As a result, it’s important to lay down the theoretical framework for this project, as well as, to define all terms that will arise in the future. Ignoring the historical “dawn of quantum mechanics”, we can say that in many cases, the practice of quantum mechanics can be distilled down to a relative simple eigenvalue problem that obeys the postulates of quantum mechanics. Generally, the eigenvalue problem can be expressed as the following equation:

\[ \hat{A}f_n = a_n f_n \]  

1.)

Where:

\[ a_n = \text{the nth eigenvalue} \]
\[ f_n = \text{the nth eigenfunction} \]
\[ \hat{A} = \text{general operator of the eigenvalue problem.} \]
Now, by introducing the postulates of quantum mechanics it will be possible to transform the terms of the general eigenvalue problem into something more meaningful. The postulates are taken directly from reference 1, although not necessarily in the same order.

\textit{Postulate 1:}

\textit{The state of a quantum mechanical system is completely specified by a function }$\psi(x)$\textit{ that depends upon the coordinate of the particle. All possible information about the system can be derived from }$\psi(x)$. \textit{This function, called the wave function or state function, has the important property that }$\psi^*(x)\psi(x)dx$\textit{ is the probability that the particle lies in the interval }$dx$\textit{, located at the position }$x$\textit{.}

It is important to realize that Postulate 1 claims the state of a quantum mechanical system such as an electron, is completely specified by the wave function and that nothing else is required. Since the square of the wave function has probabilistic interpretations, it must satisfy some physical requirements. Thus, the total probability of finding a particle somewhere must be unity and hence

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1 \quad 2.)$$

Where $\psi^*(x)$ is the complex conjugate of $\psi(x)$. 
If a particle obeys equation 2, it is said to be normalized. Functions that can be normalized are called *normalizable* and only normalizable functions are acceptable wave functions. For an acceptable wave function to be physically suitable, it and its first derivative must be single valued, continuous, and finite.

It should be noted that real particles live in 3 dimensions (excluding time) and as we shall see, it is much easier to work in spherical coordinates rather than Cartesian coordinates. As a result, the wave functions used throughout this project are in spherical \( \psi(r, \theta, \phi) \) not \( \psi(x, y, z) \) Cartesian coordinates. However, for simplicity, we will work in Cartesian coordinates throughout this manuscript.

*Postulate 2:*

*In any measurement of the observable associated with a given operator \( \hat{A} \) within the quantum mechanical eigenvalue problem, the only values that will ever be observed are the eigenvalues \( (a_n) \), satisfying the general eigenvalue problem of equation 1.*
Postulate 3:

For every observable in classical mechanics there exists a linear, Hermitian operator in quantum mechanics.

In fact, Postulate 3 and the Hermitian nature of quantum mechanical operators, guarantees the eigenvalues of equation 1 will be real.

An operator is said to be Hermitian if it satisfies the following equation:

\[ \int_{-\infty}^{\infty} f^*(x) \hat{A} g(x) \, dx = \int_{-\infty}^{\infty} g(x)[\hat{A} f]^*(x) \, dx \]  

And an operator is linear, if it obeys the following condition

\[ \hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) \]  

Postulate 4:

If a system is in a state described by a normalized wave function \( \psi \), then the average value of the observable corresponding to \( \hat{A} \) is found from the following equation:

\[ \langle a \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{A} \psi(x) \, dx \]
Postulate 5:

All electronic wave functions must be antisymmetric under the interchange of any two electrons.

This Postulate is the Pauli Exclusion Principal and simply states, no two electrons or more generally, no two fermions can occupy the same quantum state at the same time. We will come back to the definition of a quantum state later, but for now, all we need to know is that no two fermions can occupy the same position in space with their intrinsic spins aligned in the same direction.

It should be noted that the author has omitted the quantum mechanical postulate which handles the time-dependent domain, since this project strictly works in the time-independent domain.

Now that we have established the “rules” of quantum mechanics, let’s apply them. Since we are interested in the electronic energy of molecules it should come as no surprise that the eigenvalue we are interested in is the electronic energy. According to Postulate 3, we must now find a linear, Hermitian operator that will allow the eigenvalue, in this case, electronic energy, to be observed.

Let’s start by considering the case where there is one electron interacting with a single, fixed, nuclei. Let’s first recognize that we are interested in the total electronic energy, which is the sum of the kinetic and potential energy. From classical physics, kinetic energy is represented by the following expression:
Where:

\[ p = \text{momentum}. \]

Now, we invoke a quantum mechanical axiom, which is the quantum mechanical equivalent of momentum. Quantum mechanically, momentum is represented by the following operator

\[ \hat{p} = -i\hbar \frac{d}{dx} \]  

Substituting equation 7 into equation 6, we arrive at the kinetic energy portion of the total energy operator, represented by the following equation:

\[ KE = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \]  

It is important to remember that equations 7-8 consider a particle in one dimension, where a real particle lives in 3 dimensions (excluding time) and so would be represented by a partial derivative for each dimension in the momentum operator, as well as a partial second derivative for each dimension in the final kinetic energy term.

Now that we have found the kinetic energy portion of the total energy operator, let’s find the potential energy term. Since we are considering the case where one electron

\[ KE = \frac{mv^2}{2} = \frac{p^2}{2m} \]  

6)

\[ \text{Where:} \]

\[ p = \text{momentum}. \]
is interacting with a fixed (at the origin) nucleus, we only need to consider the coulombic potential between the electron and the positively charged nuclei. From classical physics, we know the electric potential energy is given by the following expression:

\[ V(x) = C \frac{qQ}{r} \quad 9. \]

Where:

\( C \) represents Coulomb's constant, given by the following expression.

\[ C = \frac{1}{4 \pi \varepsilon} \quad 10. \]

Substituting equation 10 into equation 9 and then considering the case with one electron interacting with a single positively charged nucleus, we arrive at the potential energy term within the total energy operator. The potential energy term is represented by the following.

\[ V(x) = -\frac{1}{4 \pi \varepsilon} \frac{e^2}{r} \quad 11. \]
Where:

\( e \) = the charge on the proton.

\( \epsilon \) = the permittivity of free space.

\( r \) = is the distance between the electron and the proton.

At last, we arrived at an expression for the total energy operator for our eigenvalue problem. If we combine the kinetic and potential energy terms, we arrive at the following.

\[
\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - \frac{1}{4\pi \epsilon \, r}
\]  

Taking into account real particles live in three dimensions (excluding time), as well as, the spherical geometry of the potential energy, we might as well transform the kinetic energy term of the total energy operator into spherical coordinates.

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{1}{4\pi \epsilon \, r}
\]

Where in spherical coordinates,

\[
\nabla^2 = \frac{\partial}{r^2 \partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta \partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta \partial \phi^2} \frac{\partial^2}{\partial \phi^2}
\]
It’s important to note, equation 13 is defined as the Laplacian operator.

Substituting equation 13 into our eigenvalue problem, we arrive at the central equation to quantum chemistry, the Schrödinger equation. The Schrödinger equation has the following form.

\[ \hat{H} \psi = \alpha \psi \]  \hspace{2cm} 15.\)

It will be left as an exercise to the reader to demonstrate that the electronic operator, defined as the *Hamiltonian*, obeys the postulates of quantum mechanics.

It is important to remember that this version of the Schrödinger equation describes a one electron system interacting with a nucleus that’s fixed at the origin or said another way; this version of the Schrödinger equation describes the hydrogen atom.

For our purposes, it is sufficient to take the functional form of the wave function as an axiom of quantum mechanics. Generally, an electronic wave function will have the following structure.

\[ \psi = R(r)Y(\theta, \phi)X(\alpha, \beta) \]  \hspace{2cm} 16.\)
Where:

\[ R(r) = \text{the radial component of the wave function.} \]

\[ Y(\theta, \phi) = \text{Spherical harmonics, representing the angular component of the wave function.} \]

\[ X(\alpha, \beta) = \text{Spin eigenfunction.} \]

As an example of how the wave function obeys the postulates of quantum mechanics, let’s consider the hydrogen atom. As was previously mentioned, a quantum mechanical system is said to occupy a quantum state, which is completely described by its wave function. A quantum state is defined by a set of quantum numbers, which arose from solutions of several model systems. There exists four quantum numbers which are used to represent the quantum state of the system. The following table illustrates the relationship between quantum numbers to their components of the wave function as well as, their physical significance.
Table 1.1.1  Table 1.1.1 illustrates the relationship between quantum number wave function component, as well as, the quantum number’s physical significance.

<table>
<thead>
<tr>
<th>Quantum Number</th>
<th>Wave Function Component</th>
<th>Physical Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>$R_{nl}(r)$</td>
<td>Principal quantum number used to describe the distance the particle is from the nucleus. $n \in \mathbb{Z}_{\geq 0}$.</td>
</tr>
<tr>
<td>L</td>
<td>$Y_{l,M_1}(\theta, \phi)$</td>
<td>Angular momentum quantum number used to describe the shape of the electron distribution. $L \in \mathbb{Z}_{\geq 0}$.</td>
</tr>
<tr>
<td>M_1</td>
<td>$Y_{l,M_1}(\theta, \phi)$</td>
<td>Magnetic quantum number used to describe where in space the electron distribution is located. $M_1 \in \mathbb{Z}$.</td>
</tr>
<tr>
<td>M_s</td>
<td>$X(\alpha, \beta)$</td>
<td>Spin quantum number used to describe the spin of a quantum mechanical system. $M_s \in \mathbb{Q}$.</td>
</tr>
</tbody>
</table>

Returning to the Hydrogen atom, we know in its un-ionized form, hydrogen contains one electron with a single proton. Any first-year chemistry student will tell you; this electron occupies the 1s “orbital”. If the student is ambitious, they may also tell you the electron can either have an up or down spin. Eluding the first year chemistry student is that the coordinates to the electron’s quantum state are embedded within these “orbital” definitions. For example, if we believe hydrogen’s electron occupies the 1s “orbital” with an arbitrarily chosen spin-up state we define a quantum state as the set \{n, l, M_1, M_s\}. Then the coordinates describing the quantum state of this electron is \{1, 0, 0, +1/2\}. Upon inspecting the set of quantum numbers for the electron of the hydrogen atom, we see that
the principal quantum number is proportional to the row the atom is located on within the periodic table, and an up spin is defined as +1/2, which means a down spin is defined as -1/2. Now, we interpret the angular momentum and magnetic quantum numbers. It may not be obvious from the above table, but the angular momentum quantum number describes the “orbital” or shape of the electron distribution while the magnetic quantum number describes where in space the electron distribution is likely to be. Inspecting the set of quantum numbers describing the electron of the hydrogen atom, we see that both the angular momentum and magnetic quantum numbers are 0. This observation should lead the reader to the conclusion electrons occupying an “s-orbital” have an angular momentum quantum number of 0. If the reader has drawn this conclusion, they would be absolutely correct and in fact, the angular momentum quantum increases linearly, with the energy of the electron distribution. If we consider the first year chemistry students picture of the electronic structure of atoms, we see that the electrons occupy “orbitals” that increase in energy as you move away from the hydrogen atom. For example, a hydrogen atoms electron occupies an “s-orbital” whereas boron’s lone electron would occupy a “p-orbital”, scandium’s lone electron occupies a “d-orbital” and neodymium has lone pairs of electrons occupying “f-orbitals”. As far as energy of these orbitals, we find that the energy increases as you go from the “s-orbitals” to the “f-orbitals”. This leads us to the following conclusion.
As we shall see, there are many more possible angular momentum quantum numbers, however, for now, let’s turn our attention to the magnetic quantum numbers.

As stated above, the magnetic quantum numbers tell us where in space the electron distribution is likely to be and if the reader re-inspects the set describing the electronic state of the hydrogen atom, they will see that both the angular momentum and the magnetic quantum numbers are the same. This is not a coincidence as the magnetic quantum numbers are a function of the angular momentum quantum numbers through the following equation.

\[ 2l + 1 = M_z \]  \hspace{1cm} (17.)

Letting \( \mathbb{Z} \) retain its usual definition of the integer ring, we have the following restrictions on the angular momentum and magnetic quantum numbers:

\[ l \in \mathbb{Z}, \quad M_z \in \mathbb{Z} \]  \hspace{1cm} (18.)
As an example of how equation 17 works, let’s examine the case when the angular momentum quantum number ranges from 0 to 2.

\[ m_l = 0 \]
\[ m_l = 0, 1, +1 \]
\[ m_l = 0, 1, +1, -1, -2, +2 \]

This pattern may look familiar, as we can begin to see how the angular momentum and magnetic quantum numbers relate to the orbital picture of the electronic structure of atoms. According to the orbital picture, there is a single “s-orbital”, three “p-orbitals” and five “d-orbitals” and if we inspect the relationships given in 19, this is exactly what we see. For example, a “p-orbital” has an angular momentum quantum number of 1, and we are told from the orbital description of the electronic structure of atoms there is a “p-orbital” for each dimension and hence we should have three “p-orbitals”. Again, this is exactly what we see from the relationships within 19 and conclude the magnetic quantum numbers increase linearly with the angular momentum quantum number.

We will return to the wave function later, but for now, let’s turn our attention to the Schrödinger equation for multi-electron atoms and molecules.

A natural starting point is to discuss the Hamiltonian for the helium atom.

The Hamiltonian for helium is similar to the Hamiltonian for hydrogen except, we add an additional kinetic energy term (for the additional electron), as well as, an additional potential energy term. The helium atom Hamiltonian has the following functional form.
\[
\hat{H} = -\frac{\hbar^2}{2M} \nabla^2 M - \frac{\hbar^2}{2m_e} \nabla_j^2 M - \frac{\hbar^2}{2m_e} \nabla_j^2 - \frac{1}{4\pi\varepsilon} \frac{2e^2}{|R-r_1|} - \frac{1}{4\pi\varepsilon} \frac{2e^2}{|R-r_2|} + \frac{1}{4\pi\varepsilon} \frac{e^2}{|r_1-r_2|}
\] (20.)

Where:

M = mass of the nucleus.

\(\nabla^2\) = Laplacian operator for the helium nucleus.

\(\nabla_j^2\) = Laplacian for the jth electron.

M\(_e\) = Mass of the jth electron.

R = Position of the helium nucleus.

r\(_j\) = Position of the jth electron.

Luckily, because the mass of the electron is much smaller than the mass of the nucleus, we can neglect the motion of the atomic nucleus when describing electrons in a molecule. This is called the Born-Oppenheimer approximation and simplifies the electronic Hamiltonian by removing the kinetic energy term for the nuclei. Under the Born-Oppenheimer approximation, the electronic Hamiltonian reduces to equation 21

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_j^2 M - \frac{\hbar^2}{2m_e} \nabla_j^2 - \frac{1}{4\pi\varepsilon} \frac{2e^2}{|r_1+r_2|} + \frac{1}{4\pi\varepsilon} \frac{e^2}{|r_1-r_2|}
\] (21.)

In accordance with the Pauli Exclusion Principle, an initial approximate ground state wave function for the helium atom with two non-interacting electrons may be written as a product of one electron wave functions with opposite spins. The following function represents this wave function for the helium atom.
It should be noted, that in the early 1930’s John C. Slater introduced determinants to construct wave functions that obey the postulates of quantum mechanics. For the helium atom, the approximate ground state wave function for two non-interacting electrons becomes the following determinant.

$$\psi_{He} = \frac{1}{\sqrt{3}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

Where each element in the determinant represents a quantum state for the jth electron. If we let a quantum state be represented by the list of quantum numbers, \{n,l,m_l,m_s\}, then the 1s\alpha(1) element describes a quantum state with the following quantum numbers \{1,0,0,+1/2\}, where this state is for an electron arbitrarily assigned to be the 1st electron. The concept of using determinants as wave functions can be generalized to the following.

$$\psi(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} M_1(1) & \ldots & M_N(1) \\ \vdots & \ddots & \vdots \\ M_1(N) & \ldots & M_N(N) \end{vmatrix}$$
Where \( N \) represents the number of electrons in the system and the coefficient, \( \frac{1}{\sqrt{N!}} \), represents the probability amplitude for that quantum state or said another way the square of the coefficient.

\[
\left( \frac{1}{\sqrt{N!}} \right)^2 = \left( \frac{1}{\sqrt{N!}} \right) \left( \frac{1}{\sqrt{N!}} \right) = \frac{1}{N!^{1/2} \cdot N!^{1/2}} = \frac{1}{N!}
\]

represents the probability of finding the quantum system occupying the quantum state described by the coefficient that was squared.

