Generalized Atoms In Molecules Approach (GAIM Approach)

by

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Dedication

To

the Memory of

My father,
My mother, and My sister.

I also would like to dedicate this thesis to:

My brother Abdulla

(Abu Tariq)

My sisters and My brothers

Prof. Raymond Poirier

My Dear Salam Khalil

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Abstract

This thesis involves two parts. The first is a new-proposed theoretical approach called generalized atoms in molecules (GAIM). The second is a computational study on the deamination reaction of adenine with OH^-/nH_2O (n=0, 1, 2, 3) and $3\,H_2O$.

The GAIM approach aims to solve the energy of each atom variationally in the first step and then to build the energy of a molecule from each atom. Thus the energy of a diatomic molecule (A-B) is formulated as a sum of its atomic energies, E_A and E_B. Each of these atomic energies is expressed as,

$$E_A = H^A + V_{ee}^{AA} + \frac{1}{2}V_{ee}^{A\leftrightarrow B}$$
$$E_B = H^B + V_{ee}^{BB} + \frac{1}{2}V_{ee}^{A\leftrightarrow B}$$

where; H^A and H^B are the kinetic and nuclear attraction energy of electrons of atoms A and B, respectively; V_{ee}^{AA} and V_{ee}^{BB} are the interaction energy between the electrons on atoms A and B, respectively; and $V_{ee}^{A\leftrightarrow B}$ is the interaction energy between the electrons of atom A with the electrons of atom B. The energy of the molecule is then minimized subject to the following constraint,

$$\int \rho_A(\mathbf{r})d\mathbf{r} + \int \rho_B(\mathbf{r})d\mathbf{r} = N$$

where $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ are the electron densities of atoms A and B, respectively, and N is the number of elecrons. The initial testing of the performance of GAIM was done

through calculating dissociation curves for H_2, LiH, Li_2, BH, HF, HCl, N_2, F_2, and Cl_2. The numerical results show that GAIM performs very well with H_2, LiH, Li_2, BH, HF, and HCl. GAIM shows convergence problems with N_2, F_2, and Cl_2 due to difficulties in reordering the degenerate atomic orbitals P_x, P_y, and P_z in N, F, and Cl atoms. Further work for the development of GAIM is required.

Deamination of adenine results in one of several forms of premutagenic lesions occurring in DNA. In this thesis, mechanisms for the deamination reaction of adenine with OH^-/nH_2O, (n = 0, 1, 2, 3) and $3\,H_2O$ were investigated. HF/6-31G(d), B3LYP/6-31G(d), MP2/6-31G(d), and B3LYP/6-31+G(d) levels of theory were employed to optimize all the geometries. Energies were calculated at the G3MP2B3 and CBS-QB3 levels of theory. The effect of solvent (water) was computed using the polarizable continuum model (PCM). Intrinsic reaction coordinate (IRC) calculations were performed for all transition states. Five pathways were investigated for the deamination reaction of adenine with OH^-/nH_2O and $3\,H_2O$. The first four pathways (A-D) begin with by deprotonation at the amino group of adenine by OH^-, while pathway E is initiated by tautomerization of adenine. For all pathways, the next two steps involve the formation of a tetrahedral intermediate followed by dissociation to yield products via a 1,3-hydrogen shift. Deamination with a single OH^- has a high activation barrier (190 kJ mol^{-1} using G3MP2B3 level) for the rate-determining step. Addition of one water molecule reduces this barrier by 68 kJ mol^{-1} calculated at G3MP2B3 level. Adding more water molecules decreases the overall activation energy of the reaction, but the effect becomes smaller with each additional water molecule. The most plausible mechanism is pathway E, the deamination reaction of adenine with $3\,H_2O$, which has an overall G3MP2B3 activation energy of 139 and 137 kJ mol^{-1} in the gas phase and PCM, respectively. This barrier is lower than that for the deamination with $OH^-/3\,H_2O$ by 6 and 2 kJ mol^{-1} in the gas phase and PCM, respectively.

PART ONE

Generalized Atom In Molecule Approach (GAIM Approach)

Chapter 1

Introduction

> *I like relativity and quantum theories because I don't understand them and they make me feel as if space shifted about like a swan that can't settle, refusing to sit still and be measured; and as if the atom were an impulsive thing always changing its mind.*
>
> (David H. Lawrence, Relativity)

1.1 Molecular Density

In molecular orbital theory (MOT), each molecule contains a set of orbitals called molecular orbitals, $\{\psi_a\}$, from which the molecular wavefunction can be constructed as an antisymmetrized product. Each molecular orbital (ψ_a) can be described as a linear combination of a finite set of basis functions, $\{\varphi_\mu\}$, in the form

$$\psi_a = \sum_{\mu=1}^{K} C_{\mu a}\varphi_\mu \qquad a = 1, 2, \ldots, K \tag{1.1}$$

where, K is the number of basis functions in the set, and $C_{\mu a}$ are the expansion coefficients. The molecular electron density, $\rho(\mathbf{r})$, can be obtained from these orbitals as follows,

$$\rho(\mathbf{r}) = \sum_a \eta_a \psi_a(\mathbf{r})\psi_a^*(\mathbf{r}) \tag{1.2}$$

where η_a is the occupancy of the ath molecular orbital (MO), and the sum is over all occupied MOs. The substitution of the expansion (1.1) into equation (1.2) leads to

$$\rho(\mathbf{r}) = \sum_a \eta_a \sum_{\mu=1}^{K} C_{\mu a}\varphi_\mu(\mathbf{r}) \sum_{\nu=1}^{K} C_{\nu a}^{*}\varphi_\nu^{*}(\mathbf{r}) \tag{1.3}$$

Equation (1.3) may be rearranged into,

$$\rho(\mathbf{r}) = \sum_{\mu\nu}^{K} \left(\sum_a \eta_a C_{\mu a} C_{\nu a}^{*} \right) \varphi_\mu(\mathbf{r})\varphi_\nu^{*}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{\mu\nu}^{K} P_{\mu\nu}\varphi_\mu(\mathbf{r})\varphi_\nu^{*}(\mathbf{r}) \tag{1.4}$$

where,

$$P_{\mu\nu} = \sum_a \eta_a C_{\mu a} C_{\nu a}^{*} \tag{1.5}$$

is the density matrix. Integration of $\rho(\mathbf{r})$ gives the total number of electrons (N) belonging to all atoms in a molecule.

$$\int \rho(\mathbf{r})d\mathbf{r} = \sum_{\mu\nu}^{K} P_{\mu\nu} \int \varphi_\nu^{*}(\mathbf{r})\varphi_\mu(\mathbf{r})d\mathbf{r} = \sum_{\mu\nu}^{K} P_{\mu\nu} S_{\nu\mu} = N \tag{1.6}$$

where,

$$S_{\nu\mu} = \int \varphi_\nu^{*}(\mathbf{r})\varphi_\mu(\mathbf{r})d\mathbf{r} \tag{1.7}$$

is the matrix of overlaps between basis functions.

1.2 Atoms in Molecules

Atoms can combine together to form chemical compounds. Chemists usually consider a molecule as a system that involves a finite number of atoms which are interacting with each other and are held together by chemical bonds.[1–3] Quantum mechanics (QM) treats the molecule as a mathematical system which depends on the coordinates of the nuclei and the electrons that constitute it.[4] Therefore the atom within a molecule is not a quantum mechanical observable and there is no unambiguous definition of an atom in a molecule.[5,6] Since chemistry is built upon atoms, the concept of atoms in molecules (AIM) and the decomposition of molecular properties into its atomic contributions are of great importance in chemistry.

Over the last decades a lot of scientific effort has been devoted to the AIM descriptions and to molecular energy decomposition schemes,[1–18] and they are still active research topics. The common motivation of such analysis approaches are to connect QM results with the genuine chemical concepts in order to get better understanding of issues such as atomic transferability and molecular similarity.[3,11,15] Such posteriori analyses can be classified into two main groups; the Hilbert-space analysis in which each basis function is assigned to one of the atoms in the molecule, and the three-dimensional (3D) physical space analysis in which the physical space of the molecule is partitioned into atomic domains.[4,19,20]

1.2.1 Hilbert Space Analyses

In Hilbert space analyses, the molecular basis set space is divided into atomic subspace contributions.[4] The population analyses of Mulliken[21] and Löwdin[22] are famous among the Hilbert space approaches,

$$q_A^{Mulliken} = Z_A - \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu} \tag{1.8}$$

$$q_A^{L\ddot{o}wdin} = Z_A - \sum_{\mu \in A} (\mathbf{S}^{\frac{1}{2}}\mathbf{P}\mathbf{S}^{\frac{1}{2}})_{\mu\mu} \tag{1.9}$$

where q_A is the net charge associated with atom A, Z_A is the nuclear charge of atom A, $\mathbf{S}$ and $\mathbf{P}$ are the overlap and density matrices, respectively. Neither Mulliken nor Löwdin analysis is unique and they depend very much on the basis set applied.[23,24]

1.2.2 Three-dimensional (3D) Physical Space Analyses

In the 3D physical space analysis, the molecular space is divided into atomic regions by means of the Quantum Theory of Atoms in Molecules (QTAIM) or by fuzzy atom approaches.[7,17,20]

1.2.2.1 Quantum Theory of Atoms in Molecules (QTAIM)

QTAIM which was developed by Richard Bader[7] is one of the most significant contributions to the subject of atoms and bonding in molecules. This theory is based on the assumption that every measurable property of a molecule can be measured as a sum of contributions from its composite atoms.[7,10] In QTAIM, the molecular space is divided into non-overlapping regions (atoms) bounded by the so-called zero flux surfaces that satisfy the following condition,[25,26]

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \qquad \text{for all } \mathbf{r} \text{ on the atomic surface} \tag{1.10}$$

where $\nabla\rho(\mathbf{r})$ is the gradient vector field of the electron density and $\mathbf{n}(\mathbf{r})$ is the unit vector normal to the atomic surface. Bader's analysis yields non-spherical and non-overlapping atomic regions that have sharp boundaries but they possess a high degree of transferability.[5] There are some disadvantages of this analysis including the appearance of one or more regions of the space, called non-nuclear attractors, that have no associated nuclei, and the high computational cost of the QTAIM calculations.[27,28]

1.2.2.2 Fuzzy Atom Approaches

The fuzzy atom approaches often start by introducing a weight function, $w_A(\mathbf{r})$, for each atom A at each point $\mathbf{r}$ of the molecular space such that,[29,30]

$$\sum_{A=1}^{N} w_A(\mathbf{r}) = 1, \qquad 0 \leq w_A(\mathbf{r}) \leq 1, \qquad \forall \mathbf{r} \in \mathbb{R}^3 \tag{1.11}$$

where N is the number of atoms. There are two types of weight functions; the binary weight functions where 0 or 1 are the only allowed values, and the fuzzy weight functions where all values between 0 and 1 are allowed.[31] The binary weight functions give non-overlapping atoms with sharp boundaries while the fuzzy weight functions give atoms that have overlapping and indistinct boundaries.[31,32] In the fuzzy weight functions, the value of $w_A(\mathbf{r})$ is ~ 1 near the nucleus A and gradually vanishes with distance from the nucleus A becoming 0 in the vicinity of another nucleus.[29]

Hirshfeld Weight Function

Hirshfeld proposed a weight function for each atom in a molecule, which is the ratio of the electron density of the isolated atom, $\rho_A^o(\mathbf{r}_i)$, to the electron density of the promolecule, $\rho^{pro}(\mathbf{r}_i)$, at each point $\mathbf{r}_i$ in the 3D molecular space[17]

$$w_A(\mathbf{r}_i) = \frac{\rho_A^o(\mathbf{r}_i)}{\rho^{pro}(\mathbf{r}_i)}, \qquad \rho^{pro}(\mathbf{r}_i) = \sum_A^N \rho_A^o(\mathbf{r}_i) \tag{1.12}$$

The $\rho^{pro}(\mathbf{r}_i)$ is calculated by summing over all densities, $\rho_A^o(\mathbf{r}_i)$, of non-interacting atoms placed at the same points as of the molecule of interest. The Hirshfeld approach is sometimes referred to as the stockholder approach as each atom at each point gets a fraction of the actual molecular density in proportion to its contribution to the $\rho^{pro}(\mathbf{r}_i)$. Hirshfeld analysis tends to give neutral atoms which are similar to the isolated atoms and depend on the choice of the state of free atoms used in the promolecule.[15,31]

The iterative Hirshfeld scheme proposed by Bultinck[11] and the iterative stockholder analysis (ISA) proposed by Weatley[17] are extensions of the original Hirshfeld method intended to improve it.

Becke Weight Function

In 1988, Axel D. Becke proposed a weight function for the partitioning of molecular density into single-center components.[18] Becke weight was initially introduced as a tool for simplifying the problem of numerical integration in molecular systems by decomposing the molecular integrals into atomic integral terms.[1,18] In the Becke scheme, the molecular space is divided into atomic cells (Voronoi cells or Voronoi polyhedra). Each atomic cell contains all grid points (i) that are closer to a particular nucleus than to any other nucleus, and then the boundaries between these cells are softened to create fuzzy cells.[18,33]

Becke utilized the confocal elliptical coordinate system (λ, μ, ϕ) for defining his weight. In this coordinate system, $\lambda_{iAB} = (r_{iA} + r_{iB})/R_{AB}$ can take on values from 1 to ∞, $\mu_{iAB} = (r_{iA} - r_{iB})/R_{AB}$ ranges in value from -1 to 1, and ϕ is the angle $(0 - 2\pi)$ about the AB axis. Here r_{iA} and r_{iB} are the distances from the grid point i to nuclei A and B, respectively, R_{AB} is the distance between nuclei A and B. The Becke weight function $w_A(\mathbf{r}_i)$ is defined using cell functions, $P_A(\mathbf{r}_i)$, as

$$w_A(\mathbf{r}_i) = \frac{P_A(\mathbf{r}_i)}{\sum_B P_B(\mathbf{r}_i)}, \qquad P_A(\mathbf{r}_i) = \prod_{B \neq A}^{N} s(\mu_{iAB}) \tag{1.13}$$

where N is the number of nuclei in the molecule. The sum in the denominator is run over all the nuclei of the molecule while in the $s(\mu_{iAB})$ product, the nucleus A is excluded. $s(\mu_{iAB})$ is the following step function,

$$s(\mu_{iAB}) = \begin{cases} 1 & -1 \leq \mu_{iAB} \leq 0 \\ 0 & 0 < \mu_{iAB} \leq 1 \end{cases} \tag{1.14}$$

$s(\mu_{iAB})$ is also known as the cutoff function or the cutoff profile. The cell function (P_A) defines a region of molecular space that is belonging to atom A, i.e., defines the Voronoi polyhedron surrounding the nucleus A. These cell functions play the same role as the promolecule densities in the Hirshfeld scheme. The value of $P_A(\mathbf{r}_i)$ is 1 if $\mathbf{r}_i$ lies in the cell, and 0 if $\mathbf{r}_i$ lies outside.[18]

In order to avoid discontinuities in $w_A(\mathbf{r}_i)$ at $\mu_{iAB} = 0$ $(r_{iA} = r_{iB})$, a smoothing algebraic function $f_k(\mu_{iAB})$ is used and $s(\mu_{iAB})$ is rewritten in terms of it as:[18,34]

$$s_k(\mu_{iAB}) = \frac{1}{2}\left[1 - f_k(\mu_{iAB})\right] \tag{1.15}$$

where $f_k(\mu_{iAB})$ is defined for each value of k as,

$$\begin{aligned} f_1(\mu_{iAB}) &= h(\mu_{iAB}) \\ f_2(\mu_{iAB}) &= h[h(\mu_{iAB})] \\ f_3(\mu_{iAB}) &= h\{h[h(\mu_{iAB})]\} \\ &\vdots \end{aligned}$$

where,

$$h(\mu_{iAB}) = \frac{3}{2}\mu_{iAB} - \frac{1}{2}\mu_{iAB}^3 \tag{1.16}$$

Here k is the stiffness parameter which controls the shape of the cutoff profile. The larger the value of k the steeper is the cutoff profile, and if k is too large the $s(\mu_{iAB})$ of equation (1.14) is recovered.[18,34] However, the choice of the parameter k is arbitrary. A value of $k = 3$ was chosen by Becke on the basis of the best performance of his numerical integration scheme with this value.[18] As a consequence of the use of the $s_3(\mu_{iAB})$ cutoff profile, the Becke weight gives overlapping atomic regions that have no sharp boundaries (fuzzy atoms).

The Becke scheme described above is suitable only for homonuclear systems as the faces of the Voronoi cells lie exactly at internuclear midpoints. In order for the Becke weights to be valid for describing heteronuclear systems, Becke shifted the cell boundaries according to the relative size of the atoms A and B using the following transformed coordinate,[18,33,34]

$$v_{iAB} = \mu_{iAB} + a_{AB}(1 - \mu_{iAB}^2) \tag{1.17}$$

where,

$$a_{AB} = \frac{u_{AB}}{u_{AB}^2 - 1}, \qquad u_{AB} = \frac{\chi_{AB} - 1}{\chi_{AB} + 1}, \qquad \chi_{AB} = \frac{R_A}{R_B} \tag{1.18}$$

here R_A and R_B are Bragg-Slater radii of elements A and B, respectively. With the use of Bragg-Slater radii, the Becke weights assign proportionally larger regions to larger atoms and smaller regions to smaller atoms in the molecule.

1.2.3 Properties of Atoms in Molecules

The weight function $w_A(\mathbf{r})$ obtained with any partition approach can be used for deriving atomic properties such as atomic densities, atomic population, etc., from the corresponding molecular properties. For examples, the electron density of atom A, $\rho_A(\mathbf{r})$, is derived from the molecular density, $\rho(\mathbf{r})$, as,

$$\rho_A(\mathbf{r}) = w_A(\mathbf{r})\rho(\mathbf{r}) \tag{1.19}$$

the electron population of atom A, q_A, is defined as the integral of the electron density of atom A,

$$q_A = \int \rho_A(\mathbf{r})d\mathbf{r} = \int w_A(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \tag{1.20}$$

and the atomic overlap matrix of atom A, $S_{\mu\nu}^A$, over basis functions, $\{\varphi_i\}$, is derived from the molecular overlap matrix, $S_{\mu\nu}$, as,

$$S_{\mu\nu}^A = \int w_A(\mathbf{r})\varphi_\mu^*(\mathbf{r})\varphi_\nu(\mathbf{r})d\mathbf{r} \tag{1.21}$$

1.2.4 Atoms in Molecules from Radial Density

An alternative approach, proposed by Warburton, Poirier, and Nippard,[15] for looking at AIM is the use of atomic radial densities (AIMRD) and the total radial density (TRD) in partitioning the molecular space into atomic regions.

The radial density, $\rho_A^{rad}(\mathbf{r}_i)$, of the atom A in a molecule at the point $\mathbf{r}_i$ in the molecular space is defined as,

$$\rho_A^{rad}(\mathbf{r}_i) = r_{iA}^2 w_A(\mathbf{r}_i)\rho(\mathbf{r}_i) = r_{iA}^2 \rho_A(\mathbf{r}_i) \tag{1.22}$$

where r_{iA} is the distance between nucleus A and the point $\mathbf{r}_i$, $w_A(\mathbf{r}_i)$ and $\rho(\mathbf{r}_i)$ are the Becke weight of atom A and the molecular electron density at that point, respectively. The TRD, $\rho^{rad}(\mathbf{r}_i)$, at the point $\mathbf{r}_i$ is calculated by summing over all AIMRD contributions,

$$\rho^{rad}(\mathbf{r}_i) = \sum_{A=1}^{N} r_{iA}^2 w_A(\mathbf{r}_i)\rho(\mathbf{r}_i) = \sum_{A=1}^{N} r_{iA}^2 \rho_A(\mathbf{r}_i) \tag{1.23}$$

where N is the number of atoms in the molecule, and the total sum of $w_A(\mathbf{r}_i)$ has value unity at each point in space.

The preliminary results[15] show that the AIMRDs are quite similar to the radial densities of free atoms, and therefore it would be more easily fit AIMRDs in order to generate TRDs and total densities of molecules. This approach provides an intuitive way for partitioning the molecular space into atomic regions and bonding regions.[15,16]

1.3 Energy Decomposition Analysis (EDA)

The decomposition of the total molecular energy into chemically intuitive components or into one-, two-, or more-atomic contributions gives insight into the nature of atomic and molecular interactions.[35] It also provides us with meaningful energy contributions such as exchange, correlation, electrostatic, polarization, charge transfer, etc.[36] Therefore, a significant number of EDA schemes has been proposed in both Hilbert and 3D physical spaces.[2–4,6,13,19,27–30,32,35–38,40–43] One of the most popular EDA schemes is the Kitaura-Morokuma (KM) scheme,[38] in which the HF interaction energy is decomposed into the six energy components; electrostatic (E_{ES}), polarization (E_{PL}), exchange repulsion (E_{EX}), charge transfer (E_{CT}), exchange polarization (E_{EXPL}), and a coupling term (E_{MIX}). Another scheme is the natural energy decomposition analysis (NEDA) proposed by Glendening and Streitwieser,[35] in which the HF interaction energy is partitioned into electrostatic, charge transfer, and deformation components. More recently, the NEDA has been extended to density functional theory. István Mayer has proposed several EDA methods over the last ten years using both the Hilbert space and the 3D physical space analyses.[6,13,19,32,40–43] His formalisms allow for analyzing different atomic and diatomic properties in a systematic manner based on the so called the atomic decomposition of identity. The atomic decomposition of identity means that the identity operator, $\hat{I}$, is written as a sum of single-atomic operators, $\hat{O}_A$,

$$\hat{I} = \sum_A \hat{O}_A \tag{1.24}$$

In his approaches, the total molecular energy is decomposed into atomic and diatomic components.

$$E = \sum_A E_A + \sum_{A<B} E_{AB} \tag{1.25}$$

As the decomposition of the molecular energy can be done in many ways, the definitions of the different energy components in EDA schemes are arbitrary.[39]

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Chapter 2

Theoretical Background

> *As far as the laws of mathematics refer to reality, they are not certain; and as far as they are certain, they do not refer to reality.*
>
> (Albert Einstein)

Chemistry is the science of studying the construction, transformation, and properties of substances. Although chemistry has been deliberated as an experimental science, theory has played a crucial role in its development. Theoretical chemistry is concerned with the rationalisation of chemical phenomena using mathematical methods along with the laws of physics and chemistry.[1–3] It also provides a variety of efficient and useful tools for describing, explaining, and predicting chemical problems. Computational chemistry has emerged naturally as an extension of theoretical chemistry. It is a fast-developing discipline which incorporates theoretical chemistry methods with computer science in order to study, model, and simulate chemical systems. Computational chemistry methods are becoming important tools for investigating chemical problems as well as discovering new realms of chemistry. These methods are used to perform calculations on a number of systems including inorganic and organic molecules, drugs, polymers, and biomolecules.[1] Achieving a direct and an accurate calculation to determine the structure or properties of a molecule in theoretical and computational chemistry is quite challenging. Today, with advanced computing power and efficient algorithms, computational chemistry can deal with complex chemical and biological systems with improving accuracy.[4] There are a wide range of theoretical and computational chemistry methods, which vary from highly accurate methods, that are derived from quantum mechanics such as wavefunction and density functional methods, to highly approximate methods, that are based on classical mechanics such as molecular mechanics.[4,5] A brief review of the theoretical methods most often used in computational studies are presented in this chapter.