Introducing determinants as the wave function allows for quantum mechanical postulate 5, to arise naturally. For example, if both of Helium’s electrons occupy the same quantum state, then equation 23 becomes:

\[
\Psi_{He} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\alpha(1) \\ 1s\alpha(2) & 1s\alpha(2) \end{vmatrix} = (1s\alpha(1)1s\alpha(2)) - (1s\alpha(1)1s\alpha(2)) = 0
\]

Thus, if two electrons within the same quantum mechanical system, occupy the same quantum state, the wave function collapses and goes to zero. This is a beautiful result of postulate 5.

Substituting equation 21 and 23 into equation 15, we arrive at the Schrödinger equation for the helium atom. An interesting result occurs when we examine the Schrödinger equation for the helium atom, namely the introduction of the last term in equation 21. This seemingly innocent term (called “the electron-electron repulsion
energy”’) prohibits the Schrödinger equation for the helium atom from becoming solvable analytically. This term remains unsolvable analytically due to the fact that electrons are not stationary and are constantly moving to minimize the energetically unfavorable interaction of like charges interacting with each other. From here on out, I will refer to the electron-electron repulsion energy as the following.

\[ \frac{1}{4\pi\varepsilon} \frac{e^2}{|r_i - r_k|} \quad 27. \]

Where:

\( r_i = \) position of the \( i^{th} \) electron.

\( r_k = \) position of the \( k^{th} \) electron.

Approximating the solution for multi-electron systems marks the beginning of electronic structure theory, but, before we continue, let’s examine how the Schrödinger equation varies when going from atoms to molecules.

A general molecular Hamiltonian will have the following form:

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{M=1}^{M_m} \nabla_{M}^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^{k} \nabla_i^2 + \frac{e^2}{4\pi\varepsilon} \sum_{b=M-j}^{M-1} (R_b)^{-1} + \frac{e^2}{4\pi\varepsilon} \sum_{c=(i-(i+1))} (\nabla_{d=j-k}^{-1}) (R_c)^{-1} - \]

\[ \frac{e^2}{4\pi\varepsilon} \sum_{x=M}^{y-M} (R_x)^{-1} \quad 28. \)
Where the first term represents the kinetic energy term for the $M^{th}$ to the $J^{th}$ nuclei, the second term represents the kinetic energy term for the $i^{th}$ electron to the $k^{th}$ electron and the following terms represent the potential energy for each particle in the system. The first term within the potential energy terms represent the nuclear-nuclear repulsion term between the $M$ and $M+1$ nuclei to the $M^{th}$ and $J^{th}$ nuclei, while the second term represents the electron-electron repulsion energy between the $i^{th}$ and $i+1$ electron up to the $i^{th}$ and $k^{th}$ electron and the last term represents the coulomb interaction between the $i^{th}$ electron centered around the $M^{th}$ nuclei up until the $k^{th}$ electron is centered around the $J^{th}$ nuclei. It is important to note these terms represent each nuclei interacting with every other nuclei, each electron interacting with every other electron, as well as, every electron interacting with every nucleus.

An interesting result occurs when inspecting the terms of the potential energy within the generalized Hamiltonian. What might have eluded the reader for the helium case is now more pronounced in the general case. That is, the overall operation is different for the electron-electron and nuclear-nuclear repulsion terms relative to the coulombic interaction terms. At first, this might seem strange, although we have to invoke classical physics to explain why these terms are operated on differently than the coulombic interaction terms. That is, we have to remember the change in potential energy decreases when a conservative force does work on the system. It should come as no surprise that the electron-electron and nuclear-nuclear repulsion terms are representative of a conservative force, as one electron doesn’t care how the other electron got close to it, it just cares that another like charge is within proximity of itself. It easily follows that an electron interacting with another electron or a nuclei interacting with another nuclei, is
representative of work being done on the system and hence, the system loses potential energy. Thus, the overall sign of the nuclear-nuclear and electron-electron repulsion terms change from positive to negative and as we know, when we subtract a negative we change the operation to addition and hence the overall change in operation for the nuclear-nuclear and electron-electron repulsion terms relative to the coulombic interaction terms.

While the molecular Hamiltonian looks quite daunting, there are a few tricks we can invoke to simplify it. First, we will introduce atomic units which can be found in Table 1.1.2

Now, by substituting each constant for their atomic unit equivalent, we arrive at a much simpler generalized molecular Hamiltonian. Equation 29 represents the generalized molecular Hamiltonian in terms of atomic units.

\[
\hat{H} = -\frac{1}{2} \sum_{M=1}^{l} \frac{V_{M}}{M_{m}} - \frac{1}{2} \sum_{i=1}^{k} \nabla_{i}^{2} + \sum_{i=(M-(M+1))}^{\text{b=M-J}} (R_{a})^{-1} + \sum_{c=(1+(1+1))}^{d=\text{a-k}} (R_{c})^{-1} - \\
\sum_{x=M}^{y=k} (r_{x})^{-1}
\]

Equation 29.)
As we can see from equation 29, implementing atomic units simplifies the molecular Hamiltonian by removing all potential energy coefficients and replacing the kinetic energy coefficients with a factor of 0.5. Now, we will use the Born-Oppenheimer approximation to simplify the generalized molecular Hamiltonian further. The Born-Oppenheimer approximation states that because the nucleus is much heavier than the electrons, we can view the nucleus as being fixed in space relative to the motion of the electrons. Since the nucleus is fixed in space, its kinetic energy is zero and we can remove the nuclear kinetic energy term in the molecular Hamiltonian. Under the Born-Oppenheimer approximation, the generalized molecular Hamiltonian has the following form.

### Table 1.1.2 Atomic units and their SI Equivalents

<table>
<thead>
<tr>
<th>Property</th>
<th>Atomic Unit</th>
<th>SI Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass</td>
<td>Mass of electron, $m_e$</td>
<td>$9.1094 \times 10^{-31}$ kg</td>
</tr>
<tr>
<td>charge</td>
<td>Charge on proton, $e$</td>
<td>$1.6022 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>Angular momentum</td>
<td>$\frac{\hbar}{2\pi} = \hbar$</td>
<td>$1.0546 \times 10^{-34}$ J*s</td>
</tr>
<tr>
<td>distance</td>
<td>Bohr radius, $a_0 = \frac{4\pi e^2 \hbar^2}{m_e e^2}$</td>
<td>$5.2918 \times 10^{-11}$ m</td>
</tr>
<tr>
<td>energy</td>
<td>Hartree = $\frac{m_e e^4}{16\pi^2 e^2 \hbar^2} = \frac{e^2}{4\pi e a_0} = E_h$</td>
<td>$4.3597 \times 10^{-18}$ J</td>
</tr>
<tr>
<td>permittivity</td>
<td>$4\pi\varepsilon$</td>
<td>$1.1127 \times 10^{-10}$ C²<em>J⁻¹</em>m⁻¹</td>
</tr>
</tbody>
</table>
As we can see, implementing atomic units, as well as, the Born-Oppenheimer approximation drastically simplifies the generalized molecular Hamiltonian.

Let us now turn our attention to molecular wave functions. There are several ways to approach molecular wave functions; however, we will strictly use the Linear Combination of Atomic Orbitals to form Molecular Orbitals (LCAO-MO) approach. As the name implies, we are taking atomic orbitals from atom A and linearly combining them with atomic orbitals from atom B. Although it is not a postulate of quantum mechanics, a general rule of thumb of quantum mechanics is that whatever you put in, you get out. Said another way, the molecular orbitals we get out of a LCAO-MO calculation is dependent upon the kind and amount of atomic orbitals used in the combination. As an example, let’s look at the hydrogen molecule. We know there is one electron per nuclei, so we should have a molecular wave function which is a linear combination of each of hydrogens wave function. For example, the hydrogen molecule may have a molecular wave function in the form of the following.

\[ \psi_{\pm} = c_1 \psi_{1sA} \pm c_2 \psi_{1sB} \]

Where \( c_n \) represents the weighting coefficient which describes the relative contributions of each atomic orbital to the overall molecular orbital. Remember, the square of the wave function tells us the probability the particle is occupying the quantum state represented by
the that wave function, which it easily follows the square of the coefficients for atomic orbitals used in molecular orbital calculations tells us the contribution of that atomic orbital to the overall molecular orbital. The subscript on the wave function represents the quantum state described by that wave function, as well as, which nuclei the wave function is describing. For example, 1SA is telling us the wave function is describing a particle occupying a quantum state with the following list of quantum numbers \{1,0,0,\pm\frac{1}{2}\}, centered on nucleus A.

The different linear combinations (addition and subtraction) of atomic orbitals lead to two energetically distinct electronic states. The lowest in energy molecular electronic state, is described by the addition of equation 31. This electronic state describes a symmetric orbital with the electron distribution spread evenly across the two nuclei, which because of the symmetric nature of this orbital; it is commonly referred to as a “bonding orbital”.

Subtracting equation 31, we arrive at a molecular orbital which has a node between the two nuclei. The node between the nuclei increases the nuclear-nuclear repulsion energy and hence, this orbital is called the “antibonding orbital”. It should be noted, that this approach to form molecular orbitals is the simplest possible approach, which because of the simplicity we can derive explicit expressions for the coefficients in equation 31. Let us define the overlap integral as the following expression.

\[ S = \int_{-\infty}^{\infty} \psi_m^{*} \psi_n \, dr \] (32)
Now, using the orthonormal conditions, we can determine an explicit expression for the coefficients in equation 31. This will be possible from determining the normalized wave function for the antibonding molecular orbital for the hydrogen molecule.

Let’s remember the normalization condition says if we integrate the product of a wave function with its complex conjugate the result is 1. Let’s now use this information to arrive at the following.

\[
\int_{-\infty}^{\infty} c_{n}^{*}(1sA^{*} - 1sB^{*})c_{n}(1sA - 1sB)d\tau = 1 \quad (33.)
\]

where:

\( \tau = \) all coordinates of the wave function.

Now, let’s combine the coefficients to arrive at the following.

\[
\int_{-\infty}^{\infty} c_{n}^{2}(1sA^{*} - 1sB^{*})(1sA - 1sB)d\tau = 1 \quad (34.)
\]

Next, we pull out the coefficient, factor and then distribute the integral to arrive at the following expression.

\[
c_{n}^{2} (\int_{-\infty}^{\infty} 1sA^{*}1sA - \int_{-\infty}^{\infty} 1sA^{*}1sB - \int_{-\infty}^{\infty} 1sB^{*}1sA + \int_{-\infty}^{\infty} 1sB^{*}1sB)d\tau) = 1 \quad (35.)
\]
Using the normalization condition, as well as, the overlap integral, this reduces to the following expression.

\[ c_n^2 (1 - S - S + 1) = 1 \]  

\[ c_n^2 (2 - 2S) = 1 \]

\[ c_n^2 = \frac{1}{(2-2S)} \]

Thus,

\[ c_n = \frac{1}{\sqrt{2(1-S)}} \]

Now that we’ve established the normalization (probability) coefficients for each molecular orbital of the hydrogen molecule, let us now place these molecular orbitals into determinantal form. The hydrogen molecule, may expressed as the following determinant.

\[ \psi_{H_2} = \frac{1}{\sqrt{2}} \begin{bmatrix} \psi_b \alpha(1) & \psi_b \beta(1) \\ \psi_b \alpha(2) & \psi_b \beta(2) \end{bmatrix} \]

Where in this representation, the subscript (b) tells us this element represents a bonding molecular orbital. The concept of LCAO-MO’s can be generalized to any
diatomic molecule by realizing that for every atomic orbital in, we should expect a molecular orbital out and it is only energetically favorable to form LCAO-MO’s from atomic orbitals with the same shape and energy. Basically, when forming diatomic molecules take linear combinations using the same orbital from atom A and atom B, if this is not possible, define an internuclear axis and pair the atomic orbitals that have the most overlap (overlap is intrinsically dependent upon the shape of the orbital and in turn overall energy of the orbital).

It should not come as a surprise, but as it turns out, the LCAO-MO approach can be generalized even further to polyatomic molecules. For example, the water molecule may have molecular orbitals generated by the following linear combinations of atomic orbitals.

$$\psi_{H_2O} = c_1 1s_{H_1} + c_2 1s_{H_2} + c_3 2s_{A} + c_4 2p_{yA} + c_5 2p_{yA} + c_6 2p_{yA}$$  \hspace{1cm} (41)$$

Since the linear combination involves six atomic orbitals, we should expect six molecular orbitals out, which we can then put in determinantal form similar to what we did for the hydrogen molecule. The concept of LCAO-MO’s can be generalized even further to any polyatomic molecule, by taking linear combinations of every atomic orbital, on every nucleus. It is worthwhile to mention, the coefficients for each atomic orbital used in the linear combination, are determined self-consistently in a procedure called the “Self-Consistent Linear Combination of Atomic Orbitals to form Molecular Orbitals” (SCF-LCAO-MO) and once we know the coefficients we can determine the
energies of each molecular orbital. But, before we talk about this procedure, let us remember, the LCAO-MO approach presented so far, has been the simplest approach to describing the electronic structure of molecules and as we may remember from the helium case, any system with two or more electrons becomes analytically unsolvable. Hence, we cannot derive the exact wave function for any system with two or more electrons and the wave functions presented have been approximate hydrogen-like wave functions. As it turns out, a better approximation to the exact wave function for the hydrogen molecule describes the bonding molecular orbital as the following.

\[
\psi_b = c_1(1s_A + 1s_B) + c_2(2s_A + 2s_B) + c_3(2p_{zA} + 2p_{zB})
\]

42.

Where again, all coefficients are determined self consistently.

The realization that including higher angular momentum wave functions can improve the accuracy of the calculation, leads to the development of basis sets. Basis sets were developed to approximate the non-zero probability of the electron occupying anywhere in space. It is left as an exercise to the reader to verify that the electron has a non-zero probability of occupying any position in space. It can be argued that basis sets began in 1930, by the American physicist John Slater. John Slater thought outside of the box and developed a set of non-hydrogen-like orbitals termed “Slater orbitals”, which have the following functional form.

\[
S_{n,l,m_l} = N_{nl}r^{n-1}e^{-\xi r}Y_l^m_l(\theta, \phi)
\]

43.
Where \( n, l, \) and \( m_l \) retain their usual meaning, \( \zeta \) represents a variational parameter, \( r \) represents the distance between the electron and the nuclei and \( N_{nl} \) is the normalization constant defined as the following.

\[
N_{nl} = \frac{(2\zeta)^{n+\frac{1}{2}}}{[2n]^{\frac{3}{2}}}
\]

44.

Up until this point, we have not explicitly expressed the functional form of the radial component of hydrogen like wave functions, although to compare the simplicity of Slater orbitals, as well as, what’s to follow, we will introduce a general radial solution to the Schrodinger equation for the hydrogen atom. Generally, the radial component of a hydrogen like wave function (in atomic units) can written as the following.

\[
R_{nl}(r) = -\left\{ \frac{(n-l-1)!}{(2n[n+l])^{\frac{3}{2}}} \right\}^{\frac{1}{2}} \left( \frac{2}{n} \right)^{l+\frac{3}{2}} r^l e^{-\frac{r}{n}} L_{n+1}^{2l+1}\left( \frac{2r}{n} \right)
\]

45.

Where again, \( n, l, m_l, \) and \( r \) retain their usual meaning. The last term in equation 45 are called “Associated Laguerre Polynomials” and are clearly dependent upon the principal and angular quantum number, as well as, the distance between the electron and the nuclei. It is not hard to tell that equation 43 is much simpler then equation 45, although it’s simplicity is not without a price. For example, the variational parameter, \( \zeta, \) is determined using the variational principle. The variational principle may be expressed
mathematically as the following.

\[ E_\phi = \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \quad 46. \]

The variational principal states “we can calculate an upper bound to the exact energy by using any trial function” and, as it turns out, we can couple equation 46 with the minimization technique introduced in calculus and include parameters we can continuously adjust until an exact energy is reached. Hence, the variational parameter, \( \zeta \), in Slater orbitals.