2.1 Wavefunction Electronic Structure Theories

In wavefunction electronic structure theories, molecular structures are calculated using only the electronic Schrödinger equation (2.6), which is derived by applying the Born-Oppenheimer approximation[6] to the non-relativistic time-independent Schrödinger equation (2.1) as follows,

$$\hat{H}\Psi(\{\mathbf{r}_i\};\{\mathbf{R}_A\}) = E\Psi(\{\mathbf{r}_i\};\{\mathbf{R}_A\}) \tag{2.1}$$

where, Ψ is the molecular wavefunction, which is a function of the electronic, $\{\mathbf{r}_i\}$, and nuclear, $\{\mathbf{R}_A\}$, coordinates; E is the total non-relativistic energy of the system; and $\hat{H}$ is the total non-relativistic Hamiltonian of the molecular system which has the following form in the atomic units:[7]

$$\begin{aligned}\hat{H} = &-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}\frac{1}{r_{ij}} \\ &-\frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}\end{aligned} \tag{2.2}$$

Here, N is the number of electrons, M is the number of nuclei, Z_A is the atomic number of nucleus A, M_A is the ratio of the mass of nucleus A to the mass of the electron, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator, r_{iA} is the distance between the electron i and the nucleus A, r_{ij} is the distance between the electrons i and j, and R_{AB} is the distance between the nuclei A and B. The $\hat{H}$ is the operator corresponding to the total energy of the system, i.e., the sum of the kinetic energy operators (terms 1 and 4 in equation (2.2)) and the potential energy operators (terms 2, 3 and 5 in equation (2.2)).[7,8]

The Born-Oppenheimer approximation is based on the fact that the electrons have much smaller masses than the nuclei. In other words, the electrons move much faster than the nuclei. Thus, the electrons in a molecule are considered to be moving in a field of fixed nuclei. This approximation allows us to separate the Hamiltonian into the electronic Hamiltonian, $\hat{H}_{elec}$, and the nuclear Hamiltonian, $\hat{H}_{nucl}$. Therefore, the molecular wavefunction becomes the product of the electronic and the nuclear wavefunctions, i.e.,[2,5–8]

$$\left(\hat{H}_{elec} + \hat{H}_{nucl}\right) \Psi^{\mathbf{R}}_{elec} \Psi_{nucl} = E \, \Psi^{\mathbf{R}}_{elec} \Psi_{nucl} \tag{2.3}$$

where, $\Psi^{\mathbf{R}}_{elec} = \Psi^{\mathbf{R}}_{elec}(\{\mathbf{r}_i\})$ is the electronic wavefunction, which depends on the electronic coordinates and depends parametrically on the nuclear coordinates, and $\Psi_{nucl} = \Psi_{nucl}(\{\mathbf{R}_A\})$ is the nuclear wavefunction, which depends on the nuclear coordinates.[7,9] Within the Born-Oppenheimer approximation, the kinetic energy of the nuclei is zero and the repulsion, V_{NN}, between the nuclei in a particular configuration can be considered to be constant, so that equation (2.3) becomes

$$\left(\hat{H}_{elec} + V_{NN}(\mathbf{R}_A)\right) \Psi^{\mathbf{R}}_{elec} \Psi_{nucl} = E \, \Psi^{\mathbf{R}}_{elec} \Psi_{nucl} \tag{2.4}$$

where

$$V_{NN} = \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \tag{2.5}$$

Because V_{NN} is constant in a given nuclear configuration, it has no effect on the operator's eigenfunction and can be added to the eigenvalue of that operator.[2,7] Therefore, the electronic Schrödinger equation can now be written as,

$$\hat{H}_{elec}\Psi^{\mathbf{R}}_{elec}(\{\mathbf{r}_i\}) = E_{elec}(\mathbf{R})\Psi^{\mathbf{R}}_{elec}(\{\mathbf{r}_i\}) \tag{2.6}$$

where, $E_{elec}(\mathbf{R})$ is the electronic energy of the molecular system which depends on the coordinates of the electrons and depends parametrically on the coordinates of the nuclei. The total energy of the system in a given nuclear configuration E_{total} must include the V_{NN}, so that

$$E_{total} = E_{elec} + V_{NN} \tag{2.7}$$

The total molecular energy as a parametric function of the nuclear positions is called potential energy surface (PES).[10] The exploration of PESs is the first step in the investigation of the chemical processes and properties of molecules, e.g., their equilibrium geometry and vibrational frequencies.[10–12]

The $\hat{H}_{elec}$ and $\hat{H}_{nucl}$ can now be defined as,[7]

$$\hat{H}_{elec} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}\frac{1}{r_{ij}} \tag{2.8}$$

$$\hat{H}_{nucl} = -\frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 + E_{total}(\{\mathbf{R}\}) \tag{2.9}$$

The E_{total} represents the potential energy part in the nuclear Hamiltonian. Therefore, "the nuclei in the Born-Oppenheimer approximation move on a PES obtained by solving the electronic problem"[7] for different nuclear configurations. Hence, one can obtain the molecular translational, vibrational, and rotational energy levels for a given electronic state by solving the nuclear Schrödinger equation using the $E_{total}(\{\mathbf{R}\})$ for that state.[13]

$$\hat{H}_{nucl}\Psi_{nucl} = E\Psi_{nucl} \tag{2.10}$$

where E is the Born-Oppenheimer approximation to the total non-relativistic energy of the system which includes the electronic, translational, vibrational, and rotational energy.[7] However, we will concentrate solely on solving the electronic Schrödinger equation in this chapter.

2.1.1 Hartree-Fock Theory

The Hartree-Fock (HF) method is a central well-established approximation in modern electronic structure theory. It provides a good starting point towards more accurate theories.[14] In HF theory, the N-electrons wavefunction, Ψ, is built up as an antisymmetrized product of molecular spin orbitals (MSO).[15] The MSO, $\chi(\mathbf{x})$, is a one-electron wavefunction which depends on the space and spin coordinates, $\mathbf{x}$, of that electron. Thus, the Ψ is written as,

$$\Psi\left(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\right) = (N!)^{-1/2} \begin{vmatrix} \chi_1\left(\mathbf{x}_1\right) & \chi_2\left(\mathbf{x}_1\right) & \ldots & \chi_N\left(\mathbf{x}_1\right) \\ \chi_1\left(\mathbf{x}_2\right) & \chi_2\left(\mathbf{x}_2\right) & \ldots & \chi_N\left(\mathbf{x}_2\right) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1\left(\mathbf{x}_N\right) & \chi_2\left(\mathbf{x}_N\right) & \ldots & \chi_N\left(\mathbf{x}_N\right) \end{vmatrix} \tag{2.11}$$

where, $(N!)^{-1/2}$ is the normalization factor, and the determinant of the MSOs is called a *Slater determinant.* Writing a wavefunction in determinantal form fulfills the indistinguishability and antisymmetry requirements. The Ψ could also be written in a more compact and convenient form as,[7]

$$|\Psi\rangle = |\chi_1\chi_2\cdots\chi_i\chi_j\cdots\chi_N\rangle \tag{2.12}$$

In this shorthand notation, the normalization factor is dropped and only the diagonal elements of the determinant are included.

The HF energy is the expectation value of the electronic Hamiltonian and the

HF wavefunction, $\langle \Psi | \hat{H}_{elec} | \Psi \rangle$. According to the variation principle, the ground state wavefunction, Ψ_0, is the one which gives the lowest possible energy, E_0,

$$\begin{aligned} E_0 &= \langle \Psi_0 | \hat{H}_{elec} | \Psi_0 \rangle \\ &= \sum_{i}^{N} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i,j}^{N} \langle ij \| ij \rangle \end{aligned} \tag{2.13}$$

Here $\hat{h}$ is the *core-Hamiltonian* operator, which describes the kinetic energy, $\langle i | \hat{h} | i \rangle$, for an electron and its attraction energy with the nuclei. The $\hat{h}$ omits all interaction with the other electrons.

$$\hat{h} = -\frac{1}{2}\nabla_1^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \tag{2.14}$$

and $\langle ij \| ij \rangle$ is the antisymmetrized two-electron integral,

$$\begin{aligned} \langle ij \| ij \rangle &= \langle ij | ij \rangle - \langle ij | ji \rangle \\ &= \iint \frac{\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)(1 - \mathscr{P}_{12})\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)}{r_{12}}\, d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \tag{2.15}$$

where, $\mathscr{P}_{12}$ is the permutation operator which interchanges the coordinates of electrons one and two. The minimization of the energy of the wavefunction Ψ_0 (equation 2.13) with respect to the MSOs leads to the HF equations,

$$\hat{f}(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1) \tag{2.16}$$

where, ϵ_i is the energy of the ith spin orbital, and $\hat{f}$ is the Fock operator.

$$\hat{f}(\mathbf{x}_1) = \hat{h}(\mathbf{x}_1) + \sum_{j=1}^{N} \hat{\mathscr{J}}_j(\mathbf{x}_1) - \hat{\mathscr{K}}_j(\mathbf{x}_1) \tag{2.17}$$

Here $\hat{\mathcal{J}}_j(\mathbf{x}_1)$ is the Coulomb operator, and $\hat{\mathcal{K}}_j(\mathbf{x}_1)$ is the exchange operator,

$$\begin{aligned} \hat{\mathcal{J}}_j(\mathbf{x}_1)\chi_i(\mathbf{x}_1) &= \left(\int \frac{\chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2\right)\chi_i(\mathbf{x}_1) \\ \hat{\mathcal{K}}_j(\mathbf{x}_1)\chi_i(\mathbf{x}_1) &= \left(\int \frac{\chi_j^*(\mathbf{x}_2)\mathscr{P}_{12}\chi_j(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2\right)\chi_i(\mathbf{x}_1) \end{aligned} \tag{2.18}$$

The minimization is carried out by varying the spin orbitals under the constraint that they remain orthogonal $\big(\langle\chi_i|\chi_j\rangle = \delta_{ij}$, where $\delta_{ij} = 1$ if $i = j$ and 0 otherwise$\big)$ using the Lagrange's method of undetermined multipliers.[7, 15, 16]

For computational purposes, the HF equations must be expressed over spatial orbitals so that the spin functions α and β must be integrated out. There are three types of spatial HF wavefunctions (determinants): restricted closed-shell HF (RHF), restricted open-shell HF (ROHF), and unrestricted HF (UHF) wavefunctions. In the RHF and ROHF determinants, electrons with α and β spins are forced to have the same spatial orbital, while in the UHF determinant, each electron has its own spatial orbital. The closed-shell configuration refers to a wavefunction which is made up of complete electron shells.[15] Therefore, in contrast to the open-shell systems, all molecular orbitals in closed-shell systems are doubly occupied.

2.1.1.1 Restricted Hartree-Fock Theory (RHF)

The N-electrons restricted closed-shell ground state determinant is

$$|\Psi_0\rangle = |\psi_1\psi_2\cdots\psi_a\psi_b\cdots\psi_{\frac{N}{2}}\rangle \tag{2.19}$$

where each spatial orbital, ψ_a, has two electrons with opposite spins. The spatial HF equations for the closed-shell system can be derived by integrating out the spin functions from the analogous spin orbital HF equations.[17] Thus, the closed-shell ground state energy, E_0, is

$$\begin{aligned} E_0 &= \langle \Psi_0 | \hat{H}_{elec} | \Psi_0 \rangle \\ &= 2 \sum_{a=1}^{N/2} (a|\hat{h}|a) + \sum_{a,b}^{N/2} 2(aa|bb) - (ab|ba) \\ &= 2 \sum_{a=1}^{N/2} h_{aa} + \sum_{a,b}^{N/2} 2J_{ab} - K_{ab} \end{aligned} \tag{2.20}$$

where h_{aa} is the kinetic and attraction energy of an electron described by ψ_a. J_{ab} and K_{ab} are the Coulomb and exchange energies, respectively, for two electrons described by ψ_a and ψ_b. The closed-shell eigenvalue equation has the same form as the spin orbital equation.

$$\hat{f}(\mathbf{r}_1)\psi_a(\mathbf{r}_1) = \epsilon_a \psi_a(\mathbf{r}_1) \tag{2.21}$$

where the closed-shell Fock operator is given by

$$\hat{f}(\mathbf{r}_1) = \hat{h}(\mathbf{r}_1) + \sum_{a=1}^{N/2} 2\hat{J}_a(\mathbf{r}_1) - \hat{K}_a(\mathbf{r}_1) \tag{2.22}$$

The practical method for solving the RHF equations (2.21) is the expansion of each molecular orbital as a linear combination of known basis functions with unknown coefficients. Therefore, the problem of determining the wavefunction is equivalent to calculating these coefficients. Thus, by introducing a set of K basis functions, $\{\varphi_\mu\}$, each molecular orbital can be expanded as,

$$\psi_a = \sum_{\mu=1}^{K} C_{\mu a} \varphi_\mu \tag{2.23}$$

where $C_{\mu a}$ is the expansion coefficients. The substitution of this expansion into equation (2.21) leads to

$$\hat{f}(\mathbf{r}_1) \sum_{\nu=1}^{K} C_{\nu a} \varphi_\nu(\mathbf{r}_1) = \epsilon_a \sum_{\nu=1}^{K} C_{\nu a} \varphi_\nu(\mathbf{r}_1) \tag{2.24}$$

By multiplying both sides by $\varphi_\mu^*(\mathbf{r}_1)$ and integrating with respect to $\mathbf{r}_1$, we get

$$\sum_\nu C_{\nu a} \int \varphi_\mu^*(\mathbf{r}_1)\hat{f}(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)\, d\mathbf{r}_1 = \epsilon_a \sum_\nu C_{\nu a} \int \varphi_\mu^*(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)\, d\mathbf{r}_1 \tag{2.25}$$

If we use the following notations for the matrix elements of the Fock operator, $\hat{f}(\mathbf{r}_1)$, and for the overlap between basis functions,

$$\begin{aligned} F_{\mu\nu} &= \int \varphi_\mu^*(\mathbf{r}_1)\hat{f}(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)\, d\mathbf{r}_1 \\ S_{\mu\nu} &= \int \varphi_\mu^*(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)\, d\mathbf{r}_1 \end{aligned} \tag{2.26}$$

then the result is algebraic equations known as Roothaan's equations,[15,17]

$$\sum_\nu F_{\mu\nu} C_{\nu a} = \epsilon_a \sum_\nu S_{\mu\nu} C_{\nu a} \tag{2.27}$$

which can be written as a single matrix equation.

$$\mathbf{FC} = \epsilon\mathbf{SC} \tag{2.28}$$

Here, $\mathbf{C}$ is the molecular orbital expansion coefficients matrix, $\mathbf{S}$ is the overlap matrix, ϵ is a diagonal matrix of the orbital energies, and $\mathbf{F}$ is the Fock matrix which represents the Fock operator in terms of the basis functions. Equation (2.28) is not a standard eigenvalue equation. In order to convert it into a standard eigenvalue equation, orthogonalization of the basis is necessary. The orthogonalization is carried out by defining a new coefficient matrix, $\mathbf{C}'$, related to the old $\mathbf{C}$ by ($\mathbf{C} = \mathbf{XC}'$). The $\mathbf{X}$ matrix must transform the $\mathbf{S}$ to the identity matrix, i.e., $\mathbf{X}^\dagger\mathbf{SX} = \mathbf{I}$. Substituting $\mathbf{C} = \mathbf{XC}'$ into the equation (2.28) and multiplying on the left by $\mathbf{X}^\dagger$ results in an eigenvalue equation,[7]

$$\mathbf{F}'\mathbf{C}' = \epsilon\mathbf{C}' \tag{2.29}$$

where $\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}$. The elements of the $\mathbf{F}$ over the basis function are

$$\begin{aligned} F_{\mu\nu} &= \int \varphi_\mu^*(\mathbf{r}_1) \hat{f}(\mathbf{r}_1) \varphi_\nu(\mathbf{r}_1)\, d\mathbf{r}_1 \\ &= \int \varphi_\mu^*(\mathbf{r}_1) \Big[\hat{h}(\mathbf{r}_1) + \sum_a^{N/2} 2\hat{J}_a(\mathbf{r}_1) - \hat{K}_a(\mathbf{r}_1) \Big] \varphi_\nu(1)\, d\mathbf{r}_1 \\ &= (\mu|\hat{h}|\nu) + \sum_a^{N/2} 2(\mu\nu|aa) - (\mu a|a\nu) \end{aligned} \tag{2.30}$$

By inserting the molecular orbital expansion into the two-electron integrals part, we obtain

$$\begin{aligned} F_{\mu\nu} &= (\mu|\hat{h}|\nu) + \sum_{\lambda,\sigma} \sum_a^{N/2} 2C_{\lambda a} C_{\sigma a}^* [(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)] \\ &= H_{\mu\nu} + \sum_{\lambda,\sigma} P_{\lambda\sigma} [(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)] \\ &= H_{\mu\nu} + G_{\mu\nu} \end{aligned} \tag{2.31}$$

where, $P_{\lambda\sigma}$ are the elements of the density matrix which is defined as,

$$P_{\lambda\sigma} = 2 \sum_a^{N/2} C_{\lambda a} C_{\sigma a}^* \tag{2.32}$$

or in a matrix form as,

$$\mathbf{P} = \mathbf{2CC}^\dagger \tag{2.33}$$

$H_{\mu\nu}$ is the core-Hamiltonian matrix or the one-electron part of the Fock matrix, and $G_{\mu\nu}$ is the two-electron part of the Fock matrix. $\mathbf{G}$ depends on the two-electron integrals of the basis functions and on $\mathbf{P}$. Since the matrix $\mathbf{F}$ depends, through $\mathbf{P}$, on its eigenvectors, the Roothaan equations are nonlinear and must be solved iteratively using a well-known procedure called the self-consistent field (SCF).[4,7,17]

The SCF procedure starts by defining the input data that specify a molecule such as nuclear coordinates, atomic numbers, number of electrons, and basis set. Therefore, all the required integrals, $S_{\mu\nu}$, $H_{\mu\nu}$, and $\{(\mu\nu|\lambda\sigma)\}$ as well as the matrix $\mathbf{X}$ can be obtained. Then, an initial guess for $\mathbf{C}$ is given, and $\mathbf{P}$ is calculated. $\mathbf{F}$ is obtained and transformed to $\mathbf{F}' = \mathbf{X}^{\dagger}\mathbf{F}\mathbf{X}$. Then $\mathbf{C}'$ and ϵ are obtained by diagonalizing $\mathbf{F}'$. A new $\mathbf{C} = \mathbf{X}\mathbf{C}'$ is calculated and the procedure is iterated until some convergence criteria are met. Once self-consistency has been reached, many properties of the system such as the dipole moment, quadruple moment, atomic population, electronic energy, etc., can be obtained as expectation values of the wavefunction with one-electron or two-electron operators. For example, the closed-shell ground state energy, E_0, is the expectation value $\langle\Psi_0|H_{elec}|\Psi_0\rangle$ which is given over the basis functions by

$$E_0 = \frac{1}{2}\sum_{\mu\nu} P_{\nu\mu}\left(H_{\mu\nu} + F_{\mu\nu}\right) \tag{2.34}$$

A drawback of the HF method is that it does not describe the interaction between electrons correctly. In other words, it neglects correlations between electrons with opposite spins.[7]

2.1.1.2 Unrestricted Open-Shell Hartree-Fock Theory (UHF)

The UHF method, the most commonly used method for open-shell molecules, was first formulated by J. A. Pople and R. K. Nesbet in 1953.[18] In the UHF wavefunction, different sets of spatial molecular orbitals are assigned for spin-up and spin-down electrons.[7,19] Thus, the form of an unrestricted set of spin orbitals $\{\chi_i\}$ is written as,[7]

$$\chi_i(\mathbf{x}) = \begin{cases} \psi_j^{\alpha}(\mathbf{r})\alpha(\omega) & j = 1, 2, \ldots, K \\ \psi_j^{\beta}(\mathbf{r})\beta(\omega) & j = 1, 2, \ldots, K \end{cases} \tag{2.35}$$

where, $\{\psi_j^{\alpha}\}$ and $\{\psi_j^{\beta}\}$ are the sets of spatial orbitals for α and β electrons, respectively. The UHF wavefunction has the form,

$$\Psi_{UHF} = |\psi_1^{\alpha}\psi_1^{\beta}\ldots\psi_{N^{\alpha}}^{\alpha}\psi_{N^{\beta}}^{\beta}\rangle \tag{2.36}$$

here, N^{α} and N^{β} are the number of α and β electrons, respectively. The total unrestricted open-shell energy, E_{UHF}, is expressed as,[7,18]

$$E_{UHF} = \sum_{a}^{N^{\alpha}} h_{aa}^{\alpha} + \sum_{a}^{N^{\beta}} h_{aa}^{\beta} + \frac{1}{2}\sum_{ab}^{N^{\alpha}} \left(J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}\right) + \frac{1}{2}\sum_{ab}^{N^{\beta}} \left(J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}\right) + \sum_{a}^{N^{\alpha}}\sum_{b}^{N^{\beta}} J_{ab}^{\alpha\beta} \tag{2.37}$$

where; h_{aa}^{α}, $J_{ab}^{\alpha\alpha}$, and $K_{ab}^{\alpha\alpha}$ are the kinetic and nuclear attraction energy, the Coulomb energy, and the exchange energy, respectively, for electrons of α spin; h_{aa}^{β}, $J_{ab}^{\beta\beta}$, and $K_{ab}^{\beta\beta}$ are the kinetic and nuclear attraction energy, the Coulomb energy, and the exchange energy, respectively, for electrons of β spin; $J_{ab}^{\alpha\beta}$ is the Coulomb interaction energy between α and β electrons. The summations in equation (2.37) are over occupied α or β orbitals.

The first variation of the energy in equation (2.37) with respect to α and β spatial orbitals, subject to the orthonormality conditions, and then the unitary transformation of the α and β orbitals among themselves leads to[7,18]

$$\begin{aligned} f^{\alpha}(\mathbf{r})\psi_j^{\alpha}(\mathbf{r}) &= \epsilon_j^{\alpha}\psi_j^{\alpha}(\mathbf{r}) \\ f^{\beta}(\mathbf{r})\psi_j^{\beta}(\mathbf{r}) &= \epsilon_j^{\beta}\psi_j^{\beta}(\mathbf{r}) \end{aligned} \tag{2.38}$$

where; ϵ_j^{α} and ϵ_j^{β} are the energy of the spatial orbitals ψ_j^{α} and ψ_j^{β}, respectively; $f^{\alpha}(\mathbf{r})$ and $f^{\beta}(\mathbf{r})$ are the Fock operators for electrons of α and β spin, respectively, that have the forms,

$$\begin{aligned} \hat{f}^{\alpha}(\mathbf{r}) &= \hat{h}^{\alpha}(\mathbf{r}) + \sum_{a}^{N^{\alpha}} \left(\hat{J}_a^{\alpha}(\mathbf{r}) - \hat{K}_a^{\alpha}(\mathbf{r})\right) + \sum_{a}^{N^{\beta}} \hat{J}_a^{\beta}(\mathbf{r}) \\ \hat{f}^{\beta}(\mathbf{r}) &= \hat{h}^{\beta}(\mathbf{r}) + \sum_{a}^{N^{\beta}} \left(\hat{J}_a^{\beta}(\mathbf{r}) - \hat{K}_a^{\beta}(\mathbf{r})\right) + \sum_{a}^{N^{\alpha}} \hat{J}_a^{\alpha}(\mathbf{r}) \end{aligned} \tag{2.39}$$

here $\hat{h}$, $\hat{J}$, and $\hat{K}$ are the core-Hamiltonian, the Coulomb, and the exchange operators, respectively, defined in equations (2.14) and (2.18).