The introduction of Slater orbitals was clearly an improvement over the hydrogen like radial functions, not only in simplicity but it also contained a parameter which could be continuously minimized until either the exact energy was reached or the energy couldn’t be minimized further using that specific trial function. Unfortunately, while the radial component of the wave function consisting of Slater orbitals were easier to work with then hydrogen like orbitals, their integrals were still difficult to evaluate. However, if we use Gaussian functions instead of Slater orbitals, the integrals become much simpler. Therefore, it became desirable to represent the radial component of the wave function as Gaussian functions which have the following form.

\[ G_n(r) = N_n r^{n-1} e^{-\zeta r^2} \quad 47. \]

Where \( N_n \) represents a normalization coefficient, and \( r \) and \( n \) retain their usual meaning. While the use of Gaussian functions simplified approximating the Schrodinger equation, their behavior is very different then the behavior of Slater orbitals, especially for small \( r \) values. To overcome the difficulties associated with changing from Slater orbitals to
Gaussian based orbitals, researchers have curve fit linear combinations of Gaussian functions to Slater orbitals, in what can be considered “The Dawn of Basis Sets”. The fitted Gaussian functions are termed “STO-NG”, where STO stands for Slater Type Orbitals, N represents the number of Gaussian functions used to represent a Slater orbital and the G tells us that we are using Gaussian functions to approximate Slater orbitals. The researchers found that the accuracy of the calculation increased with increasing N, as well as, discovered the most effective value of N was 3. Therefore, the most commonly used STO basis set is STO-3G. An important realization is that we are no longer dealing with single radial functions, which means we need another way to evaluate the normalization coefficients. This leads us back to the Self-Consistent Field Method mentioned earlier. Using helium as an example, let’s imagine we want to determine the ground state energy of the helium atom, using an STO-3G basis set. Assuming we have already variationally determined the \( \zeta \) values, let us self-consistently determine the coefficients for each Gaussian function used to represent a Slater type orbital. The equation we want to solve is the following eigenvalue problem.

\[
\tilde{H}_1^{\text{eff}}(r_1) \phi(r_1) = \epsilon_1 \phi(r_1)
\]

Where:

\[
\tilde{H}_1^{\text{eff}}(r_1) = -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} + V_1^{\text{eff}}(r_1)
\]

and
Physically, equation 49 represents the total (expected) energy for electron 1 and equation 50 represents the expectation value from the potential interaction of electron 2 on electron 1.

\[
V_{1}^{\text{eff}}(r_1) = \int \phi^*(r_2) \frac{1}{r_{12}} \phi(r_2) dr_2 \tag{50}
\]

\(\phi(r_1)\) represents the trial function or in this case a wave function composed of an STO-3G basis set with an \(l=0\), \(m_l=0\) spherical harmonic. \(\epsilon_1\) represents the orbital energy of the orbital electron 1 is occupying.

How the self-consistent field method works is the following. We first take a guess at the wave function for electron 2 in equation 50 should be, in this case, we guess (could be variationally determined) at what the coefficients of each Gaussian function should be. We then use the \(V_{1}^{\text{eff}}\) value as input for the effective Hamiltonian for electron 1 and then solve equation 48 for the wave function of electron 1. Typically, the initial and final wave function differs substantially after the first cycle and this process continues until the initial wave function and the output wave function are sufficiently close or “self-consistent”. The self-consistent field method can be applied to molecular wave functions as well. For example, if we let each atomic orbital be represented as \(\beta_j\), then the ith molecular orbital may be expressed as the following

\[
\psi_i = \sum_{j=1}^{N} c_{ij} \beta_j \tag{51}
\]
where $N$ is the number of atomic orbitals linearly combined to form the $i$th molecular orbital. It is important to understand each $\beta_j$ in equation 51 is a sum of Gaussian functions (dictated by the basis set), with each term having its own coefficient which is determined self-consistently. The self-consistent field method can generally be applied to any basis set used and will be used throughout this project to determine the coefficients for each Gaussian function contained in the basis set.

Now that we have discussed how to determine the coefficients for each Gaussian function of any basis set, let us turn our attention back to basis sets. It is important to realize, that STO-NG basis sets explicitly treat valence electrons with sums of Gaussian functions while inner electrons are represented by a single Slater type orbital. Basis sets that treat the inner shell electrons with a single Slater orbital and the valence-shell electrons by a linear combination of Slater orbitals are commonly called “Split-Valence Basis Sets”. Split-valence basis sets are compactly written as $N$-MPG, where $N$ represents the number of Gaussian functions used to represent an inner electron, the $M$ represents the number of Gaussian functions used for the smaller (bonding) valence orbital, the $P$ represents the number of Gaussian functions used to express the larger valence orbital. Researchers have found that while the STO-NG approximation was better than a single radial component wave function, treating the inner electrons as a linear combination of Gaussian functions greatly improves the accuracy of the calculation. Therefore, split-valence basis sets are typically in the form of 6-31G or 6-311G, where the 6 indicates 6 Gaussian functions are linearly combined to represent an electron occupying an inner orbital, the hyphen tells us that the basis set is a split-valence basis set, the 3 after the hyphen tells us 3 Gaussian orbitals are used to represent the smaller
valence orbital, while the 1 indicates that a single Gaussian function is used to represent the larger valence orbital. At this point, you might be asking yourself “I thought all orbitals were the same size?”, and what we mean by smaller and larger orbital is the orbital used in bonding compared to an orbital that would be used for lone pairs or a single electron. Typically, bonding orbitals are smaller than lone pair orbitals (due to coulombic interactions), and hence the need for difference size valence orbitals. The additional 1 in the 6-311G basis set indicates an additional Gaussian function used to represent the larger valence orbital. While representing inner electrons as linear combinations of Gaussian functions was an improvement for basis sets, it was still missing a fundamental feature, which was polarization. Polarization is used to describe the physical phenomena of orbitals distorting as one atom approaches another atom or said another way, polarization is used to describe the electron-electron repulsion of electrons from system A approaching electrons in system B. Generally, to polarize a basis set with angular momentum (l), we take a linear combination(s) of Gaussian function(s) with angular momentum (l+1) and Gaussian functions with angular momentum (l). This allows the electrons in the orbital described by angular momentum (l) to move to a position that might have been described by an orbital with an angular momentum of (l+1). For example, if we wanted to polarize the 1s orbital of hydrogen, we would take a linear combination of a 1s and 2p Gaussian function. This linear combination would allow hydrogens electron to move to one side or another when another atom approached it. While we used hydrogen as an example, we can polarize any orbital as long as we know its angular momentum. Generally, a split-valence basis set will be polarized if it has an asterisk(s), where a single asterisk represents a single polarization function on all
of the valence electrons of heavy atoms (anything other than hydrogen or helium) and a double asterisk represents a polarization function summed into hydrogen. Split-valence basis sets can also include additional diffuse functions, which are defined by their \( \zeta \) values. Since Gaussian and Slater orbitals for that matter, have negative \( \zeta \) values, as the value gets big, the space the electron is allowed to occupy shrinks and the electron comes closer to the nuclei. While if the \( \zeta \) value becomes small, the space the electron is allowed to occupy becomes big and we call that a “diffuse function”. Typically, we can tell if a split-valence basis set has diffuse functions if a + is included or ++. For example, a 6-31G+ is a regular 6-31G basis set with a single diffuse function for every valence electron, where as a 6-31G++ is a regular 6-31G+ basis set with a single diffuse function added onto hydrogen. Split-valence basis sets of this form are generally referred to as “Pople basis sets”, because they were primarily developed by John Pople in the late 1960’s. While Pople basis sets were a huge improvement over the hydrogen-like radial components of the wave-function, they neglected electron correlation. Noticing that by using a multi-reference wave function as the initial wave function used in optimizing zeta values, Dr. Thom Dunning optimized a series of Gaussian functions using a wave function in which up to 2 electrons sampled the space allowed by the basis set. Before we get to what it means to be a multi-reference wave function or what it means for 2 electrons to sample the allowed space, let us finish the discussion on basis sets. Dr. Dunning’s basis set were called the “Correlation Consistent” basis set because of the fact they incorporated electron correlation. Surprisingly, while Dr. Dunning’s basis set were harder to optimize, they are easier to comprehend then the split-valence basis sets of John Pople. Typically, Dr. Dunning’s correlation consistent basis sets are denoted
cc-pvlz for correlation consistent polarized valence l zeta or aug-cc-pvlz (augmented correlation consistent polarized valence l zeta) if diffuse functions are added. The (l) represents the largest angular momentum quantum number used in the basis and if we are using the augmented version of the correlation consistent basis sets, then we add an additional (small zeta valued) Gaussian function to every angular momentum in the basis. A beautiful feature of Dr. Dunning’s basis set is the fact that once we choose a basis set (the highest angular momentum we wish to include) then we write out the quantum numbers and countdown to l = 0, after which we are rewarded with how many Gaussian functions are used for every angular momentum. For example, if we wanted to used cc-pvdz, the highest angular momentum used in the basis set is l = 2, which is a d-orbital, so the basis set would include a linear combination of Gaussian functions representing the following list (3s2p1d). Where the 3s tells us 3, s-orbital (l = 0) Gaussian functions are used with varying zeta values, 2p tells us 2, p-orbital (l=1) Gaussian functions are used and the 1d tells us there is a single d-orbital (l=2) Gaussian function used in the basis set. As example of the augmented version of the correlation consistent basis set let’s look at aug-cc-pvdz. Well, since cc-pvdz has the following list of Gaussian functions (3s2p1d), then we can expect the augmented version of the cc-pvdz basis set to include an additional (small zeta valued) Gaussian function. So, the aug-cc-pvdz basis set would have the following list of Gaussian functions (4s3p2d). As another example, let us consider the cc-pvqz basis set. Okay, we know the highest angular momentum in the basis set is l = 4 (g-orbital) so, we have the following list of Gaussian functions (5s4p3d2f1g), however, if we are using the augmented version of the cc-pvqz basis set then the list of Gaussian functions becomes (6s5p4d3f2g). This trend continues regardless
of the highest angular momentum used in the basis set and it should be noted that the highest angular momentum containing correlation consistent basis set the author has seen, is aug-cc-pv7z. While Pople’s split-valence basis set and Dunning’s basis set are the most commonly used basis sets, they are by no means a comprehensive list of basis sets, and in fact, new basis sets are constantly being developed and will continue to be developed as technology catches up with our theories. However, since this project predominantly uses Pople’s split-valence, Dunning’s correlation consistent basis set or in a specific case, a modified version of Dunning’s correlation consistent basis sets, we will leave our discussion of basis sets and continue on to the fundamental theories used in electronic structure theory. Before we begin our discussion of the fundamental theories used in electronic structure theory, it will be easier to explain if we move from first quantization (the realm of Slater determinants) to second quantization. Upon moving from first quantization to second quantization we enter the “Fock space”, which is an abstract vector space where every determinant used to represent the electronic state of a system is represented by an “Occupation-number (ON) vector” |K>. We will define |K> as the following.

\[ |k> = |k_1, k_2, \ldots, k_M>, k_p = \begin{cases} 1 & \psi_m \text{ is occupied} \\ 0 & \psi_m \text{ is unoccupied} \end{cases} \]  

Where each \( k_p \) represents an element of the Slater determinant and the occupation number \( k_p \) is 1 if \( \psi_m \) is present in the determinant and 0 if it is absent. We will define the inner product between two orthonormal set of spin orbitals |k> and |m> as the following.

\[ \langle k|m \rangle = \delta_{k,m} = \prod_{p=1}^{m} \delta_{k_p m_p} \]
It is important to note this definition of the inner product between vector $|k>$ and vector $|m>$ is consistent with the overlap between two Slater determinants containing the same number of electrons, although the extension of equation 53 to have defined but zero overlap between states with different number of electrons is a special feature of second quantization and the Fock space. This special feature allows for a unified description of systems with varying number of electrons. The occupation number vectors in equation 52 constitute an orthonormal basis in the $2^M$–dimensional Fock space, denoted, $F(M)$. This Fock space may be broken down as a direct sum of subspaces, denoted $F(M,N)$. The direct sum is represented by the following expression.

$$F(M) = F(M,0) \oplus F(M,1) \oplus F(M,2) \oplus ... \oplus F(M,M)$$  \hspace{1cm} 54.)$$

Where $F(M,N)$ contains all occupation number vectors obtained by distributing $N$ electrons among $M$ spin orbitals, which is to say, all occupation number vectors for which the sum of the occupation number is $N$ is represented by the following.

$$N = \sum_{p=1}^{M} k_p$$  \hspace{1cm} 55.)$$

It is important to realize the subspace represented by $F(M,0)$ consists of occupation number vectors with no electrons, contains a single vector, termed the “true vacuum state”. The true vacuum state is represented by following.

$$|\text{vac}> = |0_1, 0_2, 0_3, ..., 0_M >$$  \hspace{1cm} 56.)$$

According to equation 53 the true vacuum state is normalized to unity.
Before we continue, it is worthwhile to note, approximations to an exact \( N \)-electron wave function are expressed in terms of vectors in the Fock subspace \( F(M,N) \) of dimension equal to the binomial coefficient, \( \binom{M}{N} \). The final results that we need to introduce from second quantization is the creation and annihilation operators, which allows us to move electrons from one spin orbital to another. The creation operator will be defined as the following.

\[
\alpha_p^\dagger = |k_1, k_2, \ldots, 0_p, \ldots, k_M> = \Gamma_p^k |k_1, k_2, \ldots, 1_p, \ldots, k_M>
\]

\[
\alpha_p^\dagger = |k_1, k_2, \ldots 1_p, \ldots, k_M> = 0
\]

Where equation 58 is placing an electron in the unoccupied \( p \)th spin-orbital and equation 59 is required to preserve the antisymmetric nature of the electron. \( \Gamma_p^k \) represents the phase factor, which is equal to +1 if there are an even number of electrons in the spin orbitals (to the left of \( P \) in the occupation number vector) and equal to -1 if there are an odd number of electrons in these spin orbitals. The phase factor is represented by the following equation.

\[
\Gamma_p^k = \prod_{q=1}^{p-1} (-1)^{k_q}
\]

Where \( k_q \) indicates the phase factor is for the \( k_q \)th spin orbital. Now that we have introduced the creation operator and its properties, we can compactly express the properties of the creation operator by defining it as the following.
Let us now define the annihilation operator as the operator which reduces the k_{p}th spin orbital from 1 to 0 if it is occupied and yields 0 if the spin orbital is unoccupied. Using equation 61 as a guide, we will define the annihilation operator by the following relation.

$$a_{p}^\dagger |k >= \delta_{k_p,0} \Gamma_{p}^k |k_{1},...,1_{p},...,k_{M} >$$  \hspace{1cm} (61.)

Now that we have introduced and defined all of the results of second quantization that we need, let us discuss the fundamental electronic structure methods. This discussion is not a comprehensive discussion of every fundamental electronic structure theory but of the theories used within the project. It can be argued that the field of electronic structure theory began with the realization that an exact wave function is wave function in which every electron samples all of the available space. We will define the available space, as all of the molecular orbitals produced during the LCAO-MO process. A wave function, in which every electron samples all of the available space, is called a “full configuration interaction” wave function and represents the exact wave function for a quantum mechanical system. Unfortunately, this involves a large number of determinants (depending on the system studied) to evaluate and is impractical for just about any molecule except H_{2} (H_{2}O has been done, but this only possible by exploiting its symmetry). In fact, the following equation quantitatively determines how many determinants there will be to evaluate.

$$a_{p} |k > = \delta_{k_{p+1}} \Gamma_{p}^k |k_{1},...,0_{p},...,k_{M} >$$  \hspace{1cm} (62.)
\[ N_{\text{det}} = \binom{M}{N} = \frac{M!}{N!(M-N)!} \tag{63} \]

Where \( M \) represents the number of spin orbitals in the determinant and \( N \) represents the number of electrons sampling the space (\( M \)). Therefore, configuration interaction involving only the valence electrons is much more common. Let us define configuration interaction wave function by the following linear combination of determinants.

\[ |C| = \sum_i C_i |i| \tag{64} \]

Where each state vector \(|i|\) is either the ground state Slater determinant (often referred to as the Hartree-Fock state) or the Hartree-Fock state operated on by a linear combination of excitation operators. Let us define a single excitation by the following product of annihilation and creation operators.

\[ \hat{X}_i^A |HF\rangle = C_i^A a_i^\dagger a_i |HF\rangle \tag{65} \]

Where the annihilation and creation operators retain their usual meaning and \( C_i^A \) represents the coefficient generated by the excitation. It should be noted, equation 65 is working over one electron, although in practice, the excitation operator works over \( N \) electrons (whether that’s valence or all electrons) and all spin orbitals. Now, let us define the double excitation as the following.
\[ \tilde{\chi}^{AB}_{ij} |HF> = C_{ij}^{AB} a_A^+ a_B^+ a_i a_j |HF> \]  \hspace{1cm} (66.)

Where everything in equation 66 retains its usual meaning. This trend can continue up until N and in fact, the full configuration interaction includes N excitations. Now that we have defined what it means for an operator to be a single, double, etc, operator. Let us define what it means to be a single or double configuration interaction wave function. A single configuration interaction wave function will be defined as the following.

\[ |\text{CIS}>= (1 + \sum_{AI} \tilde{\chi}_I^A) |HF> \]  \hspace{1cm} (67.)

Where the 1 in equation 67 preserves the ground state in the configuration interaction wave function and the summation runs over all N electrons. Let us now define the configuration interaction single and doubles wave function as the following.

\[ |\text{CISD}>= (1 + \sum_{AI} \tilde{\chi}_I^A + \sum_{A>B, IJ} \tilde{\chi}_{IJ}^{AB}) |HF> \]  \hspace{1cm} (68.)

As the reader might have suspected, with \( N_{\text{det}} \) comes N coefficients to evaluate. Configuration interaction determines the coefficients by variationally optimizing the expectation value of the electronic energy that minimizes the ground state through the following equation.

\[ E_{CI} = \frac{\langle \text{CI}|\tilde{\mathcal{H}}|\text{CI} \rangle}{\langle \text{CI}|\text{CI} \rangle} \]  \hspace{1cm} (69.)

While configuration interaction is a great approach to describing the electronic structure of atoms and molecules, it is not without its flaws. For example, the accuracy of
the theory comes from higher order excitations, specifically the quad excitations and higher and it is not size extensive, meaning that we cannot break up the configuration interaction energy into pieces (so the $E_{\text{total}} = E_A + \ldots E_Z$ is not preserved). While configuration interaction is not perfect, it was a great starting point for all other ab initio electronic structure theories. In fact, using the results of configuration interaction, a new theory was developed. This new theory, called "coupled cluster theory" essentially takes all of the good parts of configuration interaction, adds higher order excitations and is size extensive. Coupled cluster theory is defined by the coupled cluster wave function defined as the following.

$$|\text{CC} > = \exp(\hat{T})|\text{HF} >$$  \hspace{1cm} (70.)

Where:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots$$  \hspace{1cm} (71.)

$$\hat{T}_1 = \sum_{AI} t_i^A a_i^+ a_I$$  \hspace{1cm} (72.)

$$\hat{T}_2 = \frac{1}{4} \sum_{AB} t_{ij}^{AB} a_i^+ a_j^+ a_i a_j$$  \hspace{1cm} (73.)

Where equation 71 represents the cluster operator, which ends on N, where N is the total number of electrons in the system (valence or total). Equation 72 and 73 represent individual cluster excitations, for example equation 72 is the single cluster operator and equation 73 represents the double cluster operator. The creation and annihilation operators retain their usual meaning. The beautiful aspect of coupled cluster theory is that all we need is the single and double cluster operators and we can produce
all other higher order excitations. In fact, this is where coupled cluster gets its accuracy from and is so accurate we typically refer to the coupled cluster wave function as an exact wave function. Higher order excitations produced from lower cluster operators are referred to as “disconnected cluster operators” and are products of lower order cluster operators. For example, the coupled cluster single and double wave function is produced from the following linear combination of cluster operators.

\[
|\text{CCSD} > = \psi + \hat{T}_1 \psi + \left( \frac{1}{2} \hat{T}_2 \right) \psi + \left( \frac{1}{6} \hat{T}_4 \right) \psi + \left( \frac{1}{2} \hat{T}_2^2 \right) \psi + \left( \frac{1}{24} \hat{T}_4^2 \right) \psi + \cdots
\]

We have used the series representation for the cluster operator instead of the exponential and for simplicity, we have represented the usual Hartree-Fock occupation number vector as \(\psi\). The single and double coupled cluster wave function clearly contains the higher order triple and quadratic cluster operator by only using the single and double cluster operator as well as going up until N electrons (valence or total). Perfect! This is the wave function we have been searching for, not only does it contain higher order excitations so that every electron samples all of the space provided to them, it is size extensive and provides a very simple and systematic way to determine the coefficients. First, the disconnected cluster amplitudes are determined by multiplying the amplitudes of the connected (original) cluster operators that make them up. The total cluster excitation amplitude is then a sum of the connected and disconnected cluster amplitudes. Which means the hard part is determining the amplitude for two cluster operators (in the single and double case) which are determined by iteratively solving the following equation by Newton’s Method.\(^\text{12}\)
\[ \epsilon_u t_u = -< u | \exp(-\hat{T}) \hat{\phi} | \text{CC} > \]  

\[ E = E_{HF} + < HF | \hat{\phi} | CC > \]

\(<u| represents a reference occupation number vector in which the electrons sample the same space they will have sampled after being operated on by the cluster operator (for example, a configuration interaction wave function) and \( \hat{\phi} \) represents the fluctuation potential which is defined as the “difference between the two electron excitation operator and the one electron excitation operator”. Upon determining the cluster amplitudes, we then use the results to determine the coupled cluster energy using the following equation.

Where \( E_{HF} \) represents the varitionally determined energy using the Hartree-Fock reference occupation number vector. While so far, we have focused our attention on coupled cluster single and double theory, it is important to realize, coupled cluster does not stop at doubles and in fact, currently goes up to CCSDTQ56 with the help of super computers. The highest level of cluster excitation used in this study is triple excitations and that is with the help of perturbation theory. Perturbation theory states that we can break up our system into solvable and unsolvable parts and then sum the results. Using the Schrödinger equation for helium as an example, perturbation theory states we can solve the kinetic energy terms and then approximate the electron-electron repulsion term, followed by summing the results. How this relates to coupled cluster theory is that it is common to use perturbative triples in the coupled cluster calculation. This means the triple excitation energy is calculated separately and without the higher order disconnected excitations and the result is then summed into the coupled cluster single and double
energy. Coupled cluster theory which includes perturbative triples is commonly denoted CCSD(t). Now that we have discussed coupled cluster theory and perturbation theory, it seems appropriate to discuss Moller-Plesset Perturbation theory. Moller-Plesset theory is a textbook example of perturbation theory which uses the fact that \( E_{\text{total}} = E_{\text{HF}} + E_{\text{corr}} \), as it essentially begins with the Hartree-Fock occupation number vector and sums in higher level corrections meant to approximate the electron-electron repulsion energy. Moller-Plesset Perturbation theory is defined by the following set of equations.

\[
E_{\text{MP}}^{(0)} = \sum_i \epsilon_i \quad \text{(77.)}
\]

\[
E_{\text{MP}}^{(1)} = \langle \text{HF} | \hat{\Phi} | \text{HF} \rangle \quad \text{(78.)}
\]

\[
E_{\text{MP}}^{(2)} = -\sum_{A>B, I>J} \frac{|\theta_{AIB} - \theta_{AIB}|^2}{\epsilon_A + \epsilon_B - \epsilon_I - \epsilon_J} \quad \text{(79.)}
\]

Where equation 77 represents the sum of all of the orbital energies present in the occupation number vector, equation 78 represents the first order approximation to the electron-electron repulsion energy by determining the expectation value of the fluctuation potential and equation 79 represents the second order approximation to the electron-electron repulsion energy in the form of the absolute value of the difference between the coefficients found from the two electron excitation operator operating on the ground occupation number vector (Hartree-Fock state) divided by the orbital energies used in equation 77. If we sum all of the perturbations, the Moller-Plesset perturbation energy is found by solving the following equation.
\[ E^{\text{MP}2} = E^{(0)}_{\text{MP}} + E^{(1)}_{\text{MP}} + E^{(2)}_{\text{MP}} + h_{\text{nuc}} \quad \text{(80.)} \]

Where \( h_{\text{nuc}} \) represents the nuclear-nuclear repulsion energy (if using the Born-Oppenheimer approximation, ignore this term). A surprising result is that equation 80 reduces to the following equation.

\[ E^{\text{MP}2} = E_{\text{HF}} - \sum_{A>B,I>J} \frac{|\theta_{\text{AIBJ}} - \theta_{\text{AIBJ}}|^2}{\epsilon_A + \epsilon_B - \epsilon_I - \epsilon_J} \quad \text{(81.)} \]

Where in Moller-Plesset theory, the Hartree-Fock energy is defined by the following equation.

\[ E_{\text{HF}} = E^{(0)}_{\text{MP}} + E^{(1)}_{\text{MP}} + h_{\text{nuc}} \quad \text{(82.)} \]

Thus, Moller-Plesset theory gave us a nice, systematic way to determine the electronic energy of a system. A fantastic result from Moller-Plesset theory comes from the use of coefficients generated from the double excitation operator. This is important because it allows coupled cluster theory to extract the cluster amplitudes from Moller-Plesset generated occupation number vectors, which the electrons would have sampled same space (i.e. the singles and doubles). As in coupled cluster theory, Moller-Plesset theory does not stop with a second order perturbation and in fact, can go up to 4\(^\text{th}\) order (although it’s less commonly used).\(^{12}\) Although not a fundamental electronic structure theory, this project uses a non ab initio method, density functional theory (DFT). Density functional theory was developed in the 1960’s to overcome the difficulties encountered with ab initio approaches to understanding the electronic structure of atoms and molecules. Density functional theory does not use a wave function but instead uses an experimentally fitted density functional. The fact that density functional theory relies
on the quality of the experiment instead of the quality of the theory, has been a source of error and has most quantum chemists questioning if the results are right for the right reason. Since DFT does not use a wave function but uses an experimentally fitted functional, it will be left to reader to understand how it works.\(^{2,13,14,15}\)

Before we move on, it is worthwhile to mention quadratic configuration interaction. Quadratic configuration interaction was developed by John Pople and Martin Head-Gordon in 1987\(^ {16}\) and is similar to regular configuration interaction theory except, it’s size extensive and includes higher order excitations to approximate the exact wave function. Quadratic configuration interaction singles and doubles (QCISD) uses the fact that \(E_{\text{total}} = E_{\text{HF}} + E_{\text{correlation}}\) and therefore solves for the correlation energy. Let us define Quadratic configuration interaction singles and doubles by the following set of equations.

\[
\langle \psi_0 | \hat{H} | T_2 \psi_0 \rangle = E_{\text{correlation}} \tag{83}\]

\[
\langle \psi^a_i | \hat{H} | (T_1 + T_2 + T_1 T_2) \psi_0 \rangle = \alpha^a_i E_{\text{correlation}} \tag{84}\]

\[
\langle \psi^a_{ij} | \hat{H} | (1 + T_1 + T_2 + \frac{1}{2} T_2^2) \psi_0 \rangle = \alpha^{ab}_{ij} E_{\text{correlation}} \tag{85}\]

Where everything in equations 83-85 are defined in the exact way as in coupled cluster theory. Now that we defined the fundamental electronic structure theory methods, we can move along to modern electronic structure theory. Currently, electronic structure methods, which use the fundamental theories, focus on extrapolating various energetic components to the basis set limit i.e. replicating the use of an infinite amount of angular momentum in the basis set, which would lead to convergence to the exact energy.
Modern electronic structure methods that focus on extrapolating to the basis set limit are termed “Compound Methods” and are predominantly found in three forms; the Gaussian methods, the Complete Basis Set methods and the Weizmann methods. The Gaussian methods, which are the least accurate of the compound methods, exist in four flavors. Gaussian-1, Gaussian-2, Gaussian-3 and Gaussian-4, and within the subset, the accuracy increases with the number of the method. For example, Gaussian-3 is more accurate the Gaussian-2 but less accurate the Gaussian-4. The Gaussian methods work by the following. Gaussian-1 begins with an optimization using an MP2 wave function with all electrons involved in the excitations, as well as, with a 6-31G* basis set. A zero-point energy calculated using the Hartree-Fock wave function and then scaled by 0.8929 (to account for the lack of explicit electron correlation treatment) the result is then summed into the initial MP2 energy, which is then summed into a Quadratic configuration interaction energy which has been extrapolated out to the basis set limit. Gaussian-2 gains accuracy over Gaussian-1 by adjusting the following:

- The MP2 energy is calculated using a 6-311G* basis set.
- The MP2 basis set includes an additional 2d and one f Gaussian function on all heavy atoms.
- The MP2 basis set includes an additional p Gaussian function on all heavy atoms.

Gaussian-3 gains accuracy over Gaussian-2 by including relativistic effects such as spin-orbit coupling\(^{17}\), as well as, includes core electrons when handling electron correlation. Gaussian-3 works in the following way.
1.) Initial structure is found using Hartree-Fock wave function with a 6-31G* (HF/6-31G*).

2.) Zero point energy is calculated using a HF/6-31G* and a scaling factor of 0.8929 is applied. Zero point energy is then summed into the total energy.

3.) Initial structure is reoptimized using an MP2/6-31G* wave function, including all electrons in the treatment of electron correlation.

4.) A single point energy calculation is computed using a MP4/6-31G* wave function, which is then modified by the following:
   a.) Correction for diffuse function.
   b.) Correction for higher polarization function.
   c.) QCISD correction
   d.) Correction for larger basis set effects caused by assumption of separate basis set extensions for diffuse functions and higher polarization functions.

5.) A spin-orbit correction is summed in to the energy obtained from step 4.

6.) Higher level corrections are then summed into the overall energy, which includes corrections for pairs of valence electrons in molecules, unpaired electrons in molecules, pairs of valence electrons in atoms and unpaired electrons in atoms.

While Gaussian-3 is an improvement over Gaussian-4, it is not size extensive, making it difficult to apply to larger molecules. Gaussian-4, on the other hand, is size-extensive and gains its accuracy over Gaussian-3 by trying to eliminate known errors in our theories, rather than taking a more robust theoretical approach. How Gaussian-4 gains accuracy over Gaussian-3 is the following.
1.) The Hartree-Fock limit is determined for the total inclusion of energy.

2.) Increasing the number of d-polarization functions used in the basis set. For example, 3d functions are included for first row atoms and 4d functions are included for second row atoms.

3.) QCISD(T) is replaced with CCSD(T).

4.) Initial structure and zero point energy is calculated using a density functional (B3LYP) with a 6-31G(2df,p) basis set. The (2df,p) indicates an additional 2d and a single f function on heavy atoms and additional p function on hydrogen.

5.) Includes an additional 2 higher level correction parameters.
   a.) An additional correction is added for pairs of electrons in radical molecules that also have an ion.
   b.) An additional correction for molecules with a valence 1s pair of electrons.

It is important to note the absolute error for Gaussian-4 reduces to 0.83 kcal/mole, compared to Gaussian-3, which had a mean absolute error of 1.02 kcal/mole. The Gaussian methods were a great first approach to approximate the infinite basis set limit but it was not without its flaws, for example, the inability for Gaussian-2/3 to be size extensive. The flaws of the Gaussian methods lead to the development of the complete basis set methods. The overall goal of the complete basis set methods was to provide a size extensive compound method, which satisfied the variational principle, as well as, invariant to unitary transformations among degenerate orbitals. The need to satisfy this criteria lead to the development of 3 main subsets of complete basis set methods; Complete Basis Set APNO (CBS-APNO), Complete Basis set-4M (CBS-4M) and
Complete Basis Set-Q (CBS-Q). The complete basis set methods are similar to the Gaussian methods except that the initial “lower level” of theory calculation is performed at a higher level of theory. The complete basis set methods work in the following way.

**CBS-Q:**

1.) Initial structure is computed using an MP2/6-31G* wave function, was includes every electron in the treatment of electron correlation.

2.) Zero point energy is computed using a HF/6-31G* wave function and scaled by 0.91844.

3.) The Hartree-Fock component is then computed using a large basis set, which depends on the atoms in the molecule.\(^1\)

4.) Calculate electron correlation contribution using the MP2 model with a large basis set, which also depends on the molecule being studied.

5.) Calculate electron correlation contribution using an MP4/6-31G**(df,dp) wave function.

6.) Calculate electron correlation contribution using an QCISD(T)/6-31G** wave function.

7.) Spin-orbit corrections.

The results of each step are then summed into the initial step (step 1) to arrive at a CBS-Q energy.

CBS-4 works in almost an identical way, except the initial structure is calculated using a Hartree-Fock/3-21G wave function with each additional step using a truncated basis set,
when compared to CBS-Q. Also, CBS-4 does not include a QCISD(T) correction. The CBS-APNO method is regarded as the most accurate complete basis set method, which is able to achieve accuracy within 0.5 kcal/mole from the experimental value. CBS – APNO works in the following way.

**CBS-APNO:**

1.) Initial structure is computed using a QCISD(T)/6-311G** wave function.

2.) Zero point energy is computed using a HF/6-311G** wave function and scaled by 0.9251.

3.) Core correlation is handled molecule by molecule.¹⁹

Steps 4-5 are the same for CBS-APNO as they are in CBS-Q.

6.) QCISD(T)/6-311G+(2df,p).

7.) Same as in CBS-Q.