The UHF equations (2.38) can be solved by expanding the α and β molecular orbitals as a linear combination of K known basis functions,$\{\varphi_\mu\}$.

$$\begin{aligned} \psi_i^\alpha &= \sum_{\mu=1}^{K} C_{\mu i}^\alpha \varphi_\mu \qquad i = 1, 2, \ldots, K \\ \psi_i^\beta &= \sum_{\mu=1}^{K} C_{\mu i}^\beta \varphi_\mu \qquad i = 1, 2, \ldots, K \end{aligned} \tag{2.40}$$

Substitution of the expansions (2.40) into the UHF equations (2.38) leads to two matrix equations, known as Pople–Nesbet equations.[7,19]

$$\begin{aligned} \mathbf{F}^\alpha \mathbf{C}^\alpha &= \mathbf{S}\mathbf{C}^\alpha \epsilon^\alpha \\ \mathbf{F}^\beta \mathbf{C}^\beta &= \mathbf{S}\mathbf{C}^\beta \epsilon^\beta \end{aligned} \tag{2.41}$$

where; $\mathbf{S}$ is the matrix of overlaps between basis functions; $\mathbf{C}^\alpha$ and $\mathbf{C}^\beta$ are the α and β molecular orbitals coefficient matrices; ϵ^α and ϵ^β are diagonal matrices of α and β orbital energies; $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$ are the α and β Fock matrices, which have the forms,

$$\begin{aligned} F_{\mu\nu}^\alpha &= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}^T \left(\mu\nu|\sigma\lambda\right) - P_{\lambda\sigma}^\alpha \left(\mu\lambda|\sigma\nu\right) \\ F_{\mu\nu}^\beta &= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}^T \left(\mu\nu|\sigma\lambda\right) - P_{\lambda\sigma}^\beta \left(\mu\lambda|\sigma\nu\right) \end{aligned} \tag{2.42}$$

where; $(\mu\nu|\sigma\lambda)$ are the two-electron integrals over basis functions in chemist's notation; $H_{\mu\nu}$ is the core-Hamiltonian matrix; $P_{\lambda\sigma}^\alpha$, $P_{\lambda\sigma}^\beta$, and $P_{\lambda\sigma}^T$ are the α-electron density, the β-electron density, and the total electron density matrices, respectively, that are defined as,

$$P_{\mu\nu}^\alpha = \sum_{a}^{N^\alpha} C_{\mu a}^\alpha C_{\nu a}^{\alpha *}, \qquad P_{\mu\nu}^\beta = \sum_{a}^{N^\beta} C_{\mu a}^\beta C_{\nu a}^{\beta *}, \qquad P_{\mu\nu}^T = P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta \tag{2.43}$$

The $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$ depend explicitly on each other through $\mathbf{P}^T$. Therefore, the Pople–Nesbet equations (2.41) must be solved simultaneously. The unrestricted SCF procedure used to solve these equation is quite analogous to the SCF procedure used to solve the RHF equations. It first begins with a guess for the two coefficient matrices $\mathbf{C}^{\alpha}$ and $\mathbf{C}^{\beta}$, and then the density matrices $\mathbf{P}^{\alpha}$, $\mathbf{P}^{\beta}$, and $\mathbf{P}^{T}$ are computed. The Fock matrices $\mathbf{F}^{\alpha}$ and $\mathbf{F}^{\beta}$ are obtained and transformed to $\mathbf{F}^{\alpha\prime} = \mathbf{X}^{\dagger}\mathbf{F}^{\alpha}\mathbf{X}$ and $\mathbf{F}^{\beta\prime} = \mathbf{X}^{\dagger}\mathbf{F}^{\beta}\mathbf{X}$. Then $\mathbf{C}^{\alpha\prime}$, $\mathbf{C}^{\beta\prime}$, ϵ^{α}, and ϵ^{β} are obtained by diagonalizing $\mathbf{F}^{\alpha\prime}$ and $\mathbf{F}^{\beta\prime}$. New $\mathbf{C}^{\alpha} = \mathbf{X}\mathbf{C}^{\alpha\prime}$ and $\mathbf{C}^{\beta} = \mathbf{X}\mathbf{C}^{\beta\prime}$ are calculated and the procedure is iterated until some convergence criteria are met. A drawback of the UHF method is that, it is not an eigenfunction to the total spin angular momentum operator.[7, 19, 20]

2.1.1.3 Restricted Open-Shell Hartree-Fock Theory (ROHF)

The ROHF method was first formulated by Roothaan in 1960.[17] In contrast to the UHF wavefunction, the ROHF wavefunction is an eigenfunction to the total spin angular momentum operator.[7, 20–23] On the other hand, the ROHF method has its own limitations, such as lacking of a unique Fock operator and having a higher variational energy than that for the UHF method.[7, 20, 22, 23] In the ROHF wavefunction, occupied spatial orbitals are partitioned into two subsets; a closed-shell (doubly occupied) subset and an open-shell (partially occupied) subset.[24] Therefore, the ROHF wavefunction can be written in the form

$$\Psi_{ROHF} = |\psi_1^c\overline{\psi}_1^c\psi_2^c\overline{\psi}_2^c\cdots\psi_{n_c}^c\overline{\psi}_{n_c}^c\psi_1^o\psi_2^o\cdots\psi_{n_o}^o\rangle \tag{2.44}$$

here; the overbar denotes the occupation with a β spin electron; c and o denote the closed and open-shell orbitals, respectively; n_c and n_o are the total number of the closed and open-shell orbitals, respectively.

The total restricted open-shell electronic energy, E_{ROHF}, can be expressed as,[20, 25, 26]

$$E_{ROHF} = 2\sum_{i}^{n} f_i h_{ii} + \sum_{ij}^{n} f_i f_j \left(2a_{ij}J_{ij} - b_{ij}K_{ij}\right) \tag{2.45}$$

where; h_{ii}, J_{ij}, and K_{ij} are the kinetic and nuclear attraction energy, the Coulomb energy, and the exchange energy, respectively; $n = n_c + n_o$ is the number of occupied orbitals; f_i is the occupation number for orbital i ($f_i = 1$ for the closed-shell subset, and $0 < f_i < 1$ for the open-shell subset);[17] a_{ij} and b_{ij} are the coupling coefficients and their values depend on the case under study. Equation (2.45) is considered to be the starting point to the ROHF formulation. The minimization of the energy of equation (2.45) with respect to the spatial orbitals, subject to the orbital orthogonality constraint, leads to the Euler equation,[17,25]

$$\hat{F}_i|\psi_i\rangle = \sum_j^n \varepsilon_{ji}|\psi_j\rangle \tag{2.46}$$

where ε_{ji} are the Lagrange multipliers. The Fock operator, $\hat{F}i$, has the form[25]

$$\hat{F}_i = f_i\left(\hat{h} + \sum_j^n f_j\left(2a_{ij}\hat{J}_j - b_{ij}\hat{K}_j\right)\right) \tag{2.47}$$

here $\hat{h}$, $\hat{J}$, and $\hat{K}$ are the core-Hamiltonian, the Coulomb, and the exchange operators, respectively, defined in equations (2.14) and (2.18). Unlike the closed-shell case, there is no unitary transformation that transforms all the orbitals among themselves in order to bring equation (2.46) into a pseudo-eigenvalue equation.[17] However, in the ROHF case, there are only unitary transformations that transform the closed and open-shells subsets within themselves.[16,17] It should be noted that such transformations cannot eliminate the off-diagonal Langrange multipliers coupling the closed and open-shell subsets.[17] By ignoring the off-diagonal closed-open coupling terms, one can transform equation (2.46) into two separate pseudo-eigenvalue equations, one for the closed-shell subset and one for the open-shell subset. That is,

$$\begin{aligned}\hat{F}^c\psi_i^c &= \varepsilon_i^c\psi_i^c \\ \hat{F}^o\psi_i^o &= \varepsilon_i^o\psi_i^o\end{aligned} \tag{2.48}$$

where; ε^c and ε^o are the orbital energies for the closed and open-shell orbitals, respectively, which do not satisfy Koopmans' theorem; $\hat{F}^c$ and $\hat{F}^o$ are the Fock operators for the closed and open-shell orbitals, respectively, that have the form,[17,25,27]

$$\begin{aligned}\hat{F}^c &= \hat{h} + \left(2\hat{J}_c - \hat{K}_c\right) + f\left(2\hat{J}_o - \hat{K}_o\right) \\ \hat{F}^o &= f\left[\hat{h} + \left(2\hat{J}_c - \hat{K}_c\right) + f\left(2a\hat{J}_o - b\hat{K}_o\right)\right]\end{aligned} \tag{2.49}$$

where

$$\hat{J}_c = \sum_i^{n_c} \hat{J}_i, \qquad \hat{J}_o = \sum_i^{n_o} \hat{J}_i, \qquad \hat{K}_c = \sum_i^{n_c} \hat{K}_i, \qquad \hat{K}_o = \sum_i^{n_o} \hat{K}_i, \tag{2.50}$$

In case of high-spin open-shell systems ($f = 1/2$, $a = 1$, and $b = 2$), the ROHF calculations can be performed using alpha and beta Fock operators (f^α and f^β) of the UHF method.[16,20,25,27] For such open-shell systems, one can find the following relations between the ROHF and UHF Fock operators:

$$\hat{F}_c = (\hat{f}^\alpha + \hat{f}^\beta)/2, \qquad \hat{f}^\alpha = 2\hat{f}_o, \qquad \hat{f}^\beta = 2(\hat{f}_c - \hat{f}_o) \tag{2.51}$$

The molecular orbitals are expressed as linear combinations of K known basis functions. A set of K molecular orbitals can be constructed from such combinations, which is partitioned into three subsets; n_c closed-shell (doubly occupied), n_o open-shell (singly occupied), and $(K - n)$ virtual (unoccupied) molecular orbitals.[24] Using equation (2.48), a single Fock matrix ($\mathbf{F}^{hs}_{ROHF}$) for high-spin open-shell systems in the molecular orbital basis can be constructed as,[24,27,28]

$$
\mathbf{F}^{hs}_{ROHF} = \begin{array}{c} \\ \left(\begin{array}{ccc} \mathbf{F}^{cc}_{\psi} & 2(\mathbf{F}^{c}_{\psi} - \mathbf{F}^{o}_{\psi}) & \mathbf{F}^{c}_{\psi} \\ 2(\mathbf{F}^{c}_{\psi} - \mathbf{F}^{o}_{\psi}) & \mathbf{F}^{oo}_{\psi} & 2\mathbf{F}^{o}_{\psi} \\ \mathbf{F}^{c}_{\psi} & 2\mathbf{F}^{o}_{\psi} & \mathbf{F}^{vv}_{\psi} \end{array}\right) \end{array}
\begin{array}{cccc} & \textit{closed} & \textit{open} & \textit{virtual} \\ \textit{closed} & & & \\ \textit{open} & & & \\ \textit{virtual} & & & \end{array}
\tag{2.52}
$$

or equivalently, using the alpha and beta Fock matrices of the UHF method, as[20,24,27,28]

$$
\mathbf{F}^{hs}_{ROHF} = \begin{array}{cccc} \textit{closed} & \textit{open} & \textit{virtual} & \\ \mathbf{F}^{cc}_{\psi} & \mathbf{F}^{\beta}_{\psi} & (\mathbf{F}^{\alpha}_{\psi} + \mathbf{F}^{\beta}_{\psi})/2 & \textit{closed} \\ \mathbf{F}^{\beta}_{\psi} & \mathbf{F}^{oo}_{\psi} & \mathbf{F}^{\alpha}_{\psi} & \textit{open} \\ (\mathbf{F}^{\alpha}_{\psi} + \mathbf{F}^{\beta}_{\psi})/2 & \mathbf{F}^{\alpha}_{\psi} & \mathbf{F}^{vv}_{\psi} & \textit{virtual} \end{array}
\tag{2.53}
$$

where; $\mathbf{F}^{c}_{\psi}$ and $\mathbf{F}^{o}_{\psi}$ are the ROHF Fock matrices in molecular orbital basis that represent $\hat{f}^{c}$ and $\hat{f}^{o}$, respectively; $\mathbf{F}^{\alpha}_{\psi}$ and $\mathbf{F}^{\beta}_{\psi}$ are the α and β unrestricted Fock matrices in molecular orbital basis, that can be obtained by performing the UHF calculations on the system under study. The diagonal blocks in equations (2.52) and (2.53) have the forms

$$
\begin{aligned}
\mathbf{F}^{cc}_{\psi} &= A_{cc}\mathbf{F}^{\alpha}_{\psi} + B_{cc}\mathbf{F}^{\beta}_{\psi} \\
\mathbf{F}^{oo}_{\psi} &= A_{oo}\mathbf{F}^{\alpha}_{\psi} + B_{oo}\mathbf{F}^{\beta}_{\psi} \\
\mathbf{F}^{vv}_{\psi} &= A_{vv}\mathbf{F}^{\alpha}_{\psi} + B_{vv}\mathbf{F}^{\beta}_{\psi}
\end{aligned}
\tag{2.54}
$$

here A_{xx} and B_{xx} $(x = c, o, v)$ are called the canonicalization coefficients. These parameters can be arbitrarily chosen as they do not affect the total density, energy, or wavefunction.[20,28] But they do affect the rate of convergence, the orbital energy, and the orbital coefficients because their values alter the produced canonical orbitals.[22] A number of different values for the canonicalization coefficients are listed in Table (2.1).

Table 2.1: Some values for the diagonal canonicalization parameters used in the high-spin ROHF calculations.

	A_{cc}	B_{cc}	A_{oo}	B_{oo}	A_{vv}	B_{vv}
Roothaan[17]	-1/2	3/2	1/2	1/2	3/2	-1/2
Davidson[29]	1/2	1/2	1	0	1	0
Guest and Saunders[24]	1/2	1/2	1/2	1/2	1/2	1/2
McWeeny and Diercksen[21]	1/3	2/3	1/3	1/3	2/3	1/3
GAMESS GVB program[22]	1/2	1/2	1/2	0	1/2	1/2
Binkley, Pople, and Dobosh[30]	1/2	1/2	1	0	0	1

In chapter four, we will discuss the SCF procedure that is used for solving high-spin ROHF equations in detail.

2.1.2 Post-Hartree-Fock Theories

In the HF method, the molecular wavefunction is approximated by a single Slater determinant. The use of a single determinant wavefunction is insufficient to describe the correlation between electrons. While the antisymmetry of the determinantal wavefunction partially correlates the motion of electrons with same spin by the exchange interaction, the motion of electrons with opposite spins is not correlated. The correlation energy (E_{corr}) is defined as the difference between the exact non-relativistic energy of the system ($\mathcal{E}_0$) and the HF energy (E_{limit}) in the limit of a complete basis set.

$$E_{corr} = \mathcal{E}_0 - E_{limit} \tag{2.55}$$

Since the HF is a variational method, the E_{corr} is always negative because the E_{limit} is an upper bound to the exact energy. The HF method is able to provide about 99% of the total energy, but the remaining $\sim$ 1% is crucial for describing chemical properties.[1,31] This small percentage of the total energy can be higher than bond energies, even for a small molecule. There are several electronic structure theories which use the HF wavefunction as a starting point to improve the HF results by taking into account the electron correlation. These methods are called Post-HF or electron correlation methods. Three Post-HF methods are discussed in the following sections.

2.1.2.1 Configuration Interaction Theory

Of all the Post-HF methods, configuration interaction (CI) theory is the simplest to understand, but the most expensive to implement on a computer.[1,32] A full CI wavefunction, $|\Phi_0\rangle$, is obtained variationally as the best linear combination of all possible Slater determinants that describe different electronic configurations of the system.[33]

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{ar} c_a^r|\Psi_a^r\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c\\ r<s<t}} c_{abc}^{rst}|\Psi_{abc}^{rst}\rangle + \cdots \tag{2.56}$$

Where, a, b, and c denote occupied orbitals and r, s, and t denote virtual orbitals, $|\Psi_0\rangle$ is the ground-state HF wavefunction, $|\Psi_a^r\rangle$ is the singly exited determinants, $|\Psi_{ab}^{rs}\rangle$ is the doubly exited determinants, $|\Psi_{abc}^{rst}\rangle$ is the triply exited determinants, etc., and c_0, c_a^r, c_{ab}^{rs}, etc. are the CI expansion coefficients.

The CI problem is a direct application of the linear variation method.[34] Thus, if the CI wavefunction is substituted into the Schrödinger equation, then multiplied on the left by its complex conjugate and integrated over the space, the result is

$$\mathbf{Hc} = \mathbf{Ec} \tag{2.57}$$

Here, $\mathbf{c}$ is the CI expansion coefficients vector, $\mathbf{E}$ is a diagonal matrix of energies of the corresponding determinants, and $\mathbf{H}$ is the CI matrix, where each of its elements is given by

$$H_{IJ} = \langle \Psi_I|\hat{H}|\Psi_J\rangle \tag{2.58}$$

Equation (2.57) has the form of the usual matrix eigenvalue problem, so the CI expansion coefficients and energy of each determinant can be obtained by diagonalizing it.

In principle, the full CI wavefunction gives an exact solution to the Schrödinger equation within the chosen basis. In practice, however, the dimension of the full CI matrix increases rapidly with the size of the system and the full CI calculations become impractical very quickly. Therefore, the CI expansion must be truncated to a finite number of configurations.[35–37] Truncating the CI expansion at the excitations level one (CI with single excitations, CIS) does nothing to the HF result because single excitations do not mix with $|\Psi_0\rangle$. Thus, the double excitation level is the lowest level which improves the HF result. Including the doubles, gives CI with the single and double excitations (CISD) method.[38] The CISD has become a popular approach of calculating correlation energies for a large variety of molecules.[7] The other common truncated CI methods are QCISD (Quadratic CISD) and QCISD(T) (Quadratic CISD with triple excitations added perturbatively).[32]

In addition to being an exact variational theory for non-relativistic electronic structure problems, the full CI is also size consistent and size extensive. Unfortunately, the truncating CI methods are neither size consistent nor size extensive. A method is called size consistent if it gives for a system consisting of non-interacting particles an energy that equals the sum of their individual energies, i.e. $E(1,2) = E(1) + E(2)$. A method is said to be size extensive if the total energy of a system scales linearly with the number of particles in that system,[39] i.e. $E(nA) \equiv nE(A)$. As mentioned previously, the CISD method is the most applicable CI approach and it has been applied to a wide range of molecules.[34] The lack of size-consistency and size-extensivity are the major drawbacks of the CISD method and all other truncated CI methods. Several approximate corrections have been added to the CISD energies in order to correct the lack of size-consistency and size-extensivity.[38,40,41] The first proposed correction was made in 1974 by Langhoff and Davidson,[38] and it is known as the renormalized Davidson correction.[42] In this correction, the contribution of the entire set of quadruples is approximated as,

$$\Delta E_Q = (1 - C_0^2)\Delta E_{CISD} \tag{2.59}$$

where ΔE_Q is the quadruples contribution, ΔE_{CISD} is the CISD correlation energy, and C_0 is the leading coefficient of the CISD wavefunction.[38] Other forms of more sophisticated correction formulas were also proposed.[1]

2.1.2.2 Coupled Cluster Theory

The coupled-cluster (CC) method was first formulated at the end of the 1950s by Coester and Kummel to study nuclear physics phenomena.[43,44] The theory was introduced later to quantum chemistry by Čížek and Paldus.[45,46] Unlike the linear expansion of the CI wavefunction, the CC wavefunction, $|\Psi_{CC}\rangle$, is written as an exponential expansion of the HF wavefunction, $|\Psi_0\rangle$,

$$\begin{aligned} |\Psi_{CC}\rangle &= e^{\hat{T}}|\Psi_0\rangle \\ &= \left(1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \cdots\right)|\Psi_0\rangle \end{aligned} \tag{2.60}$$

where the cluster operator $\hat{T}$ for N-electon system is given by

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N \tag{2.61}$$

the $\hat{T}_i$ operator when acting on $|\Psi_0\rangle$ produces all ith-exited determinants, e.g.,

$$\begin{aligned} \hat{T}_1|\Psi_0\rangle &= \sum_{ar} c_a^r|\Psi_a^r\rangle \\ \hat{T}_2|\Psi_0\rangle &= \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle \end{aligned} \tag{2.62}$$

The exponential operator $e^{\hat{T}}$ can also be written as

$$e^{\hat{T}} = 1 + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2!}\hat{T}_1^2\right) + \left(\hat{T}_3 + \hat{T}_2\hat{T}_1 + \frac{1}{3!}\hat{T}_1^3\right) + \cdots \tag{2.63}$$

when it operates on $|\Psi_0\rangle$, the first term produces the reference HF and the second gives all single excitations. The first parenthesis generates all double excitations, while the second generates all triple excitations. It should be emphasized that there is only one way to generate singly-excited states, $\hat{T}_1$, but two ways to generate doubly-excited states; pure double excitations, $\hat{T}_2$, and two successive single excitations, $\hat{T}_1^2$. While three ways to generate triply-excited states; pure triple excitations, $\hat{T}_3$, double and single excitations, $\hat{T}_2\hat{T}_1$, or three successive single excitations, $\hat{T}_1^3$.

If the cluster operator $\hat{T}$ (equation 2.61) contains all terms to the $\hat{T}_N$, then $|\Psi_{CC}\rangle$ is exact and equivalent to the full CI wavefunction as it comprises all possible excitations. Due to the complexity of the CC equations and the related computational cost, the $\hat{T}$ is truncated at a certain excitation level.[47] Including only $\hat{T}_1$ and $\hat{T}_2$ in the cluster operator yields the couple-cluster singles and doubles (CCSD) method, which is the only generally applicable CC method. Higher-order CC methods such as CCSDT and CCSDTQ are only used for small molecules.[1] The well-known coupled-cluster singles and doubles plus perturbative triples method, CCSD(T), is one of the most accurate methods for evaluating electron correlation effects.[48] The CC method is size extensive at any level of the truncation of $\hat{T}$, but the method is not variational, i.e. the CC energy is not upper bound to the exact non-relativistic energy.

2.1.2.3 Møller-Plesset Perturbation Theory

In 1934, Møller and Plesset[49] applied the Rayleigh-Schrödinger perturbation theory (RSPT) for treating N-electron systems in which the sum of Fock operators is used as the zeroth-order Hamiltonian, $\hat{H}^{(0)}$.

$$\hat{H}^{(0)} = \sum_{i=1}^{N} \hat{f}(i) = \sum_{i=1}^{N} \left(\hat{h}(i) + \sum_{j=1}^{N} [\hat{J}_j(i) - \hat{K}_j(i)] \right) \tag{2.64}$$

where $\hat{f}(i)$ is the Fock operator of the ith electron. The ground-state HF wavefunction, $|\Psi^{(0)}\rangle$, is taken as the zeroth-order approximation to the exact wavefunction, $|\Phi\rangle$.[49] Thus, the zeroth-order energy, $E^{(0)} = \langle \Psi^{(0)} | \hat{H}^{(0)} | \Psi^{(0)} \rangle = \sum_a \epsilon_a$, is the sum of the energies, ϵ_a, of the occupied spin orbitals in the $|\Psi^{(0)}\rangle$.