While CBS-APNO is the most accurate complete basis set method, it is not applicable to molecules containing atoms larger than the first row and is computationally expensive. The need for a compound method that could be extended to molecules containing atoms bigger then the first row, as well as, a computationally cheaper approach lead to the development of the Weizmann methods. The Weizmann methods were developed by Jan Martin²⁰ in 1999 and come in various “flavors” with the main differences being the perturbative excitation in the initial coupled cluster optimization step. Currently, anything greater than the Weizmann-2 method is not computationally feasible on anything but a supercomputer, as a result, this study will primarily focus on
The Weizmann-1 and Weizmann-2 methods. The Weizmann-1 method picked up where the complete basis set methods left off and works by the following procedure.

**Weizmann-1:**

1.) Initial optimization is computed using the B3LYP density functional with a cc-pvtz+1 basis set. The +1 indicates an additional large exponent d Gaussian function on all second row atoms.

2.) Zero point energy is computed using the same density functional and basis set as in step 1 and is scaled by 0.985.

3.) Single point energies are computed using a CCSD(T)/aug-cc-pvdz+2d and aug-cc-pvtz+2df wave function, followed by a computing a single point energy using a CCSD/aug-cc-pvqz+2df. The +2df indicates two large exponent d and one large exponent f Gaussian function summed into the original basis set.

4.) The energies from step 3 are then extrapolated using an extrapolation formula developed by Petersson and coworkers.\(^{21}\)

5.) Compute valence correlation contribution using CCSD/aug-cc-pvtz+2df and aug-cc-pvqz+2df wave function and then extrapolate the energies using an extrapolation formula developed by Helgaker and coworkers.\(^ {22}\)

6.) The (T) valence correlation contribution is computed using a CCSD(T)/aug-cc-pvdz+2d and aug-cc-pvtz+2df wave function and then extrapolated using the Helgaker extrapolation formula.

7.) Core correlation and scalar relativistic effects are computed using a CCSD(T)/MTsmall basis set with a Douglas-Kroll-Hess Hamiltonian.\(^ {23}\) This is done by
taking the difference in energy between a CCSD(T)/MTsmall wave function with only
the valence electrons and a non-relativistic Hamiltonian and an energy computed using a
CCSD(T)/MTSmall wave function and the Douglas-Kroll-Hess Hamiltonian. The MT
small basis set is a basis set developed by Martin and Taylor\textsuperscript{24} with the goal of improving
the treatment of core correlation in mind and is in fact a cc-pvtz basis set with two
additional large exponent d and an additional large exponent f Gaussian function on all
atoms.

While the Weizmann-1 method is a computationally inexpensive approach and is
an improvement over the complete basis set and Gaussian methods, it is not without its
flaws. For example, the valence correlation extrapolation exponents used in steps 5 and 6
are derived from the Weizmann-2 method, as well as, using a density functional to
determine an initial structure and then extrapolating energies using a coupled cluster
wave function leads to errors associated with the inability to treat electron correlation
using a density functional. Therefore, the most accurate, computationally feasible
Weizmann method available, is the Weizmann-2 method. The Weizmann-2 method is
capable of producing results as little as 0.17 kcal/mole away from their experimental
value, while the Weizmann-1 method is capable of producing results that are 0.30
kcal/mole away from their experimental value. In either case, the results are still an
improvement over the Gaussian and complete basis set methods and are able to achieve
chemical accuracy, which is defined to be “results that are within 1 kcal/mole from the
experimental value”. Weizmann-2 gets its by using a coupled cluster wave function for
every step in the method, as well as, uses larger basis sets then in Weizmann-1 theory.
Weizmann-2 works in the following way.
**Weizmann-2:**

1.) Optimized structure is found using a CCSD(T)/cc-pvqz+1 wave function.

2.) Zero point energy is calculated using a CCSD(T)/cc-pvtz+1 wave function or if this is not possible a B3LYP density functional with a cc-pvtz+1 basis set. If B3LYP/cc-pvtz+1, then scale the zero point energy by 0.985.

3.) Calculate single point energies using a CCSD(T)/ aug-cc-pvtz+2df and aug-cc-pvqz+2df wave function.

4.) Calculate single point energy using a CCSD/aug-cc-pv5z.

5.) Extrapolate the energies obtained from steps 3-4 using the Petersson extrapolation formula introduced in the Weizmann-1 method.

6.) The CCSD valence correlation component is obtained from a CCSD/aug-cc-pvqz+2df and aug-cc-pv5z+2df.

7.) Results of step 6 are then extrapolated using the Helgaker extrapolation formula introduced in the Weizmann-1 method.

8.) The (T) valence correlation component is obtained from a CCSD(T)/aug-cc-pvtz+2df and aug-cc-pvqz+2df.

9.) The results of step 8 are then extrapolated using the Helgaker extrapolation formula.

10.) Core correlation and scalar relativistic effects are handled in the exact same way as in Weizmann-1 theory.

It is the opinion of the author that the Weizmann-2 theory is the most beautiful compound method that is computationally feasible because of the explicit treatment of electron correlation in every step of the method using a coupled cluster wave function.
II.) Applications of Compound Methods to Problems of Chemical Interest.

(Note this section contains a significant amount of material previously published in LeMaster, C.; LeMaster, C.; Greenwood, B.; Butler, D.; Cassidy, K.; Prince, J. J. Mol. Struc. 2017, 1146, 126-129.)

Introduction:

The range of rates of isomerization in imines varies by over 16 orders of magnitude and the mechanism of the interconversion process is of interest. Two mechanisms have been proposed: nitrogen inversion and internal rotation. The nitrogen inversion mechanism is supported by the relatively low barriers found for imines like (CH₃)₂C=NPh in which the conjugating substituent (Ph) stabilizes the inversion transition state and for imines with heteroatoms, such as halogens, attached to the imino carbon atom. These groups stabilize the inversion transition state. It is also supported by the fact that strongly hydrogen-bonding solvents raise the interconversion barrier. However, the rotational transition state is supported by the fact that when substituents with lone pairs are attached to the imino carbon atom such as oxygen or sulfur, the barrier is substantially lowered. Hall et al. have put forward the possibility that the interconversion mechanism changes as substituents on the imino carbon and nitrogen are varied to favor one mechanism or the other. They studied a group of imines (CF₃)₂C=NC₆H₄R. The two trifluoromethyl groups on the imino carbon help stabilize the rotation transition state. Most R substituents studied (CH₃O, the halogens, and CH₃) are consistent in their interconversion barriers, but when R is the nitro group, there is a
deviation of ~ 7.1 kJ mol\(^{-1}\). This would indicate a transition from rotation to nitrogen inversion as the isomerization mechanism. Perfluoro-2-azapropene is the first perfluoroaza compound for which conformational exchange kinetic parameters have been obtained in the gas phase using dynamic NMR techniques, as well as, the first imine for which gas and liquid–phase data are available. Evidence for a particular inversion mechanism may come from ab initio studies of a molecule that undergoes the inversion process and comparison of calculated inversion free energies to experiment. Perfluoro-2-azapropene is a molecule that would be expected to follow the nitrogen inversion mechanism as implied by Hall et al.\(^{27}\) because of the halogen substituents present on the imino carbon. It is also small enough to be amenable to high-level ab initio calculations with reasonable time costs, including the expensive Weizmann methods. This study compares the Complete Basis Set, Gaussian and Weizmann-1 methods to the experimental gas-phase value. Ab initio calculations are best compared to gas-phase experimental results where intermolecular interactions are negligible\(^{28}\). The Weizmann methods are not only known for accurate energy calculations but also for their calculation of precise spectroscopic parameters\(^{29}\).

Materials and Methods:

2.1. NMR studies

The gas-phase NMR sample of perfluoro-2-azapropene was prepared in a restricted volume NMR tube constructed from a 3-cm-long section of Wilmad high-precision 10-mm coaxial insert tubing. The restricted volume tubes were then inserted into longer 10-mm NMR tubes for introduction into the probe. The short tubes confine the sample and reduce the temperature gradient within the active probe volume. The
sample consisted of 100 torr (13.3 kPa) of perfluoro-2-azapropene and 2707 torr (361 kPa) of Argon bath gas. 150 torr (20.0 kPa) CFCl3 was used as a reference. Details of the techniques of gas-phase NMR spectra can be found in reference 28. The liquid sample consisted of 5 mole % perfluoroazapropene in CDCl3 in a sealed NMR tube. The spectra were obtained on an IBM AF100 NMR spectrometer using a Bruker 10-mm fluorine probe. Gas-phase 19F spectra were run on spinning samples in unlocked mode. Acquisition time was 0.2 seconds per transient with a 10 meter second<sup>-1</sup> delay time (possibly due to the extremely fast relaxation of fluorine in the gas phase) and a 75° tip angle. Typically, 15,000 transients were collected depending on the fine structure in the spectrum over a 40 ppm range. Typical signal-to-noise ratios were 4000:1 after multiplication by an exponential line-broadening factor of 1 Hz. Temperatures were controlled with a 0.1° pyrometer and read either before or after each acquisition. Temperature measurements were made using three copper-constantan thermocouples placed at different heights within an empty spinning 10-mm NMR tube. The probe and sample were allowed to equilibrate for at least 10 min before the acquisition was initiated. Temperature gradients within the active volume were within 0.2 Kelvin. The temperature-dependent rate constants, along with an estimate of their errors, were calculated using the computer program DNMR5<sup>30</sup>, which performs complete line-shape analysis of the spectra. The data were then used to construct an Eyring plot to determine the experimental liquid and gas-phase free-energy values. Parameters for chemical shifts, T2 relaxation, population, and coupling contestants are entered and the value of the rate constant determined after an iterative least-squares fit to the NMR line shape. A complete
description of the procedure and typical ranges of values obtainable on the NMR timescale are described in references\textsuperscript{28,31-39}.

2.2. Ab initio calculations

Ab initio calculations using Complete Basis Set (CBS-4M, QB3, APNO), Gaussian (1-4), and Weizmann (W1U,WBD) were performed on a Dell Precision T3600 with a dual 8 core Xenon processors and 64 GB RAM using the Linux Version of Gaussian 09\textsuperscript{31}. Minimized structures (fully geometry-optimized), vibrational frequencies, and energies were calculated for the ground state and the transition state. CPU calculation times ranged from 15 minutes (CBS-4M) to 162 days (W1BD). For the more expensive calculations 48-60 GB of Ram and 15 CPUs were typically used to minimize real time calculations. The free energy obtained for the geometry-optimized ground state was subtracted from the energy obtained for the geometry-optimized transition state for each method to obtain the activation free energy.
**Results:**

Table 1.II.1  Table 1.II.1 illustrates the kinetic barrier heights computed for all of the compound methods available within the Gaussian computational package. Kinetic barrier heights are reported in kj mole\(^{-1}\).

<table>
<thead>
<tr>
<th>Method</th>
<th>( G^\dagger_{298} ) (kj mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment (gas)</td>
<td>66.9 (4)</td>
</tr>
<tr>
<td>Experiment (liquid)</td>
<td>67.4 (8)</td>
</tr>
<tr>
<td>CBS-4M</td>
<td>55.0</td>
</tr>
<tr>
<td>CBS-QB3</td>
<td>72.4</td>
</tr>
<tr>
<td>CBS-APNO</td>
<td>63.9</td>
</tr>
<tr>
<td>G1</td>
<td>63.5</td>
</tr>
<tr>
<td>G2</td>
<td>66.1</td>
</tr>
<tr>
<td>G3</td>
<td>62.6</td>
</tr>
<tr>
<td>G4</td>
<td>73.7</td>
</tr>
<tr>
<td>W1U</td>
<td>65.6</td>
</tr>
<tr>
<td>W1BD</td>
<td>65.6</td>
</tr>
</tbody>
</table>
Conclusions:

All three methods gave reasonable comparison to experiment. The CBS-APNO, known to be the most accurate of the CBS methods differed from the gas-phase experimental results by 3.0 kj mole\(^{-1}\). The G2 method differed by 0.3 kj mole\(^{-1}\) and both the Weizmann-1 methods differed by 0.7 kj mole\(^{-1}\).

The geometry-optimized transition state obtained was consistent with the nitrogen inversion mechanism. Interestingly, attempts to converge on the rotational transition state returned to the inversion structure or failed to converge.

Calculations using CBS was in better agreement with experiment as they progressed to higher-order options starting with 4M, QB3, and then APNO. The Gaussian-n methods G1-3 returned fairly consistent values, but G4 calculated a higher free-energy value similar to that obtained from CBS-QB3. Both Weizmann methods returned the same value for the barrier. The IR and Raman Frequencies obtained from the Weizmann calculations are by far the most accurate\(^2\), as compared to experiment, of all the theories reported as might be expected.

This study provides evidence that internal isomerization in perfluoro-2-azapropene follows the nitrogen inversion mechanism and not the rotation mechanism.

With these powerful tools at our fingertips, the goal of this project was to verify the claim that the Weizmann-2 method is the most accurate computationally feasible, compound method available which is able to produce chemically accurate results (results within 1 kcal mole\(^{-1}\)) from their experimental value. As it turns out, the answer to this question raised additional questions which ultimately lead to the development of a new Weizmann method.
Let us begin.
CHAPTER 2: AN INVESTIGATION INTO THE ACCURACY OF INVERSION BARRIERS DERIVED FROM THE WEIZMANN METHODS.

The investigation into the accuracy of inversion barriers derived from the Weizmann methods follows directly from the study presented in chapter 1, when it was realized that the compound methods don’t uniformly agree with experimental results. That is, the order of accuracy of the compound methods is not what would be predicted. For example, any theorist would predict the Weizmann methods to give better results than the complete basis set methods, which would be predicted to give better results than the Gaussian-n methods. However, this is not what is observed. The data presented in chapter 1 is a great example of this, as we see the Weizmann methods do not yield the most accurate result. In fact, Gaussian-2 yields the most accurate result, followed by the Weizmann methods. CBS-APNO, however, yields results that are 3.0 kj mol$^{-1}$ away from experiment. This is unacceptable, as CBS-APNO is supposed to be the most accurate complete basis set method available and is so robust, it’s not applicable to any second row containing molecule, yet it is unable to produce the most accurate results when compared to the other classes of compound methods. This realization led the LeMaster group to search the literature to see if this anomaly is specific to perfluoro-2-azapropene or maybe the isomerization process, in general. What we found was that in a perfect world the compound methods accuracy follow the trend Weizmann > Complete Basis Set > Gaussian –n, although, in practice, this is not what is observed. In fact, results
presented in chapter 1 are quite common. That is, the accuracy of the method is dependent on the molecule studied and even the process being studied. So, we went back to the literature to see if we could find a compound method that is computationally feasible that is able to predict accurate results, regardless of the molecule or process being studied. What we found was that the Weizmann methods, specifically Weizmann-2 and beyond, are predicted to uniformly yield the most accurate results, regardless of the molecule or process being studied. Interestingly, all Weizmann theories except Weizmann-1, is free of empirical parameters and essentially works the same way but differs by increasing the order of connected cluster operators in either the initial optimization step or in the extrapolation steps. While, the higher order Weizmann methods are quite attractive, any calculation including connected triples (or higher) is not practical on anything other than super computers. The computational expense of the higher order Weizmann methods limited the Weizmann theories we were able to study. However, we were able to distill the list of Weizmann methods down to what is predicted to be the most accurate Weizmann methods available that are computationally feasible on a workstation computer. We found that the Weizmann-2, Weizmann-2x and the standard Weizmann-1 methods were predicted to be the most accurate compound methods available that are computationally feasible on a workstation computer. While the Weizmann-2 method is predicted to be most accurate compound method available, claiming chemically accurate results for any molecule, the results were only tested against thermochemical data, with little to no work being done on any kinetic parameter. So, we thought if one method is claiming it can produce chemically accurate results for
any molecule and is the most accurate method available, it should be able to produce chemically accurate results for any molecule, as well as, any process.