In Møller-Plesset perturbation theory (MPPT), the difference between the exact electronic Hamiltonian, $\hat{H}$, and the $\hat{H}^{(0)}$ is considered a small perturbation, $\hat{\mathcal{V}}$.

$$\begin{aligned} \hat{\mathcal{V}} &= \hat{H} - \hat{H}^{(0)} \\ &= \sum_{i=1}^{N} \hat{h}(i) + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \left(\hat{h}(i) + \sum_{j=1}^{N} [\hat{J}_j(i) - \hat{K}_j(i)] \right) \\ &= \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \sum_{j=1}^{N} [\hat{J}_j(i) - \hat{K}_j(i)] \\ &= \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} v^{HF}(i) \end{aligned} \tag{2.65}$$

The perturbation, $\hat{\mathcal{V}}$, is just the deviation of the effective HF potential, $v^{HF}(i)$, from the exact electron-electron potential. This deviation is often called the fluctuation potential.[1] The exact wavefunction, $|\Phi\rangle$, which is supposed to lie near the $|\Psi^{(0)}\rangle$, and the exact energy, $\mathcal{E}$, which is also supposed to lie near the $E^{(0)}$ can be expanded in a Taylor series in powers of an ordering parameter, λ, which is later set to unity,

$$\begin{aligned} |\Phi\rangle &= |\Psi^{(0)}\rangle + \lambda |\Psi^{(1)}\rangle + \lambda^2 |\Psi^{(2)}\rangle + \cdots \\ \mathcal{E} &= E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots \end{aligned} \tag{2.66}$$

where the $|\Psi^{(1)}\rangle$, $|\Psi^{(2)}\rangle$, ... and $E^{(1)}$, $E^{(2)}$, ... are the first-, second-, ... order corrections to the $|\Psi^{(0)}\rangle$ and to the $E^{(0)}$, respectively. If these expansions are substituted into the Schrödinger equation, along with $\hat{H} = \hat{H}^{(0)} + \lambda\hat{\mathcal{V}}$, and then the terms of the same order λ^n are collected, the result is the zeroth-, first-, second-, up to nth-order perturbation equations.

$$\begin{gathered}
\hat{H}^{(0)}|\Psi^{(0)}\rangle = E^{(0)}|\Psi^{(0)}\rangle \\
\hat{H}^{(0)}|\Psi^{(1)}\rangle + \hat{\mathcal{V}}|\Psi^{(0)}\rangle = E^{(0)}|\Psi^{(1)}\rangle + E^{(1)}|\Psi^{(0)}\rangle \\
\hat{H}^{(0)}|\Psi^{(2)}\rangle + \hat{\mathcal{V}}|\Psi^{(1)}\rangle = E^{(0)}|\Psi^{(2)}\rangle + E^{(1)}|\Psi^{(1)}\rangle + E^{(2)}|\Psi^{(0)}\rangle \\
\vdots \\
\hat{H}^{(0)}|\Psi^{(n)}\rangle + \hat{\mathcal{V}}|\Psi^{(n-1)}\rangle = \sum_{i=0}^{n} E^{(i)}\Psi^{(n-i)}
\end{gathered} \tag{2.67}$$

To calculate the nth-order energies, one can multiply each of the above equations on the left by $\langle\Psi^{(0)}|$ and use the orthogonality relation, $\langle\Psi^{(0)}|\Psi^{(n)}\rangle = 0$ where $n = 1, 2, 3, \cdots$, and the turnover rule, $\langle\Psi^{(0)}|\hat{H}^{(0)}|\Psi^{(n)}\rangle = \langle\Psi^{(n)}|\hat{H}^{(0)}|\Psi^{(0)}\rangle^*$, to get,[1,7,49]

$$E^{(0)} = \langle\Psi^{(0)}|\hat{H}^{(0)}|\Psi^{(0)}\rangle \tag{2.68}$$

$$E^{(1)} = \langle\Psi^{(0)}|\hat{\mathcal{V}}|\Psi^{(0)}\rangle \tag{2.69}$$

$$E^{(2)} = \langle\Psi^{(0)}|\hat{\mathcal{V}}|\Psi^{(1)}\rangle \tag{2.70}$$

In general,

$$E^{(n)} = \langle\Psi^{(0)}|\hat{\mathcal{V}}|\Psi^{(n-1)}\rangle \tag{2.71}$$

It is clear that solving for the $|\Psi^{(n-1)}\rangle$ by using the set of equations (2.67) is required in the determination of the $E^{(n)}$ for $n \geq 2$ using the equations (2.71). However, the total energies of MPPT, E_{MPn}, up to the third order are:

$$E_{MP0} = E^{(0)} = \langle\Psi^{(0)}|\hat{H}^{(0)}|\Psi^{(0)}\rangle = \sum_a \epsilon_a \tag{2.72}$$

The zeroth-order "unperturbed" energy, E_{MP0}, is just the sum of energies of the occupied MOs in the $|\Psi^{(0)}\rangle$.

$$\begin{aligned} E_{MP1} &= E^{(0)} + E^{(1)} \\ &= \langle \Psi^{(0)} | \hat{H}^{(0)} + \hat{\mathcal{V}} | \Psi^{(0)} \rangle = E_0 \end{aligned} \tag{2.73}$$

The first-order MPPT, E_{MP1}, is exactly the ground state HF energy, E_0. Thus, the first correction to the HF energy comes at the second-order of MPPT,

$$\begin{aligned} E_{MP2} &= E^{(0)} + E^{(1)} + E^{(2)} \\ &= E_0 + \langle \Psi^{(0)} | \hat{\mathcal{V}} | \Psi^{(1)} \rangle \\ &= E_0 + \sum_{\substack{a<b \\ r<s}} \frac{\langle ab || rs \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \end{aligned} \tag{2.74}$$

where, a, b refer to occupied orbitals, and r, s refer to virtual orbitals. Second-order MPPT, MP2, is one of the most widely used methods by computational chemists. Expressions for the higher-order corrections become gradually more complex than the $E^{(2)}$. Calculations of MP3, MP4, and MP5 are now available in most of the computational chemistry software packages.[1,4] The MPn methods are size consistent but not variational.

2.2 Density Functional Theory

An alternative scheme for the determination of the quantum N-electron systems, is density functional theory (DFT). In contrast with the wavefunction based methods, such as HF and the post-HF methods, DFT is based upon the electron density $\rho(\mathbf{r})$.[50] The origin of DFT dates back to the end of the 1920s with the proposition of the Thomas–Fermi model.[51,52] In the years 1964 and 1965, modern DFT was established as a promising method to study many-electron systems by Hohenberg, Kohn, and Sham.[53,54] Hohenberg and Kohn presented two theorems which are the essential pillars of DFT, known as the HK theorems. The first theorem states that *the external potential, V_{ext}, and hence any ground state property, of an N-electron system is a unique functional of the ground state electron density, $\rho_0(\mathbf{r}) = \rho_0(x, y, z)$, which depends only on three spatial variables.* The second theorem states that *the electron density which optimizes the total energy is the $\rho_0(\mathbf{r})$.*

According to the first theorem, the total energy of an electronic system can be written as the following functional of the electron density,

$$E[\rho(\mathbf{r})] = V_{ext}[\rho(\mathbf{r})] + F[\rho(\mathbf{r})] \tag{2.75}$$

where, the square brackets designate the functional relation, V_{ext} is the external potential in which the electrons are moving that depends on the system under study, and $F[\rho(\mathbf{r})]$ is the universal functional which does not depend on any external potential. $F[\rho(\mathbf{r})]$ is the sum of the kinetic energy functional of the system, $T[\rho(\mathbf{r})]$, and the electron-electron interaction energy functional, $V_{ee}[\rho(\mathbf{r})]$.

$$F[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] \tag{2.76}$$

For molecules in the absence of any external effects, the external potential ,$V_{ext}[\rho(\mathbf{r})]$, is the Coulomb attraction between electrons and nuclei, $V_{ne}[\rho(\mathbf{r})]$,

$$V_{ext}[\rho(\mathbf{r})] = V_{ne}[\rho(\mathbf{r})] = -\sum_{A=1}^{M} \int \frac{Z_A}{|\mathbf{r} - \mathbf{r}_A|} \rho(\mathbf{r}) d\mathbf{r} \tag{2.77}$$

and the $V_{ee}[\rho(\mathbf{r})]$ is given by,

$$\begin{aligned} V_{ee}[\rho(\mathbf{r})] &= J_{ee}[\rho(\mathbf{r})] + \Delta V_{ee}[\rho(\mathbf{r})] \\ &= \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + \Delta V_{ee}[\rho(\mathbf{r})] \end{aligned} \tag{2.78}$$

where it is divided into the classical Coulomb repulsion $J_{ee}[\rho(\mathbf{r})]$ and all the non-classical corrections to the electron-electron interaction energy, $\Delta V_{ee}[\rho(\mathbf{r})]$.

In order to express the kinetic energy of an N-electron system as a functional of the electron density, Kohn and Sham in 1965 introduced a new approach.[54] In this approach, the kinetic energy of the real system is approximated by the kinetic energy of a fictitious system consisting of non-interacting electrons and their corresponding orbitals. These orbitals are called Kohn-Sham (KS) orbitals, $\{\psi_i^{KS}\}$, from which the exact wavefunction of the non-interacting system is constructed as a Slater determinant. The electron density of the fictitious KS-system, $\rho^{KS}(\mathbf{r})$, must equal the ground state electron density of the real system, $\rho_0(\mathbf{r})$, i.e.,

$$\rho^{KS}(\mathbf{r}) = \sum_{i=1}^{N} \psi_i^{KS*}(\mathbf{r}) \psi_i^{KS}(\mathbf{r}) = \rho_0(\mathbf{r}) \tag{2.79}$$

The kinetic energy of the real system is written as,

$$\begin{aligned} T[\rho(\mathbf{r})] &= T_{ni}[\rho(\mathbf{r})] + \Delta T[\rho(\mathbf{r})] \\ &= -\frac{1}{2} \sum_{i=1}^{N} \langle \psi_i^{KS}(1) | \nabla_1^2 | \psi_i^{KS}(1) \rangle + \Delta T[\rho(\mathbf{r})] \end{aligned} \tag{2.80}$$

where, $T_{ni}[\rho(\mathbf{r})]$ is the kinetic energy of the non-interacting electrons, and $\Delta T[\rho(\mathbf{r})]$ is the correction to the kinetic energy. By substituting equations (2.76) to (2.78), and (2.80) into equation (2.75), one can write the total energy functional for the real systems as follows

$$\begin{aligned} E[\rho(\mathbf{r})] &= V_{ext}[\rho(\mathbf{r})] + F[\rho(\mathbf{r})] \\ &= T[\rho(\mathbf{r})] + V_{ne}[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] \\ &= T_{ni}[\rho(\mathbf{r})] + V_{ne}[\rho(\mathbf{r})] + J_{ee}[\rho(\mathbf{r})] + \Delta T[\rho(\mathbf{r})] + \Delta V_{ee}[\rho(\mathbf{r})] \\ &= -\frac{1}{2} \sum_{i=1}^{N} \langle \psi_i^{KS}(1) | \nabla_1^2 | \psi_i^{KS}(1) \rangle + \sum_{A=1}^{M} \int \frac{Z_A}{|\mathbf{r} - \mathbf{r}_A|} \rho(\mathbf{r}) d\mathbf{r} \\ &\quad + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[\rho(\mathbf{r})] \end{aligned} \tag{2.81}$$

Where, $E_{xc}[\rho(\mathbf{r})]$ is the exchange-correlation energy functional which is defined as

$$\begin{aligned} E_{xc}[\rho(\mathbf{r})] &= \Delta T[\rho(\mathbf{r})] + \Delta V_{ee}[\rho(\mathbf{r})] \\ &= \Big(T[\rho(\mathbf{r})] - T_{ni}[\rho(\mathbf{r})]\Big) + \Big(V_{ee}[\rho(\mathbf{r})] - J_{ee}[\rho(\mathbf{r})]\Big) \end{aligned} \tag{2.82}$$

In spite of its misleading name, $E_{xc}[\rho(\mathbf{r})]$ involves the correction for the difference in the kinetic energy between the real and the fictitious systems, $\Delta T[\rho(\mathbf{r})]$, and the correction to the electron-electron interaction energy, $\Delta V_{ee}[\rho(\mathbf{r})]$. The $\Delta V_{ee}[\rho(\mathbf{r})]$ includes all the non-classical corrections to the electron-electron repulsion energy such as the exchange energy, the correlation energy, and the correction to the self-interaction error (SIE) in the J_{ee}.[55] The SIE results from the fact that the $J_{ii} \neq 0$, but, of course, the electron does not repel itself. The correction to the SIE is one of the most serious problems of DFT.[56,57] In HF theory, the self-interaction energy is exactly canceled with the corresponding exchange energy, i.e. $J_{ii} - K_{ii} = 0$. However, in the DFT, the correction to the exchange energy does not completely cancel the self-interactions.[57]

As stated in the second HK theorem, the $\rho_0(\mathbf{r})$ and the ground state energy, $E[\rho_0(\mathbf{r})]$, can be obtained by minimizing the Kohn-Sham energy expression of equation (2.81). The variation of this expression with respect to the Kohn-Sham orbitals,[58] under the constraint that the orbitals remain orthonormal, leads to the celebrated Kohn-Sham equations.

$$\hat{h}^{KS}(\mathbf{r}_1)\psi_i^{KS}(\mathbf{r}_1) = \epsilon_i \psi_i^{KS}(\mathbf{r}_1) \tag{2.83}$$

Where,

$$\hat{h}^{KS}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + \hat{v}_{xc}(\mathbf{r}_1) \tag{2.84}$$

is the Kohn-Sham one-electron operator, ϵ_i is the i^{th} Kohn-Sham orbital energy, and $\hat{v}_{xc}$ is the exchange-correlation operator which is defined as,

$$\hat{v}_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \tag{2.85}$$

Equation (2.83) differs from the HF equations (2.16) only by the $\hat{v}_{xc}(\mathbf{r})$. The $\hat{h}^{KS}$, like the Fock operator, depends on its eigenvector through the $\rho(\mathbf{r})$ (equation 2.79), therefore the Kohn-Sham equations must be solved self-consistently. In general, the Kohn-Sham equations are solved in the same way as the HF equations. The only difference is that the integrals of the E_{xc} are calculated numerically because they do not have analytic expressions.

If all terms in the Kohn-Sham equations are known, DFT will be exact. Unfortunately, the form of the $\hat{v}_{xc}(\mathbf{r})$ is unknown, therefore, approximations to it must be used.[50] The total exchange-correlation energy of the system is expressed as

$$E_{xc} = \int \rho(\mathbf{r})\epsilon_{xc}[\rho(\mathbf{r})]d\mathbf{r} \tag{2.86}$$

where $\epsilon_{xc}[\rho(\mathbf{r})]$ is the exchange-correlation energy per electron which is generally written as a sum of exchange, $\epsilon_{x}[\rho(\mathbf{r})]$, and correlation, $\epsilon_{c}[\rho(\mathbf{r})]$, contributions.

$$\epsilon_{xc}[\rho(\mathbf{r})] = \epsilon_{x}[\rho(\mathbf{r})] + \epsilon_{c}[\rho(\mathbf{r})] \tag{2.87}$$

Various kinds of approximations to the exchange-correlation energy have been proposed since the early days of DFT. By now there is a long list of exchange-correlation functionals with varying levels of complexity and accuracy.[59–73] In spite of this fact, the development of more accurate functionals remains an ongoing and active area of research.[74] We now review in brief the most common types of the approximate exchange-correlation functionals:

2.2.1 Local Density Approximation (LDA)

LDAs are the simplest exchange-correlation functionals that depend only on the $\rho(\mathbf{r})$ to some power. The ϵ_x and E_x in LDA are known and given as,[75]

$$\epsilon_x^{LDA}[\rho(\mathbf{r})] = -\frac{3}{4}\left(\frac{3\rho(\mathbf{r})}{\pi}\right)^{1/3} \tag{2.88}$$

$$E_x^{LDA}[\rho(\mathbf{r})] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho(\mathbf{r})^{4/3}d\mathbf{r} \tag{2.89}$$

while the ϵ_c and E_c have different approximate forms that can be obtained by fitting to the many-body free electron gas data. For open-shell systems, the alpha and beta spin-densities, $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$ with $\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r})+\rho_\beta(\mathbf{r})$, must be used in the approximation, which is called the local spin-density approximation (LSDA).[61] The E_x in LSDA is written as,

$$E_x^{LSDA}[\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r})] = -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}\int \left(\rho_\alpha(\mathbf{r})^{4/3} + \rho_\beta(\mathbf{r})^{4/3}\right) d\mathbf{r} \tag{2.90}$$

The Perdew-Wang (PW92)[63] and Vosko-Wilk-Nusair (VWN)[59] functionals are common examples of LDA functionals.

2.2.2 Generalized Gradient Approximation (GGA)

In GGA, the E_{xc} is given as a functional of both the density and its gradients at each point.

$$E_{xc}^{GGA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})\epsilon_{xc}^{GGA}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]d\mathbf{r} \tag{2.91}$$

The GGA often shows a large improvement over the LDA results when studying atoms, molecules, and solids. Several GGA functionals have been developed and used by computational chemists, e.g., Becke-88 (B88),[61] Perdew-Wang-91 (PW91),[63,65] and Perdew–Burke–Ernzerhof (PBE)[66] functionals.

2.2.3 The Meta-GGAs

The meta-GGA functionals use the Laplacian of the density, $\nabla^2\rho(\mathbf{r})$, and the kinetic energy density, $\tau[\rho(\mathbf{r})] = -\frac{1}{2}\sum_i |\nabla\psi_i^{KS}|^2$, of the occupied Kohn–Sham orbitals into the E_{xc} as additional degrees of freedom.

$$E_{xc}^{mGGA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})\epsilon_{xc}^{mGGA}[\rho(\mathbf{r}), \triangledown\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau]d\mathbf{r} \qquad (2.92)$$

Perdew-Kurth-Zupan-Blaha (PKZB)[67] and Lee-Yang-Parr (LYP)[62] functionals are meta-GGA functionals.

2.2.4 Hybrid Functionals

The hybrid functionals incorporate a portion of the HF exchange with a combination of different levels of exchange and correlation functionals. For instance, the combination of the LSDA and B88 exchange functionals and the HF exchange, along with the VWN and LYP correlation energy functionals leads to the B3LYP functional.[62,64]

$$E_{xc}^{B3LYP} = (1 - a_0 - a_x)E_x^{LSDA} + a_0 E_x^{exact} + a_x E_x^{B88} + (1 - a_c)E_c^{VWN} + a_c E_c^{LYP} \quad (2.93)$$

Where a_0, a_x, and a_c are parameters, and E_x^{exact} is the HF exchange energy. The B3LYP, Becke three parameter exchange functional (B3)[64] and the Lee-Yang-Parr correlation functional (LYP),[62] is the most popular density functional in computational chemistry.

2.3 Basis Sets

A basis set is a set of mathematical functions from which the atomic or molecular orbitals are constructed.[55] In practice, each unknown orbital, ψ_i, is represented by a linear combination of a finite set of known functions, $\{\varphi_\mu\}$, i.e., a basis set.[7]

$$\psi_i = \sum_{\mu=1}^{K} C_{\mu i}\varphi_\mu \qquad\qquad i = 1, 2, \ldots, K \tag{2.94}$$

Where, $C_{\mu i}$ are the expansion coefficients, and K is the total number of basis functions (or the size of the basis set). The use of K basis functions yields a set of N occupied orbitals and a set of $(K-N)$ virtual orbitals. The choice of appropriate basis functions is undoubtedly of great importance in electronic structure calculations. Two main considerations should be taken into account when choosing the basis functions. The first is that the basis functions should provide the best representation of the unknown orbitals with the fewest possible terms in the expansion (2.94). The second is that the basis functions should allow for the two-electron integrals to be evaluated with as cheap a computational cost as possible.[7,55,76]

There are two types of the basis functions employed in electronic structure calculations:[77] Slater Type Functions or Orbitals (STFs or STOs) and Gaussian Type Functions or Orbitals (GTFs or GTOs). The STO, $S_{lmn}(\zeta, \mathbf{r})$, and the GTO, $G_{lmn}(\alpha, \mathbf{r})$, centered on nucleus A have the following forms in Cartesian coordinates,[7,55,77]

$$S_{lmn}(\zeta, \mathbf{r}) = N_{lmn}(x - X_A)^l (y - Y_A)^m (z - Z_A)^n e^{-\zeta|\mathbf{r}-\mathbf{R_A}|} \tag{2.95}$$

$$G_{lmn}(\alpha, \mathbf{r}) = N_{lmn}(x - X_A)^l (y - Y_A)^m (z - Z_A)^n e^{-\alpha|\mathbf{r}-\mathbf{R_A}|^2} \tag{2.96}$$

where, ζ is the Slater orbital exponent, α is the Gaussian orbital exponent, N_{lmn} is the normalization factor, l, m, and n are non-negative integers which determine the type of orbital (e.g., $l+m+n = 2$ is a d-orbital with six possible combinations leading to the Cartesian d-functions: $x^2, y^2, z^2, xy, xz,$ and yz), $\mathbf{r} = (x, y, z)$ is the position vector of an electron, and $\mathbf{R_A} = (X_A, Y_A, Z_A)$ is the position vector of the nucleus A. The STOs are similar to the orbitals obtained from the solution of the hydrogen atom. Because of this similarity, the STOs give better description to the qualitative features of the orbital ψ_i with fewer basis functions in the expansion (2.94) than do GTOs. Whilst the evaluation of the two-electron integrals with the STOs is an extremely difficult and time-consuming process, it is an easy and fast process with the GTFs. For this pragmatic reason, the GTFs have become the most used basis functions in computational chemistry.

In order to merge the attractive features of the STFs with that for the GTFs, fixed linear combinations, called contractions, of the GTFs are used to mimic the STFs or any other desired orbitals.[7, 55] These contractions lead to new Gaussian functions named Contracted Gaussian Functions (CGFs),

$$\varphi_{\mu}^{\mathrm{CGF}}(\mathbf{r}) = \sum_{p=1}^{L} d_{p\mu} G_p(\alpha_{p\mu}, \mathbf{r}) \tag{2.97}$$

where, L is the number of Gaussians used in the contraction (also called the degree of contraction), and $d_{p\mu}$ are the contraction coefficients. The Gaussian functions G_p used in such contractions are called primitives. Their exponents and contraction coefficients are generally optimized by means of relatively inexpensive atomic SCF calculations.[77] The CGFs basis set can either be constructed from segmented or generalized contraction of an optimized-primitives basis set. In the segmented basis sets, each primitive does not contribute to more than one (or maybe two) contracted function.[78] In contrast, the general contraction scheme allows each of the primitives to be contributed to every single contracted function.[79]

The basis sets are described by: (i) the number of primitives per CGF, (ii) the number of CGFs per atomic orbital, (iii) the number and the types of other augmented functions might be added, such as polarization and diffuse functions. The polarization functions are Gaussians of higher angular number than any of the occupied orbitals in the corresponding atom (i.e., $p, d, \ldots$ in H, He and $d, f, \ldots$ in Li $\longrightarrow$ Ar). The polarization functions can be of great importance for describing chemical bonding because they give more flexibility to the valence-shell orbitals. The diffuse functions are Gaussians, usually of *s* or *p* type, with small exponents so that they decay slowly and spread over space. Therefore, they are essential for calculations describing anions or Rydberg states.[1,4,55] A large number of CGF-type basis sets have been developed for the quantum chemical calculations. The smallest sets are called minimal or single-zeta (SZ) basis sets in which each occupied orbital in an atom is described by one and only one CGF. The following is a brief description of the two families of basis sets widely-used by chemists:

2.3.1 Pople Basis Sets

Pople basis sets consist of the minimal STO-NG basis sets and the split-valence (SV) basis sets. The minimal STO-NG basis set (where, $N = 2 - 6$) means a Slater-Type Orbital (STO) is fitted by N primitives. The most popular set of this group is the STO-3G in which each atomic orbital of an atom is approximated by 3 primitives.[4,7,55] The split-valence basis sets are either double split valence (DZV) basis sets denoted k-lmG, or triple split valence (TZV) basis sets denoted k-lmnG, where k is the number of primitives used in a given core orbital.[80] In the DZV basis sets, each valence orbital is spilt into two CGFs represented by l and m primitives. While in the TZV basis sets, each valence orbital is split into three CGFs represented by l, m, and n primitives. For example, a 6-31G is a DZV basis set in which each core orbital described by 6 primitives, and each valence orbital is split into two CGFs that are described by 3 and 1 primitive, respectively. Pople's basis sets might be augmented by adding polarization functions of *d* or *d* and *f* types on heavy atoms, (e.g., 6-31G(d), 6-31G(df), 6-31G(2df), 6-31G(3d2f)) and of *p* or *p* and *d* types on H and He atoms (e.g., 6-31G(d,p), 6-31G(3df,pd)).[7] Diffuse functions can also be added to heavy atoms (+) or to heavy and H atoms (++), .e.g. 6-311+G(d,p), 6-311++G(d).[55] The Pople style basis sets were constructed with the s-p constraint which means that the exponents of the s and p valence orbitals are forced to be identical.[1] This increases the efficiency of the computations but decreases the flexibility of the resulting orbitals.[76]

2.3.2 Correlation-Consistent Basis Sets

The correlation-consistent (cc) basis sets have been developed by Dunning and co-workers for high-accuracy calculations with electron-correlation methods.[81–84] The cc-basis sets are optimized using CISD energy because the basis sets obtained at the HF level might not be ideal for calculations of electron-correlation.[80] They are designated cc-pVXZ, where p stands for polarized, V for valence, X $(= D, T, Q, 5, 6)$ for the number of shells the valence orbitals are split into, and Z for zeta. The cc-pVXZ can be augmented (aug-cc-pVXZ) by adding diffuse functions, of types f, d, p, and s on heavy atoms and of types d, p, and s on H and He, to the all types of basis functions in the set.[1,76] The cc-pVDZ consists of $3s2p1d = 14$ basis functions for Li $\longrightarrow$ Ne and $2s1p = 5$ basis functions for H and He. In general, the cc-pV(X+1)Z contains for each shell (l) one extra basis function compared to the cc-pVXZ. Thus, the cc-pVTZ has $4s3p2d1f = 30$ basis functions for Li $\longrightarrow$ Ne and $3s2p1d = 14$ for H and He, while the cc-pVQZ has $5s4p3d2f1g = 55$ basis functions for Li $\longrightarrow$ Ne and $4s3p2d1f = 30$ for H and He.[85] The correlation consistent basis sets give better results than Pople's basis sets that need the same CPU time.[76] Moreover, results obtained by the correlation consistent basis sets are systematically improved with increasing their size.[86,87]

2.4 Basis Set Superposition Error

Finite basis sets suffer from a problem known as a basis set superposition error (BSSE).[77] The BSSE is a serious problem when calculating for weak interactions, such as hydrogen bonding, van der Waals, dipole-dipole interactions, etc., between two or more species (atoms or molecules).[76,88] If two molecules A and B approach each other to form a dimer AB, then the interaction energy, E_{int}, between A and B can be trivially written as

$$E_{int} = E(AB)_{ab} - E(A)_a - E(B)_b \tag{2.98}$$

where, $E(AB)_{ab}$, $E(A)_a$, and $E(B)_b$ are the energies of AB, A, and B, respectively. The subscripts a and b indicate the basis sets for the molecules A and B, respectively, and $ab = a \bigcup b$ is the full basis set of AB. Equation (2.98) is valid only if the basis sets a and b are complete or if the intermolecular distance between A and B is very large. However, when using finite basis sets, there is an extra lowering in the energy of AB compared to the sum of the individual A and B energies. This extra lowering in the $E(AB)$ is referred to as basis set superposition error (BSSE). In AB, the basis functions of B are available to A, so A in AB has a larger basis set than does isolated A, and similarly for B. Therefore, the larger basis set is artificially decreasing the $E(AB)$ compared to the individual energies of A and B, resulting in the BSSE.[76,88,89]

The most widely used technique to correct for the BSSE is the counterpoise (CP) correction method of Boys and Bernardi.[90] In the CP correction, the energy belonging to the BSSE, E_{BSSE}, is given by

$$E_{BSSE} = E(A \cdots *)^{AB}_{ab} + E(* \cdots B)^{AB}_{ab} - E(A)^{AB}_{a} - E(B)^{AB}_{b} \tag{2.99}$$

where superscript AB describes the geometry of A and B in the structure they adopt in the dimer AB. The $E(A \cdots *)$ and the $E(* \cdots B)$ are calculated using the full basis set by neglecting all the electrons and the protons of B when calculating for the $E(A \cdots *)$, and by neglecting all the electrons and the protons of A when calculating for the $E(* \cdots B)$. Hence, the CP-corrected interaction energy, E^{CP}_{int}, is obtained by the subtraction of the E_{BSSE} form the E_{int} in equation (2.98).

$$E^{CP}_{int} = E_{int} - E_{BSSE} \tag{2.100}$$

It is recommended to use the CP correction for calculations of weak-interaction energies even if it usually overestimates the BSSE without providing a clear way to correct for this overestimation.[55, 91]

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Chapter 3

Generalized Atoms In Molecules Approach (GAIM)

> *I have gotten lots of results! If I find 10,000 ways something won't work, I haven't failed. I am not discouraged, because every wrong attempt discarded is often a step forward.*
>
> (Thomas Edison)

3.1 Introduction

We propose a new theoretical approach for calculating total energies of molecules, called Generalized Atoms In Molecules Approach (GAIM). Unlike other AIM or energy decomposition approaches which try to partition the molecular energy into its atomic contributions, GAIM aims to solve the energy of each atom variationally in the first step and then build the energy of molecule from the atomic energies.

Atoms are the building blocks of molecules. Accordingly (as QTAIM shows) "every measurable property of a system, finite or periodic, can be equated to a sum of contributions from its composite atoms".[1,2] Based on this fact, the energy of the diatomic molecule A−B is formulated in the GAIM as a sum of its atomic energies. Whereas each atomic energy is expressed rigorously by adding the energy of the isolated atom to the contribution of that atom to the interaction energy between them. The energy of the molecule is then optimized subject to the constraint that the sum of integrals of atomic densities is equal to the total number of electrons.

3.2 Theory

In the GAIM approach, electrons of atom A are described by a set of orthonormal spatial atomic orbitals, $\{\psi_a^A\}$, and electrons of atom B are described by a different set of orthonormal spatial atomic orbitals, $\{\psi_a^B\}$, while the two sets are taken to be orthogonal to each other. Our intention in this approach is not to construct a molecular wavefunction from these orbitals as HF and valence bond theories do for describing the molecular system. Instead we are concerned about finding a set of AIM wavefunctions that describe each atom in a molecule as well as the whole molecular system. We know this is not an easy task but a challenging one that needs time and great effort to be achieved.

3.2.1 GAIM Expression of the Total Electronic Energy

The total electronic energy of a diatomic molecule (A−B) can be expressed as a sum of the electronic energy (E_A°) of isolated atom A, the electronic energy (E_B°) of isolated atom B, and the electronic energy (E_{AB}) of interactions between them,

$$E = E_A^\circ + E_B^\circ + E_{AB} \tag{3.1}$$

E_A° and E_B° are defined as

$$\begin{aligned} E_A^\circ &= T^A + V_{en}^{AA} + V_{ee}^{AA} \\ E_B^\circ &= T^B + V_{en}^{BB} + V_{ee}^{BB} \end{aligned} \tag{3.2}$$

T^A and T^B are the kinetic energies of the electrons in atoms A and B, respectively. V_{en}^{AA} and V_{en}^{BB} are the attraction energies between the electrons and the nuclei of isolated atoms A and B, respectively. V_{ee}^{AA} and V_{ee}^{BB} are the interaction energies between the electrons of atoms A and B, respectively.

The interaction energy E_{AB} between the two atoms in the molecule is written as

$$E_{AB} = V_{en}^{AB} + V_{en}^{BA} + \frac{1}{2}V_{ee}^{AB} + \frac{1}{2}V_{ee}^{BA} \tag{3.3}$$

V_{en}^{AB} is the attraction energy between the electrons of atom A and nucleus B. V_{en}^{BA} is the attraction energy between the electrons of atom B and nucleus A. The interaction energy between the electrons of atom A with the electrons of atom B that can be denoted as (V_{ee}^{AB} or V_{ee}^{BA}) is divided equally between the two atoms as shown in equation (3.3).

3.2.1.1 Total Electronic Energy as a Sum of Atomic Contributions

Our interest in the GAIM approach is to write the total electronic energy of a molecule as a sum of AIM energy contributions (E_A and E_B). Thus, the total electronic energy for a diatomic molecule (A−B) is defined as

$$E = E_A + E_B \tag{3.4}$$

Here E_A and E_B are rigorously defined by adding the contribution of each atom in E_{AB} (equation 3.3) to its isolated energy.

$$\begin{aligned} E_A &= E_A^{\circ} + V_{en}^{AB} + \frac{1}{2}V_{ee}^{AB} = T^A + V_{en}^{AA} + V_{en}^{AB} + V_{ee}^{AA} + \frac{1}{2}V_{ee}^{AB} \\ E_B &= E_B^{\circ} + V_{en}^{BA} + \frac{1}{2}V_{ee}^{BA} = T^B + V_{en}^{BB} + V_{en}^{BA} + V_{ee}^{BB} + \frac{1}{2}V_{ee}^{BA} \end{aligned} \tag{3.5}$$

Equations (3.5) can also be written as

$$\begin{aligned} E_A &= H^A + V_{ee}^{AA} + \frac{1}{2}V_{ee}^{AB} \\ E_B &= H^B + V_{ee}^{BB} + \frac{1}{2}V_{ee}^{BA} \end{aligned} \tag{3.6}$$

where H^A and H^B

$$\begin{aligned} H^A &= T^A + V_{en}^{AA} + V_{en}^{AB} \\ H^B &= T^B + V_{en}^{BB} + V_{en}^{BA} \end{aligned} \tag{3.7}$$

are the kinetic and nuclear attraction energy of electrons of atoms A and B, respectively.

3.2.1.2 Kinetic and Nuclear Attraction Energies

H^A and H^B are defined as

$$\begin{aligned} H^A &= \sum_a \eta_a^A h_{aa}^A = \sum_a \eta_a^A \langle \psi_a^A(\mathbf{r}_1) | \hat{h}(\mathbf{r}_1) | \psi_a^A(\mathbf{r}_1) \rangle \\ H^B &= \sum_a \eta_a^B h_{aa}^B = \sum_a \eta_a^B \langle \psi_a^B(\mathbf{r}_1) | \hat{h}(\mathbf{r}_1) | \psi_a^B(\mathbf{r}_1) \rangle \end{aligned} \tag{3.8}$$

where the sums are over all occupied atomic orbitals (AOs) of atoms A or B. η_a^A and η_a^B are the occupancies of orbitals ψ_a^A and ψ_a^B, respectively. h_{aa}^A and h_{aa}^B are the kinetic and nuclear attraction energies of an electron described by the a^{th} AO centered on atom A or B, respectively. $\hat{h}(\mathbf{r}_1)$ is the one-electron core Hamiltonian operator which contains the kinetic energy and nuclear attraction potential energy operators.

$$\hat{h}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}} \tag{3.9}$$

Here $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator. Z_A and Z_B are the nuclear charges of atoms A and B, respectively. r_{1A} and r_{1B} are the distances between the electron one and the nuclei A and B, respectively.

3.2.1.3 Interaction Energies Between Electrons

The electron-electron interaction energy (V_{ee}) can be split into three energy components as follows

$$V_{ee} = E_{CR} + E_{corr} + E_{ex} \tag{3.10}$$

where E_{CR} is the Coulomb repulsion energy, E_{corr} is the correlation energy, and E_{ex} is the exchange energy. Here we assign the occupancy coefficients that will be used for defining the electron-electron interaction energy components. These occupancy coefficients are

$$\begin{aligned}
\mathcal{C}_{ab}^{AA} &= \eta_a^A \eta_b^A, & X_{ab}^{AA} &= \left(\eta_a^{\alpha A}\eta_b^{\alpha A} + \eta_a^{\beta A}\eta_b^{\beta A}\right) \\
\mathcal{C}_{ab}^{BB} &= \eta_a^B \eta_b^B, & X_{ab}^{BB} &= \left(\eta_a^{\alpha B}\eta_b^{\alpha B} + \eta_a^{\beta B}\eta_b^{\beta B}\right) \\
\mathcal{C}_{ab}^{AB} &= \eta_a^A \eta_b^B, & X_{ab}^{AB} &= \left(\eta_a^{\alpha A}\eta_b^{\alpha B} + \eta_a^{\beta A}\eta_b^{\beta B}\right) \\
\mathcal{C}_{ab}^{BA} &= \eta_a^B \eta_b^A, & X_{ab}^{BA} &= \left(\eta_a^{\alpha B}\eta_b^{\alpha A} + \eta_a^{\beta B}\eta_b^{\beta A}\right)
\end{aligned} \tag{3.11}$$

where $\eta_a^{\alpha A}$, $\eta_a^{\beta A}$, $\eta_a^{\alpha B}$, and $\eta_a^{\beta B}$ are the occupancies of the a^{th} AO on atoms A and B with α and β electrons, respectively. For the V_{ee}^{AA} and V_{ee}^{BB} in equations (3.6), E_{CR}^{AA} and E_{CR}^{BB} are defined as follows

$$\begin{aligned}
E_{CR}^{AA} &= \frac{1}{2}\sum_{a,b} \mathcal{C}_{ab}^{AA} J_{ab}^{AA} - \frac{1}{2}\sum_{a} X_{aa}^{AA} J_{aa}^{AA} \\
E_{CR}^{BB} &= \frac{1}{2}\sum_{a,b} \mathcal{C}_{ab}^{BB} J_{ab}^{BB} - \frac{1}{2}\sum_{a} X_{aa}^{BB} J_{aa}^{BB}
\end{aligned} \tag{3.12}$$

The summations in equations (3.12) run over the occupied AOs of atom A or B. The purpose of the second sums in these equations are to eliminate the self-interaction

Coulomb energies that arise from the first sums in these equations. The Coulomb integrals J_{ab}^{AA} and J_{ab}^{BB} are given by

$$\begin{aligned} J_{ab}^{AA} &= \langle \psi_a^A(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2)|\psi_a^A(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2)\rangle \\ J_{ab}^{BB} &= \langle \psi_a^B(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2)|\psi_a^B(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2)\rangle \end{aligned} \tag{3.13}$$

For the V_{ee}^{AB} and V_{ee}^{BA} in equations (3.6), E_{CR}^{AB} and E_{CR}^{BA} are defined as follows

$$\begin{aligned} E_{CR}^{AB} &= \frac{1}{2}\sum_{a,b} \mathcal{C}_{ab}^{AB} J_{ab}^{AB} \\ E_{CR}^{BA} &= \frac{1}{2}\sum_{a,b} \mathcal{C}_{ab}^{BA} J_{ab}^{BA} \end{aligned} \tag{3.14}$$

where the sums are over all occupied AOs of atoms A or B. The energies E_{CR}^{AB} and E_{CR}^{BA} are equivalent to each other, and the Coulomb integrals J_{ab}^{AB} and J_{ab}^{BA} are defined as

$$\begin{aligned} J_{ab}^{AB} &= \langle \psi_a^A(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2)|\psi_a^A(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2)\rangle \\ J_{ab}^{BA} &= \langle \psi_a^B(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2)|\psi_a^B(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2)\rangle \end{aligned} \tag{3.15}$$

Before discussing the correlation and exchange energies (E_{corr}^A, E_{corr}^B, E_{ex}^A, and E_{ex}^B) for atoms A and B in the molecule, we rewrite the expressions for E_A and E_B (equation 3.6) by using equations (3.8, 3.10, 3.12, and 3.14).

$$\begin{aligned} E_A &= \sum_a \eta_a^A h_{aa}^A + \frac{1}{2}\sum_{a,b} \mathcal{C}_{ab}^{AA} J_{ab}^{AA} - \frac{1}{2}\sum_a X_{aa}^{AA} J_{aa}^{AA} + \frac{1}{2}\sum_{a,b} \mathcal{C}_{ab}^{AB} J_{ab}^{AB} + E_{corr}^A + E_{ex}^A \\ E_B &= \sum_a \eta_a^B h_{aa}^B + \frac{1}{2}\sum_{a,b} \mathcal{C}_{ab}^{BB} J_{ab}^{BB} - \frac{1}{2}\sum_a X_{aa}^{BB} J_{aa}^{BB} + \frac{1}{2}\sum_{a,b} \mathcal{C}_{ab}^{BA} J_{ab}^{BA} + E_{corr}^B + E_{ex}^B \end{aligned} \tag{3.16}$$

In this thesis, we present the first version of the GAIM approach in which the correlation energies E_{corr}^A and E_{corr}^B are considered to be zero, and the exchange energies

E_{ex}^{A} and E_{ex}^{B} are expressed in the same way as in HF theory. We therefore expect that the values of E for diatomic molecules near their equilibrium distances obtained by GAIM to be close to those obtained by HF calculations. Thus HF values serve as a reference for testing the performance and validity of our approach.

Analogous to the definition of Coulomb repulsion energies in equations (3.12) and (3.14), the exchange energies E_{ex}^{A} and E_{ex}^{B} are

$$\begin{aligned}
E_{ex}^{A} &= -\frac{1}{2}\left(\sum_{a,b} X_{ab}^{AA} K_{ab}^{AA} - \sum_{a} X_{aa}^{AA} K_{aa}^{AA} + \sum_{a,b} X_{ab}^{AB} K_{ab}^{AB}\right) \\
E_{ex}^{B} &= -\frac{1}{2}\left(\sum_{a,b} X_{ab}^{BB} K_{ab}^{BB} - \sum_{a} X_{aa}^{BB} K_{aa}^{BB} + \sum_{a,b} X_{ab}^{BA} K_{ab}^{BA}\right)
\end{aligned} \tag{3.17}$$

where the sums are over all occupied atomic orbitals of atoms A or B. As in HF theory, the E_{ex}^{A} and E_{ex}^{B} are negative quantities. The second terms in the above equations cancel the self-exchange energies calculated in the first terms. The exchange integral K_{ab}^{AA}, K_{ab}^{BB}, K_{ab}^{AB}, and K_{ab}^{BA} are given by

$$\begin{aligned}
K_{ab}^{AA} &= \langle \psi_a^A(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2) | \psi_b^A(\mathbf{r}_1)\psi_a^A(\mathbf{r}_2)\rangle \\
K_{ab}^{BB} &= \langle \psi_a^B(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2) | \psi_b^B(\mathbf{r}_1)\psi_a^B(\mathbf{r}_2)\rangle \\
K_{ab}^{AB} &= \langle \psi_a^A(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2) | \psi_b^B(\mathbf{r}_1)\psi_a^A(\mathbf{r}_2)\rangle \\
K_{ab}^{BA} &= \langle \psi_a^B(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2) | \psi_b^A(\mathbf{r}_1)\psi_a^B(\mathbf{r}_2)\rangle
\end{aligned} \tag{3.18}$$

The substitution of equations (3.17) into equations (3.16) leads to

$$\begin{aligned}
E_A &= \sum_a \eta_a^A h_{aa}^A + \frac{1}{2}\sum_{a,b}\left(\mathfrak{C}_{ab}^{AA} J_{ab}^{AA} - X_{ab}^{AA} K_{ab}^{AA}\right) + \frac{1}{2}\sum_{a,b}\left(\mathfrak{C}_{ab}^{AB} J_{ab}^{AB} - X_{ab}^{AB} K_{ab}^{AB}\right) \\
E_B &= \sum_a \eta_a^B h_{aa}^B + \frac{1}{2}\sum_{a,b}\left(\mathfrak{C}_{ab}^{BB} J_{ab}^{BB} - X_{ab}^{BB} K_{ab}^{BB}\right) + \frac{1}{2}\sum_{a,b}\left(\mathfrak{C}_{ab}^{BA} J_{ab}^{BA} - X_{ab}^{BA} K_{ab}^{BA}\right)
\end{aligned} \tag{3.19}$$

Adding the above two equations to each other and using the definitions (3.8, 3.13, 3.15, and 3.18) of h, J and K integrals, the total energy expression of GAIM becomes

$$\begin{aligned}
E &= E_A + E_B \\
&= \sum_a \eta_a^A \langle \psi_a^A(\mathbf{r}_1)|\hat{h}(\mathbf{r}_1)|\psi_a^A(\mathbf{r}_1)\rangle \\
&+ \frac{1}{2}\sum_{a,b}\Big(\mathcal{C}_{ab}^{AA}\langle \psi_a^A(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2)|\psi_a^A(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2)\rangle - X_{ab}^{AA}\langle \psi_a^A(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2)|\psi_b^A(\mathbf{r}_1)\psi_a^A(\mathbf{r}_2)\rangle\Big) \\
&+ \frac{1}{2}\sum_{a,b}\Big(\mathcal{C}_{ab}^{AB}\langle \psi_a^A(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2)|\psi_a^A(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2)\rangle - X_{ab}^{AB}\langle \psi_a^A(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2)|\psi_b^B(\mathbf{r}_1)\psi_a^A(\mathbf{r}_2)\rangle\Big) \\
&+ \sum_a \eta_a^B \langle \psi_a^B(\mathbf{r}_1)|\hat{h}(\mathbf{r}_1)|\psi_a^B(\mathbf{r}_1)\rangle \\
&+ \frac{1}{2}\sum_{a,b}\Big(\mathcal{C}_{ab}^{BB}\langle \psi_a^B(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2)|\psi_a^B(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2)\rangle - X_{ab}^{BB}\langle \psi_a^B(\mathbf{r}_1)\psi_b^B(\mathbf{r}_2)|\psi_b^B(\mathbf{r}_1)\psi_a^B(\mathbf{r}_2)\rangle\Big) \\
&+ \frac{1}{2}\sum_{a,b}\Big(\mathcal{C}_{ab}^{BA}\langle \psi_a^B(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2)|\psi_a^B(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2)\rangle - X_{ab}^{BA}\langle \psi_a^B(\mathbf{r}_1)\psi_b^A(\mathbf{r}_2)|\psi_b^A(\mathbf{r}_1)\psi_a^B(\mathbf{r}_2)\rangle\Big)
\end{aligned} \tag{3.20}$$

In the next section, we shall minimize E with respect to the AOs in order to get the GAIM equations.