To test this claim, we looked for a list of small molecules, which are well studied in the gas phase. What we found was the following list of small molecules in which the activation energy for the isomerization process is well studied:

a.) Methyl Nitrite

b.)NH₃

c.)PH₃

d.) Cyclopropane

e.)Aziridine

f.)Boron Tetrahydride

g.) hydrogen peroxide

h.) Cyclohexane

i.)H₃B-NH₃
Weizmann-2 theory (W2) came with additional restrictions, such as the largest molecule that is capable of being studied on a workstation computer is SO$_3$, which contains 40 electrons. So, W2 theory is restricted to molecules containing less than or equal to 40 electrons. Methyl Nitrite contains 32 electrons, which means it should be able to be studied using W2 theory, on a workstation computer. Unfortunately, after approximately 45 days, the end of the first step of W2 theory was nowhere in sight. So, we had to cancel the job and scratch methyl nitrite, for it was much too big to study. We then decreased the size of the system being studied to NH$_3$ and then gradually increased the size of the system, eventually settling on NH$_3$, PH$_3$ and Aziridine. Once a list of well-studied, small molecules was established, we set off to understand the extrapolation schemes introduced in W2 theory, as well as, research W2x theory, to eventually compare the accuracy of the W1, W2 and W2x theories. We found the extrapolation schemes introduced by Pettersson$^{21}$ and Helgaker$^{22}$, reduce to a simple two point geometric extrapolation formula, that is easily implemented in Wolfram alpha Mathematica 11.0. See Appendix for computational details. After extensive research on W2x theory, it was determined, due to the modification of basis sets required to perform W2x theory, it was not possible to compare W1, W2 and W2x theory. While it is possible to customize basis sets in the Gaussian computational package, doing so is a research project in itself. So, we decided to verify the claim that the Weizmann-2 theory is the most accurate compound method available, which is predicted to produce chemically accurate results, regardless of the molecule or process being studied.
The following chapters describe the results and implications found by comparing the standard compound methods to the Weizmann-2 theory applied to the isomerization process of small molecules.
CHAPTER 3: ISOMERIZATION OF AZIRIDINE

Aziridine was examined because of its relatively large size, as well as, the isomerization process is well studied in the gas phase.\textsuperscript{43,44,45,46,47} The overall goal of studying Aziridine was to determine the theoretical barrier height (from Weizmann-2, 1, etc) and compare it to the experimental value, in order to prove or disprove the claim that the Weizmann-2 method is the most accurate electronic structure method available, capable of producing chemically accurate results (results within 1 kcal/mole from the experimental value) for every molecule.

Aziridine is a strained, 3 membered cyclic molecule with a single nitrogen atom, two carbon atoms and 5 hydrogen atoms. As you will see, the isomerization process for Aziridine is primarily focused on the hydrogen atom bonded to the nitrogen atom. The potential energy surface for the isomerization process is depicted in Figure 3.1. The theoretical barrier height was determined by computing the energy of the ground state, the energy of the transition state and then determining the difference between the two structures. The Aziridine ground state structure is depicted in Figure 3.2, while the transition state structure is depicted in Figure 3.3.

Experimentally, the barrier height for the isomerization process was determined by utilizing gas phase $\text{H}^1$NMR spectroscopy and a technique called total line shape analysis. The experimentally determined gas phase barrier height to the isomerization process was determined to be 18.0 kcal/mole.\textsuperscript{43}
Figure 3.1. Figure 3.1 illustrates a generalized potential energy surface for an isomerization process. The lowest position on the surface (lowest in energy) represents the ground state structure, while the peak of the potential energy surface (highest in energy position) represents the transition state. The barrier height is computed by taking the difference between the transition state and the ground state structures.

Figure 3.2. Figure 3.2 illustrates the ground state structure of Aziridine, which is found at the minimums of the potential energy surface. It is important to understand the isomerization process of Aziridine involves the movement of the proton bonded to the nitrogen atom.
Figure 3.3 illustrates the transition state structure of Aziridine, which is found at the peak of the potential energy surface. It is important to note, the barrier height was determined by taking the difference in energy between the structure represented within this figure and the structure represented in figure 3.1.

The first method investigated was the Weizmann-2 method which contains no empirical parameters. In fact, the Weizmann-2 method is a pure coupled cluster method with each step increasing the size of the basis set which in turn increases the space the electrons are allowed to sample. The Weizmann-2 method predominantly uses the basis sets developed by Thom Dunning, with the exception of the relativistic correction which uses the MTsmall basis set developed by Martin and Taylor. The compiled results of the ground state computation using the Weizmann-2 method can be found in Table 3.1, while the results of the transition state can be found in Table 3.2.
Table 3.1  Table 3.1 represents the compiled Weizmann-2 data for the ground state energy of Aziridine. All energies are in Hartree’s particle

<table>
<thead>
<tr>
<th>Ground State Energy</th>
<th>Extrapolated CCSD Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>-133.098992331</td>
<td>-0.628191262</td>
</tr>
<tr>
<td>Zero-Point-Energy</td>
<td>Extrapolated (T) Component</td>
</tr>
<tr>
<td>0.070526</td>
<td>-0.031804718</td>
</tr>
<tr>
<td>Extrapolated SCF (Q/5)</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.003316918</td>
<td>-0.2114628</td>
</tr>
</tbody>
</table>

Table 3.2  Table 3.2 represents the compiled Weizmann-2 data for the transition state energy of Aziridine. All energies are in Hartree’s particle$^{-1}$.

<table>
<thead>
<tr>
<th>Transition State Energy</th>
<th>Extrapolated CCSD Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>-133.070051824</td>
<td>-0.627392572</td>
</tr>
<tr>
<td>Zero-Point-Energy</td>
<td>Extrapolated (T) Component</td>
</tr>
<tr>
<td>0.068635</td>
<td>-0.031521025</td>
</tr>
<tr>
<td>Extrapolated SCF (Q/5)</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.003607717</td>
<td>-0.21171279</td>
</tr>
</tbody>
</table>
An interesting observation is that the dominating contributions come from the zero point energy, the coupled cluster single double valence correlation energy, as well as, the relativistic extrapolation energy. Most surprising, is that the relativistic contribution is the same magnitude as the coupled cluster valence correlation energy, although aziridine isn’t traditionally considered a relativistic molecule. It’s interesting the extrapolated triple component contributes a relatively large amount to the total ground and transition state energies because it is such an incomplete treatment of the coupled cluster single double and triple wave function. The zero point energy is defined as the residual energy of a system at 0 Kelvin, so it makes sense this is the only positive contribution to the total energy.

Now that we have seen and discussed the Weizmann-2 compiled results, let’s see how the barrier height for the isomerization process computed from the Weizmann-2 method compares to the other compound methods previously mentioned. Table 3.3 represents the barrier heights in kcal mole\(^{-1}\) computed from the Weizmann-2, Weizmann-1, Complete Basis Set and Gaussian-4 methods.
Table 3.3 represents the barrier heights for the isomerization process for Aziridine, in kcal mole\(^{-1}\). The experimentally determined gas phase isomerization barrier height is reported to be 18.0 kcal mole\(^{-1}\).

<table>
<thead>
<tr>
<th>Method/Barrier Height</th>
<th>CBS-QB3 Barrier Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weizman-2</td>
<td>17.31368</td>
</tr>
<tr>
<td>W1BD</td>
<td>17.08144084</td>
</tr>
<tr>
<td>W1RO</td>
<td>18.76002922</td>
</tr>
<tr>
<td>CBS-APNO</td>
<td>18.76944187</td>
</tr>
<tr>
<td>17.18435243</td>
<td>17.24584838</td>
</tr>
<tr>
<td>CBS-Q</td>
<td>17.24584838</td>
</tr>
<tr>
<td>CBS-4m</td>
<td>17.46362499</td>
</tr>
<tr>
<td>Gaussian-4</td>
<td>17.58721364</td>
</tr>
</tbody>
</table>

These results are not what is expected and in fact, almost goes against all predictions about the compound methods made within the introduction. While the Weizmann-2 method is able to produce chemically accurate results, it is not the only method that is capable of doing so and in fact, it does not produce results closest to the experimentally accepted value of 18.0 kcal mole\(^{-1}\). We do expect the Weizmann methods to produce better results than the complete basis set methods, although the order of accuracy would be predicted to be CBS-APNO > CBS-QB3 > CB3-Q > CBS-4m. This is clearly not what is observed as the complete basis set method which produces the most accurate results is CBS-Q. Interestingly, the Weizmann-1 methods produce results that are about as accurate as the Weizmann-2 results, although the Weizmann-2 results are below the experimentally determined barrier height and the Weizmann-1 methods produce results that are above the experimentally determined barrier height. The author suspects
this is directly related to the optimization and frequency steps which uses density functional theory in Weizmann-1 and coupled cluster theory in Weizmann-2. The most surprising result is that not only does Gaussian-4 produce the most accurate barrier height but is only approximately 0.2 kcal mole\(^{-1}\) away from the Weizmann-2 barrier height. Examining the differences between the Weizmann-2 and Gaussian-4 theory, we see that Gaussian-4 corrects for the inability to describe quad excitations using coupled cluster theory and then uses Moller-Plesset perturbation theory for all other corrections, while the Weizmann-2 method only uses coupled cluster theory. The interesting connection between the Gaussian-4 and Weizmann-2 methods is that coupled cluster theory obtains the coefficients for the cluster determinants from Moller-Plesset theory. Therefore, we should expect the results obtained from the two methods to be similar, although coupled cluster theory almost universally produces better results. The author suspects Gaussian-4 produces more accurate barrier heights for Aziridine then the Weizmann-2 method due to the optimization and frequency steps which uses an empirically derived density functional.
CHAPTER 4: ISOMERIZATION OF PHOSPHINE

Phosphine was chosen because it is a relativistic molecule (contains at least a second row element) which has an isomerization process that is well studied in the gas phase. Phosphine consists of a single phosphine atom and three hydrogen atoms. The potential energy surface for the isomerization process of phosphine has the same symmetry as that of aziridine except the location of the barrier is elsewhere due to the differences in ground and transition state energies. Figure 4.1 illustrates the ground state structure of phosphine, while Figure 4.2 illustrates the transition state structure. The experimental barrier height is 31.5 kcal mole\(^{-1}\) and is obtained by examining the energy level splitting of the vibrational spectra of phosphine. The theoretical barrier height is calculated in the exact same way as with aziridine, that is, taking the difference between the transition and ground state energies.

Figure 4.1 Figure 4.1 illustrates the ground state structure of PH\(_3\) computed using the Weizmann-2 method.
Due to the large size of phosphorous relativistic effects become a necessity when achieving chemically accurate results and with relativistic molecules, we change from the Schrödinger equation to the Dirac equation. The Dirac equation was discovered by Paul Dirac in 1928 by taking the relativistic energy equation (equation 1) and substituting the momentum term for its operator equivalent. Dirac then expanded the square root in an infinite series of derivative operators, set up an eigenvalue problem and then solved the eigenvalue problem for the eigenvectors.

\[ E = c \sqrt{p^2 + m^2c^2} \]  

Equation 1

where:

c = speed of light

p = momentum

The resulting eigenvectors were a 4 component wave function containing the quantum numbers n, l, m_l, and m_s. Unlike the solutions to the Schrödinger equation, the Dirac solutions naturally contained the spin quantum number. The wave function was not the only surprising result of the Dirac equation. In fact, upon expansion of the derivative
operators, two important features of the Hamiltonian emerged; a spin-orbit coupling effect, as well as, the Darwinian term.\textsuperscript{54} The spin-orbit coupling effect accounts for the lowering in energy when the frame of reference is changed from a stationary nuclei and moving electrons to stationary electrons with the nuclei moving. The Darwinian term was arguably the most interesting discovery that came out of the Dirac equation and in fact is the derivation to the electrons antimatter counterpart, the positron. The Darwinian term describes the changing potential energy between the nuclei and the electron due to the electrons changing identity. That is, due to the electron oscillating back and forth between a negatively charged particle (electron) and a positively charged particle (positron).

Now that we’ve discussed the barrier height for the isomerization process of phosphine, how it was determined experimentally, as well as, the relevant relativistic modifications to the Hamiltonian, let’s look at the results. Naturally, the first method investigated was the Weizmann-2 method. The compiled data for the ground state and transition state structure can be found in Table 4.1 and Table 4.2, respectively.
Table 4.1  Table 4.1 represents the compiled Weizmann-2 data for the ground state energy of Phosphine. All energies are in Hartree’s particle\(^1\).

<table>
<thead>
<tr>
<th>Ground State Energy</th>
<th>Extrapolated CCSD Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>-342.493656175</td>
<td>-0.215976298</td>
</tr>
<tr>
<td>Zero-Point-Energy</td>
<td>Extrapolated (T) Component</td>
</tr>
<tr>
<td>0.023706</td>
<td>-0.009107134</td>
</tr>
<tr>
<td>Extrapolated SCF (Q/5)</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.001333111</td>
<td>-1.11725376</td>
</tr>
</tbody>
</table>

Table 4.2  Table 4.2 represents the compiled Weizmann-2 data for the transition state energy of Phosphine. All energies are in Hartree’s particle\(^1\).

<table>
<thead>
<tr>
<th>Transition State Energy</th>
<th>Extrapolated CCSD Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>-342.436841882</td>
<td>-0.219336577</td>
</tr>
<tr>
<td>Zero-Point-Energy</td>
<td>Extrapolated (T) Component</td>
</tr>
<tr>
<td>0.022416</td>
<td>-0.009874584</td>
</tr>
<tr>
<td>Extrapolated SCF (Q/5)</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.001527064</td>
<td>-1.11628616</td>
</tr>
</tbody>
</table>

Not surprisingly, the relativistic effects dominate the higher level corrections. However, it is surprising how much more the relativistic effects contribute to phosphine compared to aziridine. Upon inspection, we see that the relativistic effects contribute approximately 5.5 times more for phosphine than they do for aziridine. Clearly, phosphine is a relativistic molecule. It is interesting that the extrapolated triple component is an order of magnitude less for phosphine than for aziridine. The author suspects this is due to the difference in valence electrons; 18 valence electrons for aziridine and 8 valence electrons...
for phosphine. Evidence for this hypothesis comes from the extrapolated coupled cluster single double valence energy. Although the magnitude of this component is the same for the two molecules, the extrapolated coupled cluster single double valence energy is approximately 0.4 Hartrees lower in energy for aziridine then with phosphine. It’s interesting the extrapolated SCF energy is the same magnitude for the two molecules, although the extrapolated SCF energy is approximately 0.002 Hartrees lower for aziridine then phosphine. The zero point energy of the two molecules are of the same magnitude, although the zero point energy in aziridine is approximately 0.05 Hartrees higher than the zero point energy of phosphine. This makes sense by definition of the zero point energy. The zero point energy is defined as “a correction to the electronic energy of the molecule to account for the effects of molecular vibrations which persist even at 0 K”. The molecular vibrations would be dependent upon the kinetic and potential energies of the system and therefore because aziridine is larger, as well as, contains more electrons, the kinetic and potential energy terms would be expected to be larger and thus we would expect to see a larger zero point energy contribution from aziridine then phosphine. The Weizmann-2 barrier height for phosphine was determined to be 32.7373 kcal mole\(^{-1}\). For comparison, Table 4.3 illustrates the barrier height computed from the compound methods discussed in the introduction. While the Weizmann-2 method produces the best results (theoretical barrier height closest to the experimentally determined barrier height) it is disappointing that the result is approximately 0.2 kcal mole\(^{-1}\) away from a chemically accurate result. Although the Weizmann-2 result isn’t chemically accurate, it is relieving to see the Weizmann-2 result is 0.9 kcal mole\(^{-1}\) better than the Weizmann-1 methods. This is important as it demonstrates the ability for coupled cluster theory to outperform
an empirically determined method, density functional theory, which implies it is possible to pursue a theory first approach to experimental questions. The author suspects the CBS-QB3 method results are similar to the Weizmann-1 results because of the essentially same optimization and frequency calculation (both methods use density functional theory for the optimization and frequency calculation, as well as, both use similarly scaled zero point energies. The subsequent steps use coupled cluster theory except use a split-valence (Pople basis set) instead of the more commonly used correlation consistent basis set (Dunning basis set), as well as, Moller-Plesset theory. So, it is not surprising the CBS-QB3 barrier height resembles the Weizmann-1 barrier height. A similar argument can be made for the CBS-Q barrier height except it can be argued the results of CBS-Q are better than the CBS-QB3 results because of the fact that CBS-Q uses Moller-Plesset perturbation theory instead of density functional theory. Since the Weizmann-2 method produces the best results, we can hypothesize that it is possible the experiment done to fit the density functionals of phosphorous might not have been as good as it was for other atoms. The use of Moller-Plesset theory would eliminate this possibility and therefore produce a better result, which is observed. It’s almost surprising how well the CBS-4 method reproduces the experimental barrier height considering it is almost a pure Hartree-Fock method. In fact, the optimization, frequency and self-consistent field extrapolation steps all use the Hartree-Fock method with split-valence basis sets. Electron correlation is handled using MP2 and a split-valence basis set, as well as, MP4 and a split valence basis set. So, while the result is approximately 3.2 kcal mole$^{-1}$ away from the experimentally value, considering it is almost a pure Hartree-Fock method, which only uses split-valence basis sets, this result although not close to chemical accuracy, is not
that bad. It’s interesting the Gaussian-4 method again produces barrier heights that are so close to the Weizmann-2 barrier heights.