3.2.2 Minimization of the Energy

As the energy ($E[\{\psi_a\}]$) is a functional of the AOs, one can vary the orbitals in order to minimize the energy. Therefore the minimization of GAIM $E[\{\psi_a\}]$ with respect to the AOs is carried out subject to the constraint that the sum of atomic densities remains equal to the total number of electrons.

Before minimizing the energy, we need to write down the form of the constraint. The total electron density of a diatomic molecule (A–B) can be written as,

$$\rho(\mathbf{r}) = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) = \sum_a \eta_a^A|\psi_a^A(\mathbf{r})|^2 + \sum_a \eta_a^B|\psi_a^B(\mathbf{r})|^2 \tag{3.21}$$

where the atomic densities are expressed as a sum of AO densities $\Big(|\psi_a^A(\mathbf{r})|^2$ and $|\psi_a^B(\mathbf{r})|^2\Big)$ with occupancies η_a^A and η_a^B for the AOs of atoms A and B, respectively. The integral of these AO densities over all space is just the total number of electrons

$$\begin{aligned}\int \rho_A(\mathbf{r})d\mathbf{r} + \int \rho_B(\mathbf{r})d\mathbf{r} &= \sum_a \eta_a^A \int |\psi_a^A(\mathbf{r})|^2 d\mathbf{r} + \sum_a \eta_a^B \int |\psi_a^B(\mathbf{r})|^2 d\mathbf{r} \\ &= \sum_a \eta_a^A + \sum_a \eta_a^B = N \qquad (3.22)\end{aligned}$$

Since ψ_a^A and ψ_a^B are normalized orbitals, each integral on the right side of the above equation has value of one. Using Dirac notation, equation (3.22) can be rewritten as

$$\sum_a \eta_a^A \langle \psi_a^A|\psi_a^A\rangle + \sum_a \eta_a^B \langle \psi_a^B|\psi_a^B\rangle = \sum_a \eta_a^A + \sum_a \eta_a^B \qquad (3.23)$$

By rearranging the above equation, the form of the constraint becomes

$$\sum_a \eta_a^A(\langle \psi_a^A|\psi_a^A\rangle - 1) + \sum_a \eta_a^B(\langle \psi_a^B|\psi_a^B\rangle - 1) = 0 \qquad (3.24)$$

The standard method for finding minimum values subject to a constraint is Lagrange's method of undetermined multipliers. The constraint equations are each multiplied by some constant, called Lagrange multiplier, and added to the expression to be optimized. Thus, we define a new functional $\mathcal{L}[\{\psi\}]$,

$$\mathcal{L}[\{\psi\}] = E[\{\psi_a\}] - \left[\sum_a \eta_a^A \lambda_a^A \Big(\langle \psi_a^A|\psi_a^A\rangle - 1\Big) + \sum_a \eta_a^B \lambda_a^B \Big(\langle \psi_a^B|\psi_a^B\rangle - 1\Big)\right] \qquad (3.25)$$

The unknown constants λ_a^A and λ_a^B are the Lagrange multipliers. The quantity $\mathcal{L}$ (as well as E) is a functional of the atomic orbitals $\{\psi_a\}$ and the problem is to find stationary points of $\mathcal{L}$. That is, given infinitesimal changes in the atomic orbitals, $\psi_a \rightarrow \psi_a + \delta\psi_a$, the change in $\mathcal{L}$, ($\mathcal{L} \rightarrow \delta\mathcal{L}$), should be zero. Thus partial differentiation of $\mathcal{L}[\{\psi\}]$ (equation 3.25) with respect to $\{\psi_a\}$ gives

$$\begin{aligned}
\delta\mathcal{L} &= \delta E - \left(\sum_a \eta_a^A \lambda_a^A \delta \langle \psi_a^A | \psi_a^A \rangle + \sum_a \eta_a^B \lambda_a^B \delta \langle \psi_a^B | \psi_a^B \rangle \right) \\
&= \delta E - \left(\sum_a \eta_a^A \lambda_a^A \left[\langle \delta\psi_a^A | \psi_a^A \rangle + \langle \psi_a^A | \delta\psi_a^A \rangle \right] + \sum_a \eta_a^B \lambda_a^B \left[\langle \delta\psi_a^B | \psi_a^B \rangle + \langle \psi_a^B | \delta\psi_a^B \rangle \right] \right) \\
&= \delta E - \left[\left(\sum_a \eta_a^A \lambda_a^A \langle \delta\psi_a^A | \psi_a^A \rangle + \sum_a \eta_a^B \lambda_a^B \langle \delta\psi_a^B | \psi_a^B \rangle \right) + c.c. \right] = 0 \qquad (3.26)
\end{aligned}$$

where the first variation of the energy (δE) with respect to infinitesimal change in the $\{\psi_a\}$ is

$$\begin{aligned}
\delta E = \Bigg[& \sum_a \eta_a^A \langle \delta\psi_a^A | \hat{h} | \psi_a^A \rangle \\
&+ \frac{1}{2} \sum_{a,b} 2 \left(\mathfrak{C}_{ab}^{AA} \langle \delta\psi_a^A \psi_b^A | \psi_a^A \psi_b^A \rangle - X_{ab}^{AA} \langle \delta\psi_a^A \psi_b^A | \psi_b^A \psi_a^A \rangle \right) \\
&+ \frac{1}{2} \sum_{a,b} 2 \left(\mathfrak{C}_{ab}^{AB} \langle \delta\psi_a^A \psi_b^B | \psi_a^A \psi_b^B \rangle - X_{ab}^{AB} \langle \delta\psi_a^A \psi_b^B | \psi_b^B \psi_a^A \rangle \right) \Bigg] + c.c. \\
&+ \Bigg[\sum_a \eta_a^B \langle \delta\psi_a^B | \hat{h} | \psi_a^B \rangle \\
&+ \frac{1}{2} \sum_{a,b} 2 \left(\mathfrak{C}_{ab}^{BB} \langle \delta\psi_a^B \psi_b^B | \psi_a^B \psi_b^B \rangle - X_{ab}^{BB} \langle \delta\psi_a^B \psi_b^B | \psi_b^B \psi_a^B \rangle \right) \\
&+ \frac{1}{2} \sum_{a,b} 2 \left(\mathfrak{C}_{ab}^{BA} \langle \delta\psi_a^B \psi_b^A | \psi_a^B \psi_b^A \rangle - X_{ab}^{BA} \langle \delta\psi_a^B \psi_b^A | \psi_b^A \psi_a^B \rangle \right) \Bigg] + c.c. \qquad (3.27)
\end{aligned}$$

In order that E may reach its absolute minimum compatible with the constraint (equation (3.24)), the $\delta\mathcal{L}$ (but not necessarily δE) must be zero. Thus, by substituting equation (3.27) into equation (3.26), the first variation of $\mathcal{L}$ becomes

$$\begin{aligned}
\delta\mathcal{L} = \sum_{a} \Big[& \eta_a^A \langle \delta\psi_a^A | \hat{h} | \psi_a^A \rangle \\
& + \sum_b \Big(\mathfrak{C}_{ab}^{AA} \langle \delta\psi_a^A \psi_b^A | \psi_a^A \psi_b^A \rangle - X_{ab}^{AA} \langle \delta\psi_a^A \psi_b^A | \psi_b^A \psi_a^A \rangle \Big) \\
& + \sum_b \Big(\mathfrak{C}_{ab}^{AB} \langle \delta\psi_a^A \psi_b^B | \psi_a^A \psi_b^B \rangle - X_{ab}^{AB} \langle \delta\psi_a^A \psi_b^B | \psi_b^B \psi_a^A \rangle \Big) \Big] + c.c. \\
& + \sum_a \Big[\eta_a^B \langle \delta\psi_a^B | \hat{h} | \psi_a^B \rangle \\
& + \sum_b \Big(\mathfrak{C}_{ab}^{BB} \langle \delta\psi_a^B \psi_b^B | \psi_a^B \psi_b^B \rangle - X_{ab}^{BB} \langle \delta\psi_a^B \psi_b^B | \psi_b^B \psi_a^B \rangle \Big) \\
& + \sum_b \Big(\mathfrak{C}_{ab}^{BA} \langle \delta\psi_a^B \psi_b^A | \psi_a^B \psi_b^A \rangle - X_{ab}^{BA} \langle \delta\psi_a^B \psi_b^A | \psi_b^A \psi_a^B \rangle \Big) \Big] + c.c. \\
& - \Bigg[\Bigg(\sum_a \eta_a^A \lambda_a^A \langle \delta\psi_a^A | \psi_a^A \rangle + \sum_a \eta_a^B \lambda_a^B \langle \delta\psi_a^B | \psi_a^B \rangle \Bigg) + c.c. \Bigg] = 0
\end{aligned} \tag{3.28}$$

Equation (3.28) can be written in the form

$$\begin{aligned}
\delta\mathcal{L} = & \sum_a \int \delta\psi_a^{A*}(\mathbf{r}_1) \Big[\eta_a^A \hat{h}(\mathbf{r}_1) \\
& + \sum_b \Bigg(\mathfrak{C}_{ab}^{AA} \int \frac{\psi_b^{A*}(\mathbf{r}_2)\psi_b^A(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 - X_{ab}^{AA} \int \frac{\psi_b^{A*}(\mathbf{r}_2)\hat{\mathscr{P}}_{12}\psi_b^A(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \Bigg) \\
& + \sum_b \Bigg(\mathfrak{C}_{ab}^{AB} \int \frac{\psi_b^{B*}(\mathbf{r}_2)\psi_b^B(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 - X_{ab}^{AB} \int \frac{\psi_b^{B*}(\mathbf{r}_2)\hat{\mathscr{P}}_{12}\psi_b^B(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \Bigg) \\
& - \eta_a^A \lambda_a^A \Big] \psi_a^A(\mathbf{r}_1) d\mathbf{r}_1 + c.c. \\
& + \sum_a \int \delta\psi_a^{B*}(\mathbf{r}_1) \Big[\eta_a^B \hat{h}(\mathbf{r}_1) \\
& + \sum_b \Bigg(\mathfrak{C}_{ab}^{BB} \int \frac{\psi_b^{B*}(\mathbf{r}_2)\psi_b^B(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 - X_{ab}^{BB} \int \frac{\psi_b^{B*}(\mathbf{r}_2)\hat{\mathscr{P}}_{12}\psi_b^B(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \Bigg) \\
& + \sum_b \Bigg(\mathfrak{C}_{ab}^{BA} \int \frac{\psi_b^{A*}(\mathbf{r}_2)\psi_b^A(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 - X_{ab}^{BA} \int \frac{\psi_b^{A*}(\mathbf{r}_2)\hat{\mathscr{P}}_{12}\psi_b^A(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \Bigg) \\
& - \eta_a^B \lambda_a^B \Big] \psi_a^B(\mathbf{r}_1) d\mathbf{r}_1 + c.c. = 0
\end{aligned} \tag{3.29}$$

If we use the following definition for the Coulomb operator $\hat{\mathcal{J}}_b^X$ and the exchange operator $\hat{\mathcal{K}}_b^X$,

$$\begin{aligned}
\hat{\mathcal{J}}_b^X(\mathbf{r}_1)\psi_a(\mathbf{r}_1) &= \left[\int \frac{\psi_b^{X*}(\mathbf{r}_2)\psi_b^X(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2\right]\psi_a(\mathbf{r}_1) \\
\hat{\mathcal{K}}_b^X(\mathbf{r}_1)\psi_a(\mathbf{r}_1) &= \left[\int \frac{\psi_b^{X*}(\mathbf{r}_2)\hat{\mathscr{P}}_{12}\psi_b^X(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2\right]\psi_a(\mathbf{r}_1)
\end{aligned} \tag{3.30}$$

equation (3.29) becomes

$$\begin{aligned}
\delta\mathcal{L} &= \sum_a \int \delta\psi_a^{A*}(\mathbf{r}_1)\Big[\eta_a^A \hat{h}(\mathbf{r}_1) + \sum_b \Big(\mathcal{C}_{ab}^{AA}\hat{\mathcal{J}}_b^A(\mathbf{r}_1) - X_{ab}^{AA}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)\Big) \\
&+ \sum_b \Big(\mathcal{C}_{ab}^{AB}\hat{\mathcal{J}}_b^B(\mathbf{r}_1) - X_{ab}^{AB}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)\Big) - \eta_a^A\lambda_a^A\Big]\psi_a^A(\mathbf{r}_1)d\mathbf{r}_1 + c.c. \\
&+ \sum_a \int \delta\psi_a^{B*}(\mathbf{r}_1)\Big[\eta_a^B \hat{h}(\mathbf{r}_1) + \sum_b \Big(\mathcal{C}_{ab}^{BB}\hat{\mathcal{J}}_b^B(\mathbf{r}_1) - X_{ab}^{BB}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)\Big) \\
&+ \sum_b \Big(\mathcal{C}_{ab}^{BA}\hat{\mathcal{J}}_b^A(\mathbf{r}_1) - X_{ab}^{BA}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)\Big) - \eta_a^B\lambda_a^B\Big]\psi_a^B(\mathbf{r}_1)d\mathbf{r}_1 + c.c. = 0
\end{aligned} \tag{3.31}$$

Partitioning η_a^A into $(\eta_a^{\alpha A} + \eta_a^{\beta A})$ and η_a^B into $(\eta_a^{\alpha B} + \eta_a^{\beta B})$, and using the definitions of the occupancy coefficients $\mathcal{C}_{ab}$ and X_{ab} of equations (3.11) give

$$\begin{aligned}
\delta\mathcal{L} &= \sum_a \int \delta\psi_a^{A*}(\mathbf{r}_1)\Big[\{\eta_a^{\alpha A} + \eta_a^{\beta A}\}\hat{h} \\
&+ \sum_b \Big(\{\eta_a^{\alpha A} + \eta_a^{\beta A}\}\eta_b^A\hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \{\eta_a^{\alpha A}\eta_b^{\alpha A} + \eta_a^{\beta A}\eta_b^{\beta A}\}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)\Big) \\
&+ \sum_b \Big(\{\eta_a^{\alpha A} + \eta_a^{\beta A}\}\eta_b^B\hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \{\eta_a^{\alpha A}\eta_b^{\alpha B} + \eta_a^{\beta A}\eta_b^{\beta B}\}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)\Big) \\
&- \{\eta_a^{\alpha A} + \eta_a^{\alpha A}\}\lambda_a^A\Big]\psi_a^A(\mathbf{r}_1)d\mathbf{r}_1 + c.c. \\
&+ \sum_a \int \delta\psi_a^{B*}(\mathbf{r}_1)\Big[\{\eta_a^{\alpha B} + \eta_a^{\beta B}\}\hat{h}(\mathbf{r}_1) \\
&+ \sum_b \Big(\{\eta_a^{\alpha B} + \eta_a^{\beta B}\}\eta_b^B\hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \{\eta_a^{\alpha B}\eta_b^{\alpha B} + \eta_a^{\beta B}\eta_b^{\beta B}\}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)\Big) \\
&+ \sum_b \Big(\{\eta_a^{\alpha B} + \eta_a^{\beta B}\}\eta_b^A\hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \{\eta_a^{\alpha B}\eta_b^{\alpha A} + \eta_a^{\beta B}\eta_b^{\beta A}\}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)\Big) \\
&- \{\eta_a^{\alpha B} + \eta_a^{\alpha B}\}\lambda_a^B\Big]\psi_a^B(\mathbf{r}_1)d\mathbf{r}_1 + c.c. = 0
\end{aligned} \tag{3.32}$$

By taking out each of $\eta_a^{\alpha A}$,$\eta_a^{\beta A}$,$\eta_a^{\alpha B}$, and $\eta_a^{\beta B}$ as a common factor, we get

$$\begin{aligned}
\delta\mathcal{L} = {} & \sum_a \eta_a^{\alpha A} \int \delta\psi_a^{A*}(\mathbf{r}_1)\Big[\Big(\hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^A \hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \eta_b^{\alpha A}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)] \\
& + \sum_b [\eta_b^B \hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \eta_b^{\alpha B}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)]\Big)\psi_a^A(\mathbf{r}_1) - \lambda_a^A \psi_a^A(\mathbf{r}_1)\Big] d\mathbf{r}_1 + c.c. \\
& + \sum_a \eta_a^{\beta A} \int \delta\psi_a^{A*}(\mathbf{r}_1)\Big[\Big(\hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^A \hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \eta_b^{\beta A}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)] \\
& + \sum_b [\eta_b^B \hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \eta_b^{\beta B}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)]\Big)\psi_a^A(\mathbf{r}_1) - \lambda_a^A \psi_a^A(\mathbf{r}_1)\Big] d\mathbf{r}_1 + c.c. \\
& + \sum_a \eta_a^{\alpha B} \int \delta\psi_a^{B*}(\mathbf{r}_1)\Big[\Big(\hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^B \hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \eta_b^{\alpha B}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)] \\
& + \sum_b [\eta_b^A \hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \eta_b^{\alpha A}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)]\Big)\psi_a^B(\mathbf{r}_1) - \lambda_a^B \psi_a^B(\mathbf{r}_1)\Big] d\mathbf{r}_1 + c.c. \\
& + \sum_a \eta_a^{\beta B} \int \delta\psi_a^{B*}(\mathbf{r}_1)\Big[\Big(\hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^B \hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \eta_b^{\beta B}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)] \\
& + \sum_b [\eta_b^A \hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \eta_b^{\beta A}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)]\Big)\psi_a^B(\mathbf{r}_1) - \lambda_a^B \psi_a^B(\mathbf{r}_1)\Big] d\mathbf{r}_1 + c.c. = 0
\end{aligned} \tag{3.33}$$

The quantities in the biggest square brackets of equation (3.33) must be zero for all values of a, therefore

$$\begin{aligned}
&\Big(\hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^A \hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \eta_b^{\alpha A}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)] + \sum_b [\eta_b^B \hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \eta_b^{\alpha B}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)]\Big)\psi_a^A(\mathbf{r}_1) = \lambda_a^A \psi_a^A(\mathbf{r}_1) \\
&\Big(\hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^A \hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \eta_b^{\beta A}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)] + \sum_b [\eta_b^B \hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \eta_b^{\beta B}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)]\Big)\psi_a^A(\mathbf{r}_1) = \lambda_a^A \psi_a^A(\mathbf{r}_1) \\
&\Big(\hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^B \hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \eta_b^{\alpha B}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)] + \sum_b [\eta_b^A \hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \eta_b^{\alpha A}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)]\Big)\psi_a^B(\mathbf{r}_1) = \lambda_a^B \psi_a^B(\mathbf{r}_1) \\
&\Big(\hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^B \hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \eta_b^{\beta B}\hat{\mathcal{K}}_b^B(\mathbf{r}_1)] + \sum_b [\eta_b^A \hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \eta_b^{\beta A}\hat{\mathcal{K}}_b^A(\mathbf{r}_1)]\Big)\psi_a^B(\mathbf{r}_1) = \lambda_a^B \psi_a^B(\mathbf{r}_1)
\end{aligned} \tag{3.34}$$

By defining operators $\hat{f}^{\alpha A}$, $\hat{f}^{\beta A}$, $\hat{f}^{\alpha B}$, and $\hat{f}^{\beta B}$ as,

$$\begin{aligned}
\hat{f}^{\alpha A}(\mathbf{r}_1) &= \hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^A \hat{\mathfrak{J}}_b^A(\mathbf{r}_1) - \eta_b^{\alpha A} \hat{\mathfrak{K}}_b^A(\mathbf{r}_1)] + \sum_b [\eta_b^B \hat{\mathfrak{J}}_b^B(\mathbf{r}_1) - \eta_b^{\alpha B} \hat{\mathfrak{K}}_b^B(\mathbf{r}_1)] \\
\hat{f}^{\beta A}(\mathbf{r}_1) &= \hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^A \hat{\mathfrak{J}}_b^A(\mathbf{r}_1) - \eta_b^{\beta A} \hat{\mathfrak{K}}_b^A(\mathbf{r}_1)] + \sum_b [\eta_b^B \hat{\mathfrak{J}}_b^B(\mathbf{r}_1) - \eta_b^{\beta B} \hat{\mathfrak{K}}_b^B(\mathbf{r}_1)] \\
\hat{f}^{\alpha B}(\mathbf{r}_1) &= \hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^B \hat{\mathfrak{J}}_b^B(\mathbf{r}_1) - \eta_b^{\alpha B} \hat{\mathfrak{K}}_b^B(\mathbf{r}_1)] + \sum_b [\eta_b^A \hat{\mathfrak{J}}_b^A(\mathbf{r}_1) - \eta_b^{\alpha A} \hat{\mathfrak{K}}_b^A(\mathbf{r}_1)] \\
\hat{f}^{\beta B}(\mathbf{r}_1) &= \hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^B \hat{\mathfrak{J}}_b^B(\mathbf{r}_1) - \eta_b^{\beta B} \hat{\mathfrak{K}}_b^B(\mathbf{r}_1)] + \sum_b [\eta_b^A \hat{\mathfrak{J}}_b^A(\mathbf{r}_1) - \eta_b^{\beta A} \hat{\mathfrak{K}}_b^A(\mathbf{r}_1)] \qquad (3.35)
\end{aligned}$$

equations (3.34) take the forms

$$\begin{aligned}
\hat{f}^{\alpha A}(\mathbf{r}_1)\psi_a^A(\mathbf{r}_1) &= \lambda_a^A \psi_a^A(\mathbf{r}_1) \\
\hat{f}^{\beta A}(\mathbf{r}_1)\psi_a^A(\mathbf{r}_1) &= \lambda_a^A \psi_a^A(\mathbf{r}_1) \\
\hat{f}^{\alpha B}(\mathbf{r}_1)\psi_a^B(\mathbf{r}_1) &= \lambda_a^B \psi_a^B(\mathbf{r}_1) \\
\hat{f}^{\beta B}(\mathbf{r}_1)\psi_a^B(\mathbf{r}_1) &= \lambda_a^B \psi_a^B(\mathbf{r}_1) \qquad (3.36)
\end{aligned}$$

The Lagrange multipliers (λ_a^A and λ_a^B) in the above equations are just the orbital energies ($\varepsilon_a^{\alpha A}$, $\varepsilon_a^{\beta A}$, $\varepsilon_a^{\alpha B}$, and $\varepsilon_a^{\beta B}$). Therefore, the GAIM equations are written as

$$\begin{aligned}
\hat{f}^{\alpha A}(\mathbf{r}_1)\psi_a^A(\mathbf{r}_1) &= \varepsilon_a^{\alpha A} \psi_a^A(\mathbf{r}_1) \\
\hat{f}^{\beta A}(\mathbf{r}_1)\psi_a^A(\mathbf{r}_1) &= \varepsilon_a^{\beta A} \psi_a^A(\mathbf{r}_1) \\
\hat{f}^{\alpha B}(\mathbf{r}_1)\psi_a^B(\mathbf{r}_1) &= \varepsilon_a^{\alpha B} \psi_a^B(\mathbf{r}_1) \\
\hat{f}^{\beta B}(\mathbf{r}_1)\psi_a^B(\mathbf{r}_1) &= \varepsilon_a^{\beta B} \psi_a^B(\mathbf{r}_1) \qquad (3.37)
\end{aligned}$$

Equations (3.37) and (3.35) can be written in general format as,

$$\hat{f}^{\theta A}(\mathbf{r}_1)\psi_a^A(\mathbf{r}_1) = \varepsilon_a^{\theta A} \psi_a^A(\mathbf{r}_1) \qquad (3.38)$$

$$\hat{f}^{\theta B}(\mathbf{r}_1)\psi_a^B(\mathbf{r}_1) = \varepsilon_a^{\theta B} \psi_a^B(\mathbf{r}_1) \qquad (3.39)$$

$$f^{\theta A}(\mathbf{r}_1) = \hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^A \hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \eta_b^{\theta A} \hat{\mathcal{K}}_b^A(\mathbf{r}_1)] + \sum_b [\eta_b^B \hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \eta_b^{\theta B} \hat{\mathcal{K}}_b^B(\mathbf{r}_1)] \tag{3.40}$$

$$f^{\theta B}(\mathbf{r}_1) = \hat{h}(\mathbf{r}_1) + \sum_b [\eta_b^B \hat{\mathcal{J}}_b^B(\mathbf{r}_1) - \eta_b^{\theta B} \hat{\mathcal{K}}_b^B(\mathbf{r}_1)] + \sum_b [\eta_b^A \hat{\mathcal{J}}_b^A(\mathbf{r}_1) - \eta_b^{\theta A} \hat{\mathcal{K}}_b^A(\mathbf{r}_1)] \tag{3.41}$$

where we have used θ to denote α or β spin.