Table 4.3 Table 4.3 represents the barrier heights for the isomerization process for Phosphine, in kcal mole\(^{-1}\). The experimentally determined gas phase isomerization barrier height is reported to be 31.5 kcal mole\(^{-1}\). The N/A under CBS-APNO represents the fact that this method is unavailable for molecules containing second row (or larger) atoms.

<table>
<thead>
<tr>
<th>Weizman-2 Barrier Height</th>
<th>CBS-QB3 Barrier Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.7373</td>
<td>33.78512087</td>
</tr>
<tr>
<td>W1BD Barrier Height</td>
<td>CBS-Q Barrier Height</td>
</tr>
<tr>
<td>33.61820329</td>
<td>33.19212422</td>
</tr>
<tr>
<td>W1RO Barrier Height</td>
<td>CBS-4m Barrier Height</td>
</tr>
<tr>
<td>33.63200851</td>
<td>34.79729397</td>
</tr>
<tr>
<td>CBS-APNO Barrier Height</td>
<td>Gaussian-4 Barrier Height</td>
</tr>
<tr>
<td>N/A</td>
<td>32.83883628</td>
</tr>
</tbody>
</table>

The author suspects this is due to the fact that Gaussian-4 replaces quadratic configuration interaction with coupled cluster theory (the only theory used in Weizmann-2 theory), as well as, attempts to gain accuracy through cancelation of errors (accounting for electron correlation, approximating the infinite basis set limit, etc.) rather than attempting to gain accuracy through the use of quadratic configuration interaction alone. Nevertheless, while it is disappointing Weizmann-2 theory is unable to produce chemically accurate results for the barrier height of the isomerization process for phosphine it is relieving Weizmann-2 theory produces the closest results to the experimentally determined barrier height.
Ammonia was chosen because it is a small molecule with an established and accepted isomerization barrier height.\textsuperscript{55,56} Ammonia consists of a single nitrogen atom and three hydrogen atoms. The barrier height for the isomerization process can be seen from the potential energy surface of ammonia depicted in Figure 5.1. The experimental barrier height was found from microwave spectroscopy and was determined to be 5.8 kcal mole\textsuperscript{-1}. The theoretical barrier height was computed by calculating the ground state and transition state energy followed by finding the difference in energy between the two states. The ground state structure is presented in Figure 5.2, while the transition state structure is presented in Figure 5.3. Interestingly, while Ammonia appears to be a simple molecule, it has caused theorists headaches as it does the exact opposite of what we would expect when implementing higher levels of theory. That is, the accuracy of the calculation deteriorates as the level of theory increases. So, not only was ammonia investigated because the isomerization process is well studied but also because it came with an additional question, which is, can the Weizmann-2 method overcome the ammonia problem and produce chemically accurate results?
Figure 5.1  Figure 5.1 illustrates the potential energy surface for the isomerization process of NH₃ computed using Moller-Plesset 2nd order perturbation theory.

Naturally, the first method investigated was the Weizmann-2 method, which the results for the ground and transition state can be found in Table 5.1 and 5.2, respectively.

Figure 5.2  Figure 5.2 illustrates the ground state structure for NH₃, computed from the Weizmann-2 method.
Figure 5.3 illustrates the transition state structure for NH3, computed from the Weizmann-2 method.

Comparing the compiled Weizmann-2 results for ammonia and aziridine is left to the reader as it should be expected the same conclusions are found with ammonia and aziridine as was found for phosphine and aziridine due to the differences in size (number of electrons) of the systems. However, a more interesting comparison can be made by comparing the compiled Weizmann-2 results for ammonia and that of phosphine. Comparing the two molecules not only compares a relativistic molecule to a non-relativistic molecule but also examines the effects of increasing the size of the central atom for the general AH$_3$ class of molecules, where A represents nitrogen, phosphorous, etc. Examining the compiled Weizmann-2 data for phosphine and ammonia, the first thing we notice is the difference in the extrapolated triple component, which is an order of magnitude larger for ammonia then for phosphine. Although, phosphine has more electrons (core + valence) every step within the Weizmann-2 method except the relativistic effects only account for valence electrons. So, the fact that phosphine has more electrons isn’t contributing to the difference in the extrapolated triple component.
Table 5.1  Table 5.1 represents the compiled Weizmann-2 data for the ground state energy of Ammonia. All energies are in Hartree’s particle-1.

<table>
<thead>
<tr>
<th>Ground State Energy</th>
<th>Extrapolated CCSD Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>-56.2230139868</td>
<td>-0.272642412</td>
</tr>
<tr>
<td>Zero-Point-Energy</td>
<td>Extrapolated (T) Component</td>
</tr>
<tr>
<td>0.034572</td>
<td>-0.01114706</td>
</tr>
<tr>
<td>Extrapolated SCF (Q/5)</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.00217535</td>
<td>-0.081849673</td>
</tr>
</tbody>
</table>

Table 5.2  Table 5.2 represents the compiled Weizmann-2 data for the ground state energy of Ammonia. All energies are in Hartree’s particle-1.

<table>
<thead>
<tr>
<th>Transition State Energy</th>
<th>Extrapolated CCSD Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>-56.2151948293</td>
<td>-0.272305171</td>
</tr>
<tr>
<td>Zero-Point-Energy</td>
<td>Extrapolated (T) Component</td>
</tr>
<tr>
<td>0.032461</td>
<td>-0.011035008</td>
</tr>
<tr>
<td>Extrapolated SCF (Q/5)</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.002697043</td>
<td>-0.08205634</td>
</tr>
</tbody>
</table>
The author suspects the differences between the extrapolated triple components for phosphine and ammonia is due to the higher nuclear charge, shielding effect and larger principal quantum number (larger distance between the nuclei and the electrons) for phosphine then ammonia, which because phosphines electrons are allowed to sample more space they aren’t correlated as much as electrons occupying a smaller amount of space (the allowed space for ammonia’s electrons). Interestingly, this result trickles into the zero point energy, as we see the zero point energy is the same magnitude for the two molecules except it is approximately 0.01 Hartree’s larger for ammonia then it is for phosphine. While phosphine has a larger mass, the author suspects because the difference in the extrapolated triple components is an order of magnitude larger for ammonia then for phosphine, the increased electron repulsion energy cancels out the larger kinetic energy contribution from phosphine which ultimately leads to a larger zero point energy, which is what is observed. Surprisingly, the coupled cluster single double valence correlation energy is the same magnitude for phosphine and ammonia, although the valence contribution from ammonia is greater than that for phosphine. We can apply the same reasoning as we did for the differences between the extrapolated triple components and in fact, the coupled cluster single double valence contribution can be used as evidence to justify the hypothesis for the differences between the extrapolated tripled components. The extrapolated self-consistent field component varies by approximately 0.001 Hartree’s and as expected the relativistic contributions is much larger (approximately 1.03 Hartree’s) for phosphine then it is for ammonia. Sadly, the Weizmann-2 barrier height was determined to be 3.4 kcal mole\(^{-1}\) which is 1.4 kcal mole\(^{-1}\) away from chemical accuracy and 2.4 kcal mole\(^{-1}\) away from the accepted 5.8 kcal mole\(^{-1}\)
barrier height. For comparison, Table 5.3 illustrates the barrier heights computed from the compound methods discussed within the introduction. It’s surprising that with the development of these robust compound methods only the Weizmann-1 methods were able to achieve chemically accurate results for the barrier height of the isomerization process of ammonia. The author suspects the accuracy observed in the Weizmann-1 method is a direct result of the optimization and frequency steps which uses an empirically fitted density functional rather than an ab initio wave function. This would make a difference because the empirically fitted density functional would find a minima that agrees with experiment, rather than a minima that was determined by approximating the true wave function. It’s interesting how close the Weizmann-2 result and the CBS-APNO results are as CBS-APNO uses quadratic configuration interaction (which only includes connected excitation operators) whereas the Weizmann-2 method uses coupled cluster theory includes the disconnected excitation operators as well as the connected excitation operators. It should be noted CBS-APNO uses the split-valence basis sets developed by John Pople, while the Weizmann-2 method uses the correlation consistent basis sets developed by Thom Dunning.

Sadly, from this preliminary study, the claim that the Weizmann-2 method is the most accurate method available, which is able to produce chemically accurate results for all molecules and processes, doesn’t seem to be true. While the author applauds Jan Martin for the theoretical beauty involved in the development of the Weizmann-2 method, it is disappointing that our best approximation to the exact wave function (the coupled cluster wave function) can still produce results less accurate than results derived from an empirically fitted density functional. It appears that some of the problems with
determining the most accurate method for all molecules and processes is the fact that we mix ab initio and empirically derived methods. This approach to chemical accuracy is confusing as we will never know if our theory is the reason why the results aren’t what we think they should be or is it due to the experiment which the empirical parameter was derived.

Table 5.3 Table 5.3 represents the barrier heights for the isomerization process for ammonia, in kcal mole\(^{-1}\). The experimentally determined gas phase isomerization barrier height is reported to be 5.8 kcal mole\(^{-1}\).

<table>
<thead>
<tr>
<th>Method</th>
<th>CBS-QB3 Barrier Height</th>
<th>CBS-Q Barrier Height</th>
<th>CBS-4m Barrier Height</th>
<th>Gaussian-4 Barrier Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weizman-2</td>
<td>3.4</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W1BD</td>
<td>CBS-QB3 Barrier Height</td>
<td>5.09</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>W1RO</td>
<td>CBS-QB3 Barrier Height</td>
<td>5.09</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>CBS-APNO</td>
<td>CBS-QB3 Barrier Height</td>
<td>4.05</td>
<td>4.1</td>
<td></td>
</tr>
</tbody>
</table>

It would be interesting to develop a compound method that only uses theories which have empirically derived parameters within them and compare them to theories without any empirical parameters (maybe, the Weizmann-2 method), as well as, a theory which mixes ab initio and empirically derived approaches. This would be interesting as it should be able to elucidate where the problem(s) within these methods could be, whether the problem is due to the experiment in which the parameters were derived, whether the problem is due to mixing ab initio and empirically derived methods or is the problem due
to the incomplete description of the Hilbert space when approximating the exact wave function?
CHAPTER 6: DEVELOPMENT OF WEIZMANN-2 LPK THEORY

The inability for the Weizmann-2 method to produce chemically accurate results for the majority of the molecules studied raised additional questions such as “Can a method be developed to produce chemically accurate results for the majority of the molecules studied?” if so “Can the new method produce chemically accurate results for the nitrogen inversion process of ammonia?” Since the coupled cluster wave function is such a good approximation to the exact wave function, it makes sense to attempt to develop a theory that produces chemically accurate results using the coupled cluster wave function. The Weizmann-2 method is a pure coupled cluster method that is able to produce chemically accurate results, so, naturally we investigated where computationally feasible improvements to the Weizmann-2 method could be made. Since the goal was to make computationally feasible improvements to the Weizmann-2 method, higher order connected excitation operators were ruled out. Upon inspecting the Weizmann-2 method, it was realized that the zero point energy is not extrapolated out to the basis set limit, however, it could be. In order to properly extrapolate the various components, the researcher must determine what type of function best represents the component attempted to be extrapolated. For example, the Petersson extrapolation formula works for components which are best described by an exponential function, while the Helgaker formula works best for components which are described by a power series. In order to
determine the functional form of the zero point energy, the zero point energy was calculated using the correlation consistent basis sets (cc-pvNz) where N varied from 2 to 5. Table 6.1 illustrates the results of these calculations. The next step was to determine the functional form of the zero point energy. This was done by plotting the zero point energies as a function of the angular momentum quantum number, followed by examining the $R^2$ values. Figure 6.1 illustrates the plot of the zero point energies fitted to an exponential function, while Figure 6.2 illustrates the plot of the zero point energies fitted to a power series. As we see, the plot of the zero point energies as a function of the angular momentum quantum number is best represented by a power series relative to an exponential series. This realization should lead to the conclusion that extrapolating the zero point energy out to the basis set limit would be best done using the Helgaker extrapolation formula instead of the Petersson extrapolation formula. While this is a great qualitative conclusion, to justify the use of one extrapolation formula over the other requires quantitative proof. To quantitatively demonstrate the zero point energy would be best extrapolated using the Helgaker extrapolation formula, we first must prove the zero point energy is an asymptotic series.
Table 6.1 represents the calculated zero point energies using a CCSD(T)/cc-pvNz wave function.

<table>
<thead>
<tr>
<th>Angular Momentum Quantum Number</th>
<th>Zero Point Energy (a.u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.035093</td>
</tr>
<tr>
<td>3</td>
<td>0.034572</td>
</tr>
<tr>
<td>4</td>
<td>0.034493</td>
</tr>
<tr>
<td>5</td>
<td>0.034478</td>
</tr>
</tbody>
</table>

Figure 6.1 illustrates the plot of zero point energies (in atomic units) as a function of angular momentum quantum number. As we see, the $R^2$ value for the exponential function is 0.7232 which is represented by the exponential function $y = 0.0353e^{-0.006x}$. 

$R^2 = 0.7232$.
Figure 6.2 illustrates the plot of zero point energies (in atomic units) as a function of angular momentum quantum number. As we see, the $R^2$ value for the power series is 0.8318.

To quantitatively demonstrate the zero point energy is an asymptotic series we will use equation 1 and the power series equation generated from the plot of the zero point energy as a function of the angular momentum quantum number.
\[ \lim_{|n| \to \infty} x^n \left[ f(x) - \sum_{p=0}^{\infty} \frac{A_p}{x^p} \right] \]  

Equation 1.

Where:

\( x \) = the angular momentum quantum number.

\( n \) = adjustable parameter in which we find the limit as it goes to infinity.

\( f(x) \) = the original equation (\( y = 0.0355x^{-0.019} \)).

\[ \sum_{p=0}^{n} \frac{A_p}{x^p} = \text{A series representation for the original function } f(x). \]

It is well known that a function is asymptotic if equation 1 equals zero as \( n \) goes to infinity but before we examine the behavior of the power series, we need to find a series representation of the power series. The power series may be rewritten as equation 2.

\[ y = \frac{0.0355}{x^{0.019}} = 0.0355 \frac{1}{x^{0.019}} \]  

Equation 2.

This is very convenient because equation 2 looks a lot like equation 3, which has a nice and easy to work with series representation, which is represented by equation 4.

\[ y = \frac{1}{x} \]  

Equation 3.
Substituting equations 2 and 4 into equation 1, setting $x$ equal to a large angular momentum quantum number (say 100) followed by taking the limit as $n$ approaches infinity, we find equation 1 equals zero. Therefore, not only have we demonstrated we can use an extrapolation formula on the zero point energy but it also predicts that the Helgaker extrapolation formula will provide a more accurate result than the Petersson extrapolation formula. Upon establishing a solid foundation to base the extrapolation of the zero point energy on, the Weizmann-2 method was further examined to determine if any computationally feasible improvements can be made. What was found was that while extrapolating the triple valence component out to the basis set limit is a theoretically beautiful approach for attempting to achieve chemically accurate results, we are extrapolating from such a small portion of the Fock space that very little of the actual triple correlation energy is retained. In fact, the extrapolated triple valence component is consistently an order of magnitude smaller (or more) than that of the extrapolated CCSD valence correlation energy, as well as, the relativistic effects. With this realization in mind, we asked “How does the result change if we leave out the extrapolated triple correlation energy and instead replace it with a more complete extrapolation of the CCSD valence correlation energy?” The CCSD valence correlation energy can be argued to be incomplete due to the fact that the extrapolation starts with an augmented correlation consistent quad zeta basis set and ends with the augmented correlation consistent 5 zeta basis set, ignoring the important triple zeta basis set. In an attempt to capture the
complete Fock space when extrapolating the CCSD valence correlation energy, we included the original extrapolated CCSD valence correlation energy component but then re-extrapolated the augmented correlation consistent quad zeta basis set with the triple zeta basis set. The idea is that we are capturing everything below the quad zeta basis set with the triple zeta basis set, as well as, capturing the basis set limit by including the five zeta basis set. Table 6.2 illustrates the compiled ground state data for our new method, while Table 6.3 illustrates the compiled transition state data. For comparison, Table 6.4 illustrates the extrapolated zero point energies from the Petersson extrapolation formula for the ground and transition states. It is interesting the transition state has a more stable zero point energy then the ground state, which is observed from both the Helgaker and Petersson extrapolation formula. Table 6.5 illustrates the compiled data for the nitrogen inversion process of ammonia using our new method. As was predicted, the Helgaker extrapolation formula performs better (albeit slightly) then the Petersson extrapolation formula. However, it is disappointing our method improves the accuracy of the barrier height for the nitrogen inversion process of ammonia by 0.56 Hartree’s. Unfortunately, our method is unable to achieve chemical accuracy for the nitrogen inversion process of ammonia.
Table 6.2  Table 6.2 represents the compiled Weizmann-2 LPK data for the ground state energy of ammonia. All energies are in Hartree’s particle$^{-1}$.