3.2.3 Introduction of Basis Sets

Using a Roothaan-like approach,[4] the differential equations (3.37) are converted to matrix equations by expanding the AOs $\{\psi_a^A\}$ and $\{\psi_a^B\}$ as a linear combination of known basis functions. We have used two different ways for expanding the atomic orbitals of atoms A and B; (1) Expanding the orbitals for each atom as linear combinations of basis functions $\Big(\{\varphi_\mu^A \mid \mu = 1, 2 \ldots, K_A\} \; or \; \{\varphi_\mu^B \mid \mu = 1, 2 \ldots, K_B\}\Big)$ centered only on that atom, (2) Expanding the orbitals for each atom as linear combinations of all basis functions on the two atoms $\{\varphi_\mu \mid \mu = 1, 2 \ldots, K\}$, where $K{=}K_A{+}K_B$.

This section is divided into two separate subsections. In subsection (3.2.3.1) we convert the equations (3.37) using the full basis set $\{\varphi_\mu\}$, while in subsection (3.2.3.2) we convert equations (3.37) into matrix equations by expanding the AOs using the basis sets $\{\varphi_\mu^A\}$ and $\{\varphi_\mu^B\}$.

3.2.3.1 Expansion of AOs Using the Full Basis Set $\{\varphi_\mu\}$

The atomic orbitals $\{\psi_a^A\}$ and $\{\psi_a^B\}$ of atoms A and B can be expanded in terms of the full basis functions $\{\varphi_\mu \mid \mu = 1, 2, \ldots, K\}$ in the molecule as follows

$$\psi_a^A = \sum_{\mu=1}^{K} C_{\mu a}^A \varphi_\mu \tag{3.42}$$

$$\psi_a^B = \sum_{\mu=1}^{K} C_{\mu a}^B \varphi_\mu \tag{3.43}$$

Here we will concentrate on atom A and analogous results will be obtained for atom B. Thus, the substitution of the expansion (3.42) into equation (3.38) leads to

$$\hat{f}^{\theta A}(\mathbf{r}_1)\sum_{\nu=1}^{K} C_{\nu a}^{A}\varphi_\nu(\mathbf{r}_1) = \varepsilon_a^{\theta A}\sum_{\nu=1}^{K} C_{\nu a}^{A}\varphi_\nu(\mathbf{r}_1) \tag{3.44}$$

If both sides of the above equation are multiplied by $\varphi_\mu^*(\mathbf{r}_1)$ and integrated over the coordinates of electron one, $\mathbf{r}_1$, the result,

$$\sum_{\nu=1}^{K} C_{\nu a}^{A}\int \varphi_\mu^*(\mathbf{r}_1)\hat{f}^{\theta A}(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)d\mathbf{r}_1 = \varepsilon_a^{\theta A}\sum_{\nu=1}^{K} C_{\nu a}^{A}\int \varphi_\mu^*(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)d\mathbf{r}_1 \tag{3.45}$$

are Roothaan-like matrix equations, which can be expressed in matrix form as

$$\mathbf{F}^{\theta A}\mathbf{C}^{A} = \epsilon^{\theta A}\mathbf{S}\mathbf{C}^{A} \tag{3.46}$$

$\epsilon^{\theta A}$ is a diagonal matrix of orbital energies. $\mathbf{C}^{A}$ is the matrix of the expansion coefficients $C_{\mu a}^{A}$. $\mathbf{F}^{\theta A}$ is the matrix representation of $\hat{f}^{\theta A}$ in the basis $\{\varphi_\mu\}$.

$$F_{\mu\nu}^{\theta A} = \int \varphi_\mu^*(\mathbf{r}_1)\hat{f}^{\theta A}(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)d\mathbf{r}_1 \tag{3.47}$$

S is the overlap matrix that has the elements

$$S_{\mu\nu} = \int \varphi_\mu^*(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)d\mathbf{r}_1 \tag{3.48}$$

Similarly for atom B. Therefore, four matrix equations can be written for a diatomic molecule (A–B). The first two equations are for α and β electrons of atom A,

$$\begin{aligned}\mathbf{F}^{\alpha A}\mathbf{C}^{A} &= \epsilon^{\alpha A}\mathbf{S}\mathbf{C}^{A}\\ \mathbf{F}^{\beta A}\mathbf{C}^{A} &= \epsilon^{\beta A}\mathbf{S}\mathbf{C}^{A}\end{aligned} \tag{3.49}$$

and the other two are for the α and β electrons of atom B.

$$\begin{aligned}\mathbf{F}^{\alpha B}\mathbf{C}^{B} &= \epsilon^{\alpha B}\mathbf{S}\mathbf{C}^{B}\\ \mathbf{F}^{\beta B}\mathbf{C}^{B} &= \epsilon^{\beta B}\mathbf{S}\mathbf{C}^{B}\end{aligned} \tag{3.50}$$

3.2.3.1.1 Definition of Density Matrices

We have defined the total charge density of a diatomic molecule (A–B) in equation (3.21) as a sum of atomic densities. The charge density can also be rewritten as the sum of charge densities contributed by electrons of α and β spins in each atom,

$$\begin{aligned}\rho(\mathbf{r}) &= \rho_A^{\alpha}(\mathbf{r}) + \rho_A^{\beta}(\mathbf{r}) + \rho_B^{\alpha}(\mathbf{r}) + \rho_B^{\beta}(\mathbf{r})\\ &= \sum_a (\eta_a^{\alpha A} + \eta_a^{\beta A})|\psi_a^A(\mathbf{r})|^2 + \sum_a (\eta_a^{\alpha B} + \eta_a^{\beta B})|\psi_a^B(\mathbf{r})|^2\end{aligned} \tag{3.51}$$

The substitution of the basis set expansions (3.42 and 3.43) of the AOs into the expression (3.51) leads to

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_{\mu,\nu}^{K}\sum_a (\eta_a^{\alpha A} + \eta_a^{\beta A})C_{\nu a}^{A}C_{\mu a}^{A*}(\mathbf{r})\varphi_\nu(\mathbf{r})\varphi_\mu^* + \sum_{\mu,\nu}^{K}\sum_a (\eta_a^{\alpha B} + \eta_a^{\beta B})C_{\nu a}^{B}C_{\mu a}^{B*}\varphi_\nu(\mathbf{r})\varphi_\mu^*(\mathbf{r})\\ &= \sum_{\mu,\nu}^{K}(P_{\nu\mu}^{\alpha A} + P_{\nu\mu}^{\beta A})\varphi_\nu(\mathbf{r})\varphi_\mu^*(\mathbf{r}) + \sum_{\mu,\nu}^{K}(P_{\nu\mu}^{\alpha B} + P_{\nu\mu}^{\beta B})\varphi_\nu(\mathbf{r})\varphi_\mu^*(\mathbf{r})\end{aligned} \tag{3.52}$$

where the density matrices $P_{\nu\mu}^{\alpha A}$ and $P_{\nu\mu}^{\alpha B}$ for α electrons and the density matrices $P_{\nu\mu}^{\beta A}$ and $P_{\nu\mu}^{\beta B}$ for β electrons are defined by

$$\begin{aligned}P_{\nu\mu}^{\alpha A} &= \sum_a \eta_a^{\alpha A}C_{\nu a}^{A}C_{\mu a}^{A*} & P_{\nu\mu}^{\alpha B} &= \sum_a \eta_a^{\alpha B}C_{\nu a}^{B}C_{\mu a}^{B*}\\ P_{\nu\mu}^{\beta A} &= \sum_a \eta_a^{\beta A}C_{\nu a}^{A}C_{\mu a}^{A*} & P_{\nu\mu}^{\beta B} &= \sum_a \eta_a^{\beta B}C_{\nu a}^{B}C_{\mu a}^{B*}\end{aligned} \tag{3.53}$$

In addition to these matrices, one can define the total density matrices $(P^{A}_{\nu\mu})$ and $(P^{B}_{\nu\mu})$ as

$$\begin{aligned} P^{A}_{\nu\mu} = P^{\alpha A}_{\nu\mu} + P^{\beta A}_{\nu\mu} \; &= \; \sum_{a} \eta^{A}_{a} C^{A}_{\nu a} C^{A*}_{\mu a} \\ P^{B}_{\nu\mu} = P^{\alpha B}_{\nu\mu} + P^{\beta B}_{\nu\mu} \; &= \; \sum_{a} \eta^{B}_{a} C^{B}_{\nu a} C^{B*}_{\mu a} \end{aligned} \tag{3.54}$$

3.2.3.1.2 Explicit Forms for the $\mathbf{F}^{\theta A}$ and $\mathbf{F}^{\theta B}$ over Basis Functions

The explicit expressions of $\mathbf{F}^{\theta A}$ matrices are obtained by substituting the expression (3.40) of $\hat{f}^{\theta A}$ and the basis set expansion (3.42) into equation (3.47). That is,

$$\begin{aligned} F^{\theta A}_{\mu\nu} &= \int \varphi^{*}_{\mu}(\mathbf{r}_1) \hat{f}^{\theta A}(\mathbf{r}_1) \varphi_{\nu}(\mathbf{r}_1) d\mathbf{r}_1 \\ &= \int \varphi^{*}_{\mu}(\mathbf{r}_1) \Big[\hat{h}(\mathbf{r}_1) + \sum_{b} [\eta^{A}_{b} \hat{\mathfrak{J}}^{A}_{b}(\mathbf{r}_1) - \eta^{\theta A}_{b} \hat{\mathfrak{K}}^{A}_{b}(\mathbf{r}_1)] \\ &+ \sum_{b} [\eta^{B}_{b} \hat{\mathfrak{J}}^{B}_{b}(\mathbf{r}_1) - \eta^{\theta B}_{b} \hat{\mathfrak{K}}^{B}_{b}(\mathbf{r}_1)] \Big] \varphi_{\nu}(\mathbf{r}_1) d\mathbf{r}_1 \end{aligned} \tag{3.55}$$

By using chemists' notation, equation (3.55) becomes

$$\begin{aligned} F^{\theta A}_{\mu\nu} &= (\varphi_{\mu}|\hat{h}|\varphi_{\nu}) + \sum_{b} \Big[\eta^{A}_{b} (\varphi_{\mu}\varphi_{\nu}|\psi^{A}_{b}\psi^{A}_{b}) - \eta^{\theta A}_{b} (\varphi_{\mu}\psi^{A}_{b}|\psi^{A}_{b}\varphi_{\nu}) \Big] \\ &+ \sum_{b} \Big[\eta^{B}_{b} (\varphi_{\mu}\varphi_{\nu}|\psi^{B}_{b}\psi^{B}_{b}) - \eta^{\theta B}_{b} (\varphi_{\mu}\psi^{B}_{b}|\psi^{B}_{b}\varphi_{\nu}) \Big] \end{aligned} \tag{3.56}$$

The substitution of the basis set expansions (3.42 and 3.43) for ψ^{A}_{b} and ψ^{B}_{b} leads to

$$\begin{aligned} F^{\theta A}_{\mu\nu} &= H_{\mu\nu} + \sum_{\lambda,\sigma}^{K} \sum_{b} \Big[\eta^{A}_{b} C^{A*}_{\lambda b} C^{A}_{\sigma b} (\varphi_{\mu}\varphi_{\nu}|\varphi_{\lambda}\varphi_{\sigma}) - \eta^{\theta A}_{b} C^{A*}_{\lambda b} C^{A}_{\sigma b} (\varphi_{\mu}\varphi_{\sigma}|\varphi_{\lambda}\varphi_{\nu}) \Big] \\ &+ \sum_{\lambda,\sigma}^{K} \sum_{b} \Big[\eta^{B}_{b} C^{B*}_{\lambda b} C^{B}_{\sigma b} (\varphi_{\mu}\varphi_{\nu}|\varphi_{\lambda}\varphi_{\sigma}) - \eta^{\theta B}_{b} C^{B*}_{\lambda b} C^{B}_{\sigma b} (\varphi_{\mu}\varphi_{\sigma}|\varphi_{\lambda}\varphi_{\nu}) \Big] \end{aligned} \tag{3.57}$$

and with definitions of density matrices (3.53) and (3.54), we get

$$\begin{aligned} F_{\mu\nu}^{\theta A} &= H_{\mu\nu} + \sum_{\lambda,\sigma}^{K} \Big[P_{\sigma\lambda}^{A}(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\theta A}(\mu\sigma|\lambda\nu) \Big] + \sum_{\lambda,\sigma}^{K} \Big[P_{\sigma\lambda}^{B}(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\theta B}(\mu\sigma|\lambda\nu) \Big] \\ &= H_{\mu\nu} + G_{\mu\nu}^{\theta A} \end{aligned} \tag{3.58}$$

where $G_{\mu\nu}^{\theta A}$ is the two-electron part of the $F^{\theta A}$ matrix, which depends on the density matrices and the two-electron integrals.

For the diatomic molecule (A–B), we have the following expressions for the α and β electrons of atom A,

$$\begin{aligned} F_{\mu\nu}^{\alpha A} &= H_{\mu\nu} + \sum_{\lambda,\sigma}^{K} \Big[P_{\sigma\lambda}^{A}(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\alpha A}(\mu\sigma|\lambda\nu) \Big] + \sum_{\lambda,\sigma}^{K} \Big[P_{\sigma\lambda}^{B}(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\alpha B}(\mu\sigma|\lambda\nu) \Big] \\ F_{\mu\nu}^{\beta A} &= H_{\mu\nu} + \sum_{\lambda,\sigma}^{K} \Big[P_{\sigma\lambda}^{A}(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\beta A}(\mu\sigma|\lambda\nu) \Big] + \sum_{\lambda,\sigma}^{K} \Big[P_{\sigma\lambda}^{B}(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\beta B}(\mu\sigma|\lambda\nu) \Big] \end{aligned} \tag{3.59}$$

and the following expressions for the α and β electrons of atom B.

$$\begin{aligned} F_{\mu\nu}^{\alpha B} &= H_{\mu\nu}^{B} + \sum_{\lambda,\sigma}^{K} \Big[P_{\sigma\lambda}^{B}(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\alpha B}(\mu\sigma|\lambda\nu) \Big] + \sum_{\lambda,\sigma}^{K} \Big[P_{\sigma\lambda}^{A}(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\alpha A}(\mu\sigma|\lambda\nu) \Big] \\ F_{\mu\nu}^{\beta B} &= H_{\mu\nu}^{B} + \sum_{\lambda,\sigma}^{K} \Big[P_{\sigma\lambda}^{B}(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\beta B}(\mu\sigma|\lambda\nu) \Big] + \sum_{\lambda,\sigma}^{K} \Big[P_{\sigma\lambda}^{A}(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\beta A}(\mu\sigma|\lambda\nu) \Big] \end{aligned} \tag{3.60}$$

3.2.3.1.3 Total Electronic Energy over Basis Functions

The total electronic energy (E) for the diatomic molecule (A–B) is expressed as the sum of atomic energies E_A and E_B, see equation (3.20). To derive an expression for E over basis functions $\{\varphi_\mu\}$, we substitute the basis set expansions of the AOs (3.42 and 3.43) of atoms A an B into equation (3.20).

For simplicity, we will concentrate on the E_A part of the equation (3.20); an analogous result will be obtained for E_B, so that

$$\begin{aligned} E_A = &\sum_{\mu,\nu}^{K}\sum_{a}\eta_a^A C_{\mu a}^{A*}C_{\nu a}^{A}(\mu|\hat{h}|\nu) \\ &+\frac{1}{2}\sum_{\mu,\nu}^{K}\sum_{\lambda,\sigma}^{K}\sum_{a,b} C_{\mu a}^{A*}C_{\nu a}^{A}C_{\lambda b}^{A*}C_{\sigma b}^{A}\left[\mathcal{C}_{ab}^{AA}(\mu\nu|\lambda\sigma) - X_{ab}^{AA}(\mu\sigma|\lambda\nu)\right] \\ &+\frac{1}{2}\sum_{\mu,\nu}^{K}\sum_{\lambda,\sigma}^{K}\sum_{a,b} C_{\mu a}^{A*}C_{\nu a}^{A}C_{\lambda b}^{B*}C_{\sigma b}^{B}\left[\mathcal{C}_{ab}^{AB}(\mu\nu|\lambda\sigma) - X_{ab}^{AB}(\mu\sigma|\lambda\nu)\right] \end{aligned} \tag{3.61}$$

By partitioning the η_a^A into $(\eta_a^{\alpha A}+\eta_a^{\beta A})$, and using the definitions of the $\mathcal{C}_{ab}^{XY}$ and X_{ab}^{XY} coefficients (equation 3.11), we get

$$\begin{aligned} E_A = \frac{1}{2}\sum_{\mu,\nu}^{K}\Bigg(&\sum_{a} 2\{\eta_a^{\alpha A}+\eta_a^{\beta A}\}C_{\mu a}^{A*}C_{\nu a}^{A}H_{\mu\nu} \\ &+\sum_{\lambda,\sigma}^{K}\sum_{a,b} C_{\mu a}^{A*}C_{\nu a}^{A}C_{\lambda b}^{A*}C_{\sigma b}^{A}\Big[\{\eta_a^{\alpha A}\eta_b^{A}+\eta_a^{\beta A}\eta_b^{A}\}(\mu\nu|\lambda\sigma) \\ &\quad -\{\eta_a^{\alpha A}\eta_b^{\alpha A}+\eta_a^{\beta A}\eta_b^{\beta A}\}(\mu\sigma|\lambda\nu)\Big] \\ &+\sum_{\lambda,\sigma}^{K}\sum_{a,b} C_{\mu a}^{A*}C_{\nu a}^{A}C_{\lambda b}^{B*}C_{\sigma b}^{B}\Big[\{\eta_a^{\alpha A}\eta_b^{B}+\eta_a^{\beta A}\eta_b^{B}\}(\mu\nu|\lambda\sigma) \\ &\quad -\{\eta_a^{\alpha A}\eta_b^{\alpha B}+\eta_a^{\beta A}\eta_b^{\beta B}\}(\mu\sigma|\lambda\nu)\Big]\Bigg) \end{aligned} \tag{3.62}$$

Using the definitions of the density matrices (3.53) and (3.54) leads to

$$\begin{aligned} E_A = \frac{1}{2}\sum_{\mu,\nu}^{K}\Bigg(&P_{\nu\mu}^{A}H_{\mu\nu}+\{P_{\nu\mu}^{\alpha A}+P_{\nu\mu}^{\beta A}\}H_{\mu\nu} \\ &+\sum_{\lambda,\sigma}^{K}\Big[\{P_{\nu\mu}^{\alpha A}P_{\sigma\lambda}^{A}+P_{\nu\mu}^{\beta A}P_{\sigma\lambda}^{A}\}(\mu\nu|\lambda\sigma) - \{P_{\nu\mu}^{\alpha A}P_{\sigma\lambda}^{\alpha A}+P_{\nu\mu}^{\beta A}P_{\sigma\lambda}^{\beta A}\}(\mu\sigma|\lambda\nu)\Big] \\ &+\sum_{\lambda,\sigma}^{K}\Big[\{P_{\nu\mu}^{\alpha A}P_{\sigma\lambda}^{B}+P_{\nu\mu}^{\beta A}P_{\sigma\lambda}^{B}\}(\mu\nu|\lambda\sigma) - \{P_{\nu\mu}^{\alpha A}P_{\sigma\lambda}^{\alpha B}+P_{\nu\mu}^{\beta A}P_{\sigma\lambda}^{\beta B}\}(\mu\sigma|\lambda\nu)\Big]\Bigg) \end{aligned} \tag{3.63}$$

This expression can be simplified by taking out each of $P^{\alpha A}_{\nu\mu}$ and $P^{\beta A}_{\nu\mu}$ as a common factor, that is

$$\begin{aligned} E_A = \frac{1}{2}\sum_{\mu,\nu}^{K}\Bigg(&P^{A}_{\nu\mu}H_{\mu\nu} + P^{\alpha A}_{\nu\mu}\Bigg[H_{\mu\nu} + \sum_{\lambda,\sigma}^{K}\Big\{P^{A}_{\sigma\lambda}(\mu\nu|\lambda\sigma) - P^{\alpha A}_{\sigma\lambda}(\mu\sigma|\lambda\nu)\Big\} \\ &+ \sum_{\lambda,\sigma}^{K}\Big\{P^{B}_{\sigma\lambda}(\mu\nu|\lambda\sigma) - P^{\alpha B}_{\sigma\lambda}(\mu\sigma|\lambda\nu)\Big\}\Bigg]) \\ &+ P^{\beta A}_{\nu\mu}\Bigg[H_{\mu\nu} + \sum_{\lambda,\sigma}^{K}\Big\{P^{A}_{\sigma\lambda}(\mu\nu|\lambda\sigma) - P^{\beta A}_{\sigma\lambda}(\mu\sigma|\lambda\nu)\Big\} \\ &+ \sum_{\lambda,\sigma}^{K}\Big\{P^{B}_{\sigma\lambda}(\mu\nu|\lambda\sigma) - P^{\beta B}_{\sigma\lambda}(\mu\sigma|\lambda\nu)\Big\}\Bigg]\Bigg) \end{aligned} \tag{3.64}$$

where the quantities in square brackets are just $F^{\alpha A}_{\mu\nu}$ and $F^{\beta A}_{\mu\nu}$, therefore

$$E_A = \frac{1}{2}\sum_{\mu,\nu}^{K}\Big[P^{A}_{\nu\mu}H_{\mu\nu} + P^{\alpha A}_{\nu\mu}F^{\alpha A}_{\mu\nu} + P^{\beta A}_{\nu\mu}F^{\beta A}_{\mu\nu}\Big] \tag{3.65}$$

Similarly for E_B, so the total electronic energy is

$$E = \frac{1}{2}\Bigg(\sum_{\mu,\nu}^{K}\Big[P^{A}_{\nu\mu}H_{\mu\nu} + P^{\alpha A}_{\nu\mu}F^{\alpha A}_{\mu\nu} + P^{\beta A}_{\nu\mu}F^{\beta A}_{\mu\nu}\Big] + \sum_{\mu,\nu}^{K}\Big[P^{B}_{\nu\mu}H_{\mu\nu} + P^{\alpha B}_{\nu\mu}F^{\alpha B}_{\mu\nu} + P^{\beta B}_{\nu\mu}F^{\beta B}_{\mu\nu}\Big]\Bigg) \tag{3.66}$$

3.2.3.2 Expansion of AOs Using the Basis Sets $\{\varphi^A_\mu\}$ and $\{\varphi^B_\mu\}$

In the previous subsection we have converted the GAIM equations (3.37) into matrix equations by expanding each AO on atoms A and B in terms of the full basis set $\{\varphi_\mu\}$. We have also derived explicit expressions for $F^{\alpha A}_{\mu\nu}$, $F^{\beta A}_{\mu\nu}$, $F^{\alpha B}_{\mu\nu}$, $F^{\beta B}_{\mu\nu}$ and E over the full basis set. In the current subsection, we convert equations (3.37) into matrix equations and derive explicit expressions for $F^{\alpha A}_{\mu\nu}$, $F^{\beta A}_{\mu\nu}$, $F^{\alpha B}_{\mu\nu}$, $F^{\beta B}_{\mu\nu}$ and E in terms of the basis sets $\{\varphi^A_\mu\}$ and $\{\varphi^B_\mu\}$.