<table>
<thead>
<tr>
<th>Ground State Energy</th>
<th>Extrapolated CCSD Valence (T/Q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-56.2230140243</td>
<td>-0.274369765</td>
</tr>
<tr>
<td>Extrapolated Zero-Point-Energy</td>
<td>Extrapolated CCSD Valence (Q/5)</td>
</tr>
<tr>
<td>(Helgaker)</td>
<td></td>
</tr>
<tr>
<td>0.034435351</td>
<td>-0.272642375</td>
</tr>
<tr>
<td>Extrapolated SCF</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.002175329</td>
<td>-0.08143802</td>
</tr>
</tbody>
</table>

Table 6.3  Table 6.3 represents the compiled Weizmann-2 LPK data for the transition state energy of ammonia. All energies are in Hartree’s particle$^{-1}$.

<table>
<thead>
<tr>
<th>Transition State Energy</th>
<th>Extrapolated CCSD Valence (T/Q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-56.2151948293</td>
<td>-0.274105171</td>
</tr>
<tr>
<td>Extrapolated Zero-Point-Energy</td>
<td>Extrapolated CCSD Valence (Q/5)</td>
</tr>
<tr>
<td>(Helgaker)</td>
<td></td>
</tr>
<tr>
<td>0.0330629189189189</td>
<td>-0.272305171</td>
</tr>
<tr>
<td>Extrapolated SCF</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.002697043</td>
<td>-0.08165047</td>
</tr>
</tbody>
</table>
Table 6.4  Table 6.4 represents the ground and transition state extrapolated zero point energies using the Petersson extrapolation formula. All energies are in Hartree’s particle$^{-1}$.

<table>
<thead>
<tr>
<th>Petersson Extrapolated Zero Point Energy (Ground State)</th>
<th>Petersson Extrapolated Zero Point Energy (Transition State)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0344684199743918</td>
<td>0.0330922202304737</td>
</tr>
</tbody>
</table>

Table 6.5  Table 6.5 represents the compiled barrier heights from our method using the Helgaker and Petersson extrapolation formulas. For comparison, the barrier height derived from the Weizmann-2 method is included. All energies are in kcal mol$^{-1}$.

<table>
<thead>
<tr>
<th>W2-LPK (Helgaker ZPE)</th>
<th>W2-LPK (Petersson ZPE)</th>
<th>Weizmann-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.96</td>
<td>3.95</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Luckily, ammonia’s an outlier for all empirically free electronic structure methods, so the inability to achieve chemical accuracy for the nitrogen inversion process does not invalidate our method. In fact, our method shows promise for relativistic molecules. For example, we are able to reduce the barrier height for the isomerization of phosphine by approximately 1.6 kcal mol$^{-1}$ in turn achieving chemical accuracy for the isomerization process of phosphine. The compiled ground state and transition state data can be found in Table 6.6 and 6.7, respectively. It is interesting the extrapolated zero point energies obtained from the Helgaker extrapolation formula appears to be irrational at first, however, upon inspection we see that the extrapolated zero point energy is actually rational. This is an interesting result as every other component is irrational and there is no reason to suspect the zero point energy would be any different. Although, the
author suspects this is due to the algorithm used within Wolframalpha Mathematica (used to compute the extrapolation components) which typically works in fields such as the rational, real or complex numbers. Table 6.8 illustrates the barrier height for the isomerization process of phosphine obtained with our method using the Helgaker extrapolation formula, our method using the Petersson extrapolation formula and for comparison the Weizmann-2 method. As predicted, the Helgaker extrapolation formula performs better than the Petersson extrapolation formula. It is interesting that regardless of which extrapolation formula is used, chemically accurate results are obtained. Since the Helgaker extrapolation formula has consistently shown to yield more accurate results than the Petersson extrapolation formula, from here on out, we will define our method (relative to the zero point energy) as the zero point energy extrapolated with the Helgaker extrapolation formula. The last molecule to study with our new method is aziridine. The compiled data for Aziridine is found in Table 6.9 and 6.10, while the barrier height for the isomerization process of Aziridine computed using our method and compared against the Weizmann-2 method is found in Table 6.11.
Table 6.6  Table 6.6 represents the compiled Weizmann-2 LPK data for the ground state energy of Phosphine. All energies are in Hartree’s particle\(^1\).

<table>
<thead>
<tr>
<th>Ground State Energy</th>
<th>Extrapolated CCSD Valence (T/Q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-342.493644105</td>
<td>-0.216951077</td>
</tr>
<tr>
<td>Extrapolated Zero-Point-Energy (Helgaker)</td>
<td>Extrapolated CCSD Valence (Q/5)</td>
</tr>
<tr>
<td>0.024123027027027</td>
<td>-0.215988055</td>
</tr>
<tr>
<td>Extrapolated SCF</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.00133698</td>
<td>-1.11462634</td>
</tr>
</tbody>
</table>

Table 6.7  Table 6.7 represents the compiled Weizmann-2 LPK data for the transition state energy of phosphine. All energies are in Hartree’s particle\(^1\).

<table>
<thead>
<tr>
<th>Transition State Energy</th>
<th>Extrapolated CCSD Valence (T/Q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-342.436841882</td>
<td>-0.220432478</td>
</tr>
<tr>
<td>Extrapolated Zero-Point-Energy (Helgaker)</td>
<td>Extrapolated CCSD Valence (Q/5)</td>
</tr>
<tr>
<td>0.0228977297297297</td>
<td>-0.219336577</td>
</tr>
<tr>
<td>Extrapolated SCF</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.001527064</td>
<td>-1.11368363</td>
</tr>
</tbody>
</table>
Table 6.8 Table 6.8 represents the compiled barrier heights for phosphine derived from our method using the Helgaker and Petersson extrapolation formulas. For comparison, the barrier height derived from the Weizmann-2 method is included. All energies are in kcale mole\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>W2-LPK(Helgaker ZPE)</th>
<th>W2-LPK(Petersson ZPE)</th>
<th>Weizmann-2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>31.0614</td>
<td>31.0543</td>
<td>32.7373</td>
</tr>
</tbody>
</table>

Table 6.9 Table 6.9 represents the compiled Weizmann-2 LPK data for the ground state energy of Aziridine. All energies are in Hartree’s particle\(^{-1}\).

<table>
<thead>
<tr>
<th>Ground State Energy</th>
<th>Extrapolated CCSD Valence (T/Q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-133.098992331</td>
<td>-0.632041601</td>
</tr>
<tr>
<td>Extrapolated Zero-Point-Energy (Helgaker)</td>
<td>Extrapolated CCSD Valence (Q/5)</td>
</tr>
<tr>
<td>0.0703582162162162</td>
<td>-0.628191262</td>
</tr>
<tr>
<td>Extrapolated SCF</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.003316918</td>
<td>-0.2114628</td>
</tr>
</tbody>
</table>
Table 6.10  Table 6.10 represents the compiled Weizmann-2 LPK data for the transition state energy of Aziridine. All energies are in Hartree’s particle⁻¹.

<table>
<thead>
<tr>
<th>Transition State Energy</th>
<th>Extrapolated CCSD Valence (T/Q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-133.070051824</td>
<td>-0.631476671</td>
</tr>
<tr>
<td>Extrapolated Zero-Point-Energy (Helgaker)</td>
<td>Extrapolated CCSD Valence (Q/5)</td>
</tr>
<tr>
<td>0.0683495945945946</td>
<td>-0.627392572</td>
</tr>
<tr>
<td>Extrapolated SCF</td>
<td>Relativistic Contribution</td>
</tr>
<tr>
<td>-0.003607717</td>
<td>-0.21171279</td>
</tr>
</tbody>
</table>

Table 6.11  Table 6.11 represents the compiled barrier heights for Aziridine derived from our method (Weizmann-2 LPK). For comparison, the barrier height derived from the Weizmann-2 method is included. All energies are kcal mol⁻¹.

<table>
<thead>
<tr>
<th>W2-LPK (Helgaker ZPE)</th>
<th>Weizmann-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.416342758099</td>
<td>17.31368</td>
</tr>
</tbody>
</table>
Comparing the aziridine barrier height derived by our method and the Weizmann-2 method, we see an increase in the barrier height by 0.1 kcal mole\(^{-1}\). This is an improvement to the original Weizmann-2 method, as well as, out performs all of the Weizmann-1 methods. Thus, we have developed an empirically free method that is able to produce chemically accurate results for all of the well behaved molecules studied. The author would like to define this method as the Weizmann-2 LPK theory because it modifies the Weizmann-2 theory and the LPK stands for Clifford LeMaster, Matthew King, and myself, all of which without their help this method would not have been developed. The Weizmann-2 LPK Theory is defined by the following steps:

1.) Geometry optimization using CCSD(T)/cc-pvqz+1
   - where the +1 indicates an additional large exponent d-function on second row atoms.

2.) Zero Point Energy obtained by CCSD(T)/cc-pvtz+1

3.) Zero Point Energy obtained by CCSD(T)/cc-pvqz+1

4.) Extrapolate the Zero Point Energies using the Helgaker extrapolation formula.

5.) Self-Consistent Field component is calculated from CCSD(T)/aug-cc-pvtz+2df, CCSD(T)/ aug-cc-pvqz+2df, CCSD(T)/ aug-cc-pv5z+2df
   - where the +2df indicates additional large exponent d and f-functions on second row atoms.
6.) Coupled Cluster valence correlation energy is obtained by CCSD/aug-cc-pvtz, CCSD/aug-cc-pvqz, CCSD/aug-cc-pv5z

7.) Coupled Cluster valence correlation energy is extrapolated out to the basis set limit using the Helgaker extrapolation formula.

8.) Core correlation and relativistic effects are computed using CCSD/MTsmall.

In conclusion, a decrease in the phosphine barrier height by approximately 1.6 kcal mole\(^{-1}\) rendering the calculation chemically accurate is a promising approach for problematic relativistic (second row containing) molecules such as SO\(_3\). Therefore, it is recommended future work with this method focus on both problematic and well behaved relativistic molecules, as well as, different processes such as atomization energies and barrier heights for isomerization processes.
APPENDIX A:

Standard Operating Procedure, Weizmann-2 Theory
The following is a standard operating procedure, as well as, a worked out example for computing the Weizmann-2 barrier height for the isomerization process of Aziridine. The input file will consist of the Link 0 and route section commands used within Weizmann-2 theory, while the output file will simply list what is needed from the output file using the ground state of Aziridine as an example.

**Step 1: Input File.**

%nprocshared=15 mem=60GB

%chk= This is where you specify the location of the checkpoint file.

# opt=ef ccsd(t)/cc-pvqz geom=connectivity

**Step 1: Output File.**

SCF Done: E(RHF) = -133.098992331
**Step 2: Input File.**

```
%nprocshared=15 mem=60GB
%chk= . . .
# freq=doublenumer ccsd(t)/cc-pvtz geom=connectivity
```

**Step 2: Output File.**

Zero Point Correction = 0.070526

**Step 3: Input File.**

```
%nprocshared=15 mem=60GB
%chk= . . .
# ccsd(t)/aug-cc-pvqz geom=connectivity
```

**Step 3: Output File.**

SCF Done: E(RHF) = -133.099626094
**Step 4: Input File.**

```
%nprocshared=15 mem=60GB
%chk= . . .

# ccsd/aug-cc-pv5z
```

**Step 4: Output File.**

SCF Done: E(RHF) = -133.10143033

**Step 5: Input File.**

```
%nprocshared=15 mem=60GB
%chk= . . .

# ccsd/aug-cc-pvqz
```

**Step 5: Output File.**

E(Corr) = -133.70755722
**Step 6: Input File.**

```
%nprocshared=15 mem=60GB
%chk=...
# ccsd/aug-cc-pv5z
```

**Step 6: Output File.**

\[ E(\text{Corr}) = -133.71713489 \]

**Step 7: Input File.**

```
%nprocshared=15 mem=60GB
%chk=...
# ccsd(t)/aug-cc-pvtz
```

**Step 7: Output File.**

\[ \text{CCSD(T)} = -133.70041769 \]
Step 8: Input File.

%nprocshared=15 mem=60GB
%chk=...
# ccsd(t)/aug-cc-pvqz

Step 8: Output File.

CCSD(T) = -133.73427883

Step 9: Input File.

%nprocshared=15 mem=60GB
%chk=...
# ccsd(t,full)/MTSmall Integral=DKH

Step 9: Output File.

CCSD(T) = -133.91613955
**Step 10: Input File.**

```
%nprocshared=15 mem=60GB
%chk=...
# ccsd(t)/MTSmall
```

**Step 10: Output File.**

CCSD(T) = -133.70467675

The Weizmann-2 transition state energy is computed identically to the ground state energy except the initial step is modified to account for the fact that we are trying to find a higher in energy minimum within the potential energy surface, relative to the ground state energy. The transition state input file looks like the following.

**Step 1: Input File.**

```
%nprocshared=15 mem=60GB
%chk=...
# opt=(ts,ef) ccsd(t)/cc-pvqz geom=connectivity
```

Once all of the energies have been computed and collected, we can extrapolate the various components of the Weizmann-2 method by the Petersson and Helgaker extrapolation formulas. The Petersson extrapolation formula is used solely for the initial
Hartree-Fock self-consistent field energy (because its convergence behaves exponentially) and is found by solving equation 1 and 2.

\[ E_1 = y + \frac{A}{L_1^2} \]  
Equation 1.

\[ E_2 = y + \frac{A}{L_2^2} \]  
Equation 2.

Where:

\( L_1 \) = The highest angular momentum used in the cc-p\( n_1 \)z basis set.

\( E_1 \) = Hartree-Fock energy obtained from the cc-p\( n_1 \)z basis set.

\( L_2 \) = The highest angular momentum used in the cc-p\( n_2 \)z basis set.

\( E_2 \) = Hartree-Fock energy obtained from the cc-p\( n_2 \)z basis set.

The details of the Petersson extrapolation formula can be found in reference 58 but for our purposes it is sufficient to realize the extrapolated self-consistent field energy is found by solving for \( Y \) in equations 1 and 2. For the ground state of Aziridine, the self-consistent field extrapolated component is found by solving the following systems of equations represented by equation 3.

\[ -133.099626094 = y + \frac{A}{45}, -133.101430033 = y + \frac{A}{55} \]  
Equation 3.

Solving equation 3, we find the extrapolated self-consistent field energy is -133.102309249342 Hartree’s. Now, since we are interested in the extrapolated self-consistent field component we subtract the extrapolated self-consistent field energy from the initial self-consistent field energy found in step 1. The next step is to sum the zero
point energy found in step 2 into the result of step 1 of Weizmann-2 theory followed by extrapolating the coupled cluster single double valence correlation energy using the Helgaker extrapolation formula. The Helgaker extrapolation formula is found in equation 4, while a worked out example for the ground state structure of aziridine is found in equation 5.

\[
\frac{(E_1 - (L_1^3)) - (E_2 - (L_2^3))}{(L_1^3) - (L_2^3)} \quad \text{Equation 4.}
\]

\[
\frac{(-133.72718359295) - (-133.71713469458)}{(4^3) - (5^3)} \quad \text{Equation 5.}
\]

Upon computing equation 5, we find the extrapolated coupled cluster single double valence correlation energy to be -133.72718359295 Hartree’s. Realizing this is the extrapolated correlation energy and the total energy is the sum of the correlation and Hartree-Fock energy, we subtract the result of equation 5 from the result of step 1, to obtain the extrapolated correlation energy. We repeat the process of computing equation 5 for steps 8 and 9 followed by subtracting the coupled cluster triple valence correlation energy from the coupled cluster single double valence correlation energy. The idea behind this subtraction is that the coupled cluster single double valence energy contains the single double correlation energy plus the Hartree-Fock energy, since we are only interested in the triple component (which is contained in the result of this step) we subtract the extrapolated coupled cluster single double valence correlation energy from the extrapolated coupled cluster triple valence energy, to arrive at the extrapolated triple component. Once the extrapolated components are obtained we sum the results into step
1. The next step is to determine the core correlation contribution, as well as, the relativistic effects, which is found by subtracting step 10 from step 9. Once the core correlation and relativistic contributions are obtained, we sum them into step 1. We then repeat the process for the transition state structure followed by subtracting the Weizmann-2 ground state energy from the transition state energy to arrive at a barrier height for the isomerization process of Aziridine, in Hartrees.
REFERENCES


14. Levy, M. *Universal variational functionals of electron densities, first order density matrices, and natural spin orbitals and solution of the v-representation*


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