The atomic orbitals $\{\psi^A_a\}$ and $\{\psi^B_a\}$ of atoms A and B can also be expanded in terms of the basis functions $\{\varphi^A_\mu|\mu = 1, 2, \ldots, K_A\}$ and $\{\varphi^B_\mu|\mu = 1, 2, \ldots, K_B\}$ that centered on each of the atoms A and B in the molecule as follows

$$\psi_a^A = \sum_{\mu=1}^{K_A} C_{\mu a}^A \varphi_\mu^A \tag{3.67}$$

$$\psi_a^B = \sum_{\mu=1}^{K_B} C_{\mu a}^B \varphi_\mu^B \tag{3.68}$$

Using a procedure similar to that used to convert the GAIM equations (3.37) into matrix equations in the previous subsection, one can use the expansions (3.67 and 3.68) to convert the equations (3.37) into the following matrix equations for atom A,

$$\begin{aligned} \mathbf{F}^{\alpha A}\mathbf{C}^A &= \epsilon^{\alpha A}\mathbf{S}^A\mathbf{C}^A \\ \mathbf{F}^{\beta A}\mathbf{C}^A &= \epsilon^{\beta A}\mathbf{S}^A\mathbf{C}^A \end{aligned} \tag{3.69}$$

and the following matrix equations for atom B in the molecule A$-$B.

$$\begin{aligned} \mathbf{F}^{\alpha B}\mathbf{C}^B &= \epsilon^{\alpha B}\mathbf{S}^B\mathbf{C}^B \\ \mathbf{F}^{\beta B}\mathbf{C}^B &= \epsilon^{\beta B}\mathbf{S}^B\mathbf{C}^B \end{aligned} \tag{3.70}$$

Here $\mathbf{S}^A$ and $\mathbf{S}^B$ are the matrices of overlaps between the basis functions $\{\varphi_\mu^A\}$ and $\{\varphi_\mu^B\}$ on the atoms A and B, respectively, that have the elements,

$$\begin{aligned} S_{\mu\nu}^A &= \int \varphi_\mu^{A*}(\mathbf{r}_1)\varphi_\nu^A(\mathbf{r}_1)d\mathbf{r}_1 \\ S_{\mu\nu}^B &= \int \varphi_\mu^{B*}(\mathbf{r}_1)\varphi_\nu^B(\mathbf{r}_1)d\mathbf{r}_1 \end{aligned} \tag{3.71}$$

$F^{\alpha A}_{\mu\nu}$ and $F^{\beta A}_{\mu\nu}$ are the matrix representations of the operators $\hat{f}^{\alpha A}$ and $\hat{f}^{\beta A}$, respectively, in the basis sets $\{\varphi^A_\mu\}$ and $\{\varphi^B_\mu\}$,

$$\begin{aligned}
F^{\alpha A}_{\mu\nu} &= \int \varphi^{A*}_\mu(\mathbf{r}_1)\hat{f}^{\alpha A}(\mathbf{r}_1)\varphi^A_\nu(\mathbf{r}_1)d\mathbf{r}_1 \\
&= H^A_{\mu\nu} + \sum_{\lambda,\sigma}^{K_A}\left[P^A_{\sigma\lambda}(\mu^A\nu^A|\lambda^A\sigma^A) - P^{\alpha A}_{\sigma\lambda}(\mu^A\sigma^A|\lambda^A\nu^A)\right] \\
&\quad + \sum_{\lambda,\sigma}^{K_B}\left[P^B_{\sigma\lambda}(\mu^A\nu^A|\lambda^B\sigma^B) - P^{\alpha B}_{\sigma\lambda}(\mu^A\sigma^B|\lambda^B\nu^A)\right]
\end{aligned} \tag{3.72}$$

$$\begin{aligned}
F^{\beta A}_{\mu\nu} &= \int \varphi^{A*}_\mu(\mathbf{r}_1)\hat{f}^{\beta A}(\mathbf{r}_1)\varphi^A_\nu(\mathbf{r}_1)d\mathbf{r}_1 \\
&= H^A_{\mu\nu} + \sum_{\lambda,\sigma}^{K_A}\left[P^A_{\sigma\lambda}(\mu^A\nu^A|\lambda^A\sigma^A) - P^{\beta A}_{\sigma\lambda}(\mu^A\sigma^A|\lambda^A\nu^A)\right] \\
&\quad + \sum_{\lambda,\sigma}^{K_B}\left[P^B_{\sigma\lambda}(\mu^A\nu^A|\lambda^B\sigma^B) - P^{\beta B}_{\sigma\lambda}(\mu^A\sigma^B|\lambda^B\nu^A)\right]
\end{aligned} \tag{3.73}$$

where $H^A_{\mu\nu} = (\varphi^A_\mu|\hat{h}|\varphi^A_\nu)$. $F^{\alpha B}_{\mu\nu}$ and $F^{\beta B}_{\mu\nu}$ are the matrix representations of the operators $\hat{f}^{\alpha B}$ and $\hat{f}^{\beta B}$, respectively, in the basis sets $\{\varphi^A_\mu\}$ and $\{\varphi^B_\mu\}$.

$$\begin{aligned}
F^{\alpha B}_{\mu\nu} &= \int \varphi^{B*}_\mu(\mathbf{r}_1)\hat{f}^{\alpha B}(\mathbf{r}_1)\varphi^B_\nu(\mathbf{r}_1)d\mathbf{r}_1 \\
&= H^B_{\mu\nu} + \sum_{\lambda,\sigma}^{K_B}\left[P^B_{\sigma\lambda}(\mu^B\nu^B|\lambda^B\sigma^B) - P^{\alpha B}_{\sigma\lambda}(\mu^B\sigma^B|\lambda^B\nu^B)\right] \\
&\quad + \sum_{\lambda,\sigma}^{K_A}\left[P^A_{\sigma\lambda}(\mu^B\nu^B|\lambda^A\sigma^A) - P^{\alpha A}_{\sigma\lambda}(\mu^B\sigma^A|\lambda^A\nu^B)\right]
\end{aligned} \tag{3.74}$$

$$\begin{aligned}
F^{\beta B}_{\mu\nu} &= \int \varphi^{B*}_\mu(\mathbf{r}_1)\hat{f}^{\beta B}(\mathbf{r}_1)\varphi^B_\nu(\mathbf{r}_1)d\mathbf{r}_1 \\
&= H^B_{\mu\nu} + \sum_{\lambda,\sigma}^{K_B}\left[P^B_{\sigma\lambda}(\mu^B\nu^B|\lambda^B\sigma^B) - P^{\beta B}_{\sigma\lambda}(\mu^B\sigma^B|\lambda^B\nu^B)\right] \\
&\quad + \sum_{\lambda,\sigma}^{K_A}\left[P^A_{\sigma\lambda}(\mu^B\nu^B|\lambda^A\sigma^A) - P^{\beta A}_{\sigma\lambda}(\mu^B\sigma^A|\lambda^A\nu^B)\right]
\end{aligned} \tag{3.75}$$

where $H^B_{\mu\nu} = (\varphi^B_\mu|\hat{h}|\varphi^B_\nu)$. The total electronic energy for diatomic molecules is expressed in terms of the basis sets $\{\varphi^A_\mu\}$ and $\{\varphi^B_\mu\}$ as follows

$$E = \frac{1}{2}\Big(\sum_{\mu,\nu}^{K_A}\Big[P^A_{\nu\mu}H^A_{\mu\nu} + P^{\alpha A}_{\nu\mu}F^{\alpha A}_{\mu\nu} + P^{\beta A}_{\nu\mu}F^{\beta A}_{\mu\nu}\Big] + \sum_{\mu,\nu}^{K_B}\Big[P^B_{\nu\mu}H^B_{\mu\nu} + P^{\alpha B}_{\nu\mu}F^{\alpha B}_{\mu\nu} + P^{\beta B}_{\nu\mu}F^{\beta B}_{\mu\nu}\Big]\Big) \tag{3.76}$$

3.3 The H_2 model

The purpose of this section is to show that the expansion of the AOs using the basis sets $\{\varphi^A_\mu\}$ and $\{\varphi^B_\mu\}$ is insufficient for describing potential energy curves of diatomic molecules. Therefore, we shall calculate the potential energy curve of H_2 as an illustrated example of using $\{\varphi^A_\mu\}$ and $\{\varphi^B_\mu\}$ basis sets.

Figure (3.1) shows the coordinate system for H_2 molecule. The first atomic orbital, $1s^A$, is centered on the hydrogen atom A ($\mathrm{H_A}$) and the second atomic orbital, $1s^B$, is

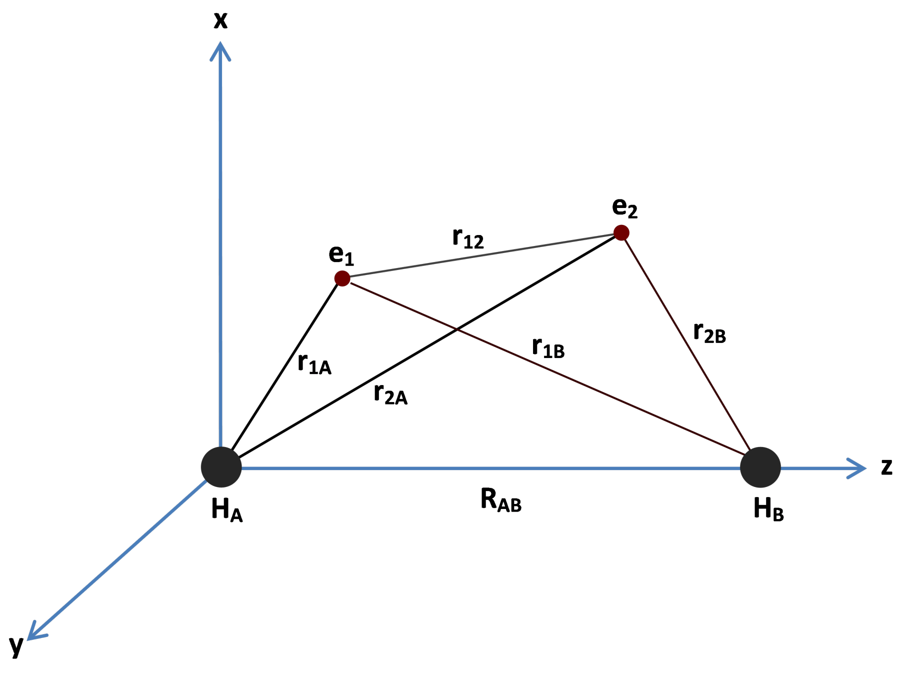

Figure 3.1: Coordinate system for H_2 molecule.

centered on the hydrogen atom B (H_B). e_1 and e_2 refer to the two electrons of H_2 at points r_1 and r_2, respectively. R_{AB} is the distance between nuclei A and B. r_{12} is the distance between the two electrons. r_{1A} and r_{2A} are the distances between nucleus A and electrons e_1 and e_2, respectively.

In GAIM, the total electronic energy (E_{H_2}) can be written as a sum of electronic energies (E_{H_A} and E_{H_B}) of individual atoms,

$$\begin{aligned}
E_{H_2} &= E_{H_A} + E_{H_B} \\
&= \eta_1^A \langle 1s_1^A(1)|h(1)|1s_1^A(1)\rangle \\
&+ \frac{1}{2}\Big[\mathcal{C}_{11}^{AA}\langle 1s_1^A(1)1s_1^A(r_2)|1s_1^A(1)1s_1^A(2)\rangle - X_{11}^{AA}\langle 1s_1^A(1)1s_1^A(2)|1s_1^A(2)1s_1^A(1)\rangle\Big] \\
&+ \frac{1}{2}\Big[\mathcal{C}_{11}^{AB}\langle 1s_1^A(1)1s_1^B(2)|1s_1^A(1)1s_1^B(2)\rangle - X_{11}^{AB}\langle 1s_1^A(1)1s_1^B(2)|1s_1^A(2)1s_1^B(1)\rangle\Big] \\
&+ \eta_1^B \langle 1s_1^B(1)|h(1)|1s_1^B(1)\rangle \\
&+ \frac{1}{2}\Big[\mathcal{C}_{11}^{BB}\langle 1s_1^B(1)1s_1^B(2)|1s_1^B(1)1s_1^B(2)\rangle - X_{11}^{BB}\langle 1s_1^B(1)1s_1^B(2)|1s_1^B(2)1s_1^B(1)\rangle\Big] \\
&+ \frac{1}{2}\Big[\mathcal{C}_{11}^{BA}\langle 1s_1^B(1)1s_1^A(r_2)|1s_1^B(1)1s_1^A(2)\rangle - X_{11}^{BA}\langle 1s_1^B(1)1s_1^A(2)|1s_1^B(2)1s_1^A(1)\rangle\Big]
\end{aligned} \tag{3.77}$$

The H_2 molecule has two occupied AOs; one is $1s_1^A$ centered on H atom A that has an electron with α spin, the other is $1s_1^B$ centered on H atom B that has an electron with β spin. If we substitute the following occupancy coefficients $\eta_1^{\alpha A} = \eta_1^{\beta B} = 1$, $\eta_1^{\beta A} = \eta_1^{\alpha B} = 0$, $\mathcal{C}_{11}^{AA} = \mathcal{C}_{11}^{BB} = 1$, $X_{11}^{AA} = X_{11}^{BB} = 1$, and $X_{11}^{AB} = X_{11}^{BA} = 0$ in equation (3.77), the electronic energy of H_2 becomes

$$\begin{aligned}
E_{H_2} &= \langle 1s_1^A(1)|h(1)|1s_1^A(1)\rangle + \frac{1}{2}\langle 1s_1^A(1)1s_1^B(2)|1s_1^A(1)1s_1^B(2)\rangle \\
&+ \langle 1s_1^B(1)|h(1)|1s_1^B(1)\rangle + \frac{1}{2}\langle 1s_1^B(1)1s_1^A(r_2)|1s_1^B(1)1s_1^A(2)\rangle
\end{aligned} \tag{3.78}$$

or,

$$E_{H_2} = h_{11}^A + h_{11}^B + \frac{1}{2}J_{11}^{AB} + \frac{1}{2}J_{11}^{BA} \tag{3.79}$$

To evaluate the energy of H_2, we use the minimal STO-2G basis set to define the AOs ($1s_1^A$ and $1s_1^B$), so that

$$\begin{aligned}
1s_1^A &= C_{11}^A \left(G_1^A + G_2^A\right) \\
&= C_{11}^A \left([d_{12} g_{1s}^A(\alpha_{12})] + [d_{22} g_{1s}^A(\alpha_{22})]\right) \\
&= C_{11}^A \left([(0.162342) g_{1s}^A(0.233136)] + [(0.375320) g_{1s}^A(1.309757)]\right) \qquad (3.80)
\end{aligned}$$

and

$$\begin{aligned}
1s_1^B &= C_{11}^B \left(G_1^B + G_2^B\right) \\
&= C_{11}^B \left([d_{12} g_{1s}^B(\alpha_{12})] + [d_{22} g_{1s}^B(\alpha_{22})]\right) \\
&= C_{11}^B \left([(0.162342) g_{1s}^B(0.233136)] + [(0.375320) g_{1s}^B(1.309757)]\right) \qquad (3.81)
\end{aligned}$$

G^A and G^B are primitive Gaussian functions that are used to construct STO-2G basis set with coefficients (d_{12} and d_{22}) and exponents (α_{12} and α_{22}) shown in the above equations. Each of C_{11}^A and C_{11}^B can be determined, to be 1, from the fact that $1s_1^A$ and $1s_1^B$ are normalized as follows,

$$\begin{aligned}
\int 1s_1^{A*}(\mathbf{r}) 1s_1^A(\mathbf{r}) d\mathbf{r} &= \int \left[C_{11}^A \left(G_1^A + G_2^A\right)\right]^* \left[C_{11}^A \left(G_1^A + G_2^A\right)\right] d\mathbf{r} \\
&= |C_{11}^A|^2 \int \left(G_1^A + G_2^A\right)^* \left(G_1^A + G_2^A\right) d\mathbf{r} \\
&= |C_{11}^A|^2 = 1 \Longrightarrow C_{11}^A = 1 \qquad (3.82)
\end{aligned}$$

Similarly for C_{11}^B. The next step for calculating the energy of H_2 is the solving of the following GAIM equations;

$$\begin{aligned}
\mathbf{F}^{\alpha A} \mathbf{C}^A &= \epsilon^{\alpha A} \mathbf{S}^A \mathbf{C}^A \\
\mathbf{F}^{\beta B} \mathbf{C}^B &= \epsilon^{\beta B} \mathbf{S}^B \mathbf{C}^B \qquad (3.83)
\end{aligned}$$

Here we will calculate the energy of H_2 at $R_{AB} = 1.4$ bohr as shown in the coordinate system of figure (3.1):

1. The elements of $\mathbf{S}^A$ and $\mathbf{S}^B$ can be calculated, using equations (3.71) and (A.2) in Appendix A to be, $\mathbf{S}^A = \mathbf{S}^B = 1$. Thus the GAIM equations (3.83) become,

$$\begin{aligned}\mathbf{F}^{\alpha A} &= \epsilon^{\alpha A} \\ \mathbf{F}^{\beta B} &= \epsilon^{\beta B}\end{aligned} \tag{3.84}$$

2. The elements of ($\mathbf{F}^{\alpha A}$ and $\mathbf{F}^{\beta B}$) are the sums of elements of ($\mathbf{H}^A$ and $\mathbf{H}^B$) and elements of ($\mathbf{G}^A$ and $\mathbf{G}^B$), i.e.,

$$\begin{aligned}F^{\alpha A}_{\mu\nu} &= H^A_{\mu\nu} + G^{\alpha A}_{\mu\nu} \\ F^{\beta B}_{\mu\nu} &= H^B_{\mu\nu} + G^{\beta B}_{\mu\nu}\end{aligned} \tag{3.85}$$

   (a) The matrices ($\mathbf{H}^A$ and $\mathbf{H}^B$) are the sums of the kinetic energy matrices ($\mathbf{T}^A$ and $\mathbf{T}^B$) and the nuclear-electron attraction matrices ($\mathbf{V}^A$ and $\mathbf{V}^B$)

$$\begin{aligned}\mathbf{H}^A &= \mathbf{T}^A + \mathbf{V}^A \\ \mathbf{H}^B &= \mathbf{T}^B + \mathbf{V}^B\end{aligned} \tag{3.86}$$

   Using the formulae (A.3 and A.4) in appendix A, the elements of $\mathbf{T}$ and $\mathbf{V}$ can be calculated to be,

$$\begin{aligned}\mathbf{T}^A &= \mathbf{T}^B = 0.734883\ h \\ \mathbf{V}^A &= \mathbf{V}^B = -1.841796\ h\end{aligned}$$

   Therefore, $\mathbf{H}^A = \mathbf{H}^B = 0.734883 - 1.841796 = -1.106912\ h$

   (b) For H_2 molecules; $\mathbf{P}^A = \mathbf{P}^{\alpha A}$, $\mathbf{P}^{\beta A} = 0$, $\mathbf{P}^B = \mathbf{P}^{\beta B}$, and $\mathbf{P}^{\alpha B} = 0$; therefore

$\mathbf{G}^{\alpha A}$ and $\mathbf{G}^{\beta B}$ of equations (3.72) and (3.75) become

$$G_{\mu\nu}^{\alpha A} = \sum_{\lambda,\sigma}^{K_B} P_{\sigma\lambda}^{B}(\mu^A\nu^A|\lambda^B\sigma^B)$$

$$G_{\mu\nu}^{\beta B} = \sum_{\lambda,\sigma}^{K_A} P_{\sigma\lambda}^{A}(\mu^B\nu^B|\lambda^A\sigma^A) \tag{3.87}$$

The two-electron integrals in the above equations can be calculated using equation (A.6) in appendix A, while $P_{\sigma\lambda}^{B}$ and $P_{\sigma\lambda}^{A}$ can be obtained using equations (3.53 and 3.54) to be 1. Thus, $G_{\mu\nu}^{\alpha A} = G_{\mu\nu}^{\beta B} = 0.569146\ h$

3. Using equation (3.79),

   $E_{H_2} = (-1.106912) + (-1.106912) + \frac{1}{2}(0.569146) + \frac{1}{2}(0.569146) = -1.644678\ h$

4. The nuclear-nuclear repulsion energy ($V_{nn} = \dfrac{1}{R_{AB}} = \dfrac{1}{1.4} = 0.714286\ h$).

5. Therefore, the total energy of H_2 is,

   $E_{H_2}^{T} = -1.644678 + 0.714286 = -0.930392\ h.$

Following the procedure discussed above, one can find $E_{H_2}^{T}$ at different $\mathbf{R}_{AB}$. Table (3.1) shows different values of $E_{H_2}^{T}$ in hartrees calculated at different $\mathbf{R}_{AB}$ using GAIM and the corresponding HF values. Figure (3.2) shows the potential energy curve for H_2 calculated using GAIM/STO-2G and RHF/STO-2G. The GAIM results around the equilibrium distance are too positive compared to the HF results. This is due to the use of the $\{\varphi_\mu^A\}$ and the $\{\varphi_\mu^B\}$ basis sets. Therefore the expansion of the AOs using a full basis set is essential. In the next chapter we shall discuss the solution of the GAIM equations using a full basis set.

Table 3.1: Total energy of H_2 (hartree) calculated at different $\mathbf{R}_{AB}$ (bohr) using GAIM and HF with STO-2G basis set.

$\mathbf{R}_{AB}$	$E^T_{H_2}$ (GAIM)	$E^T_{H_2}$ (HF)
0.40	0.137733	0.091063
0.80	-0.791653	-0.918275
1.20	-0.920820	-1.085419
1.40	-0.930392	-1.093407
1.80	-0.928166	-1.056993
2.00	-0.924653	-1.026296
3.00	-0.912159	-0.861517
5.00	-0.908825	-0.660601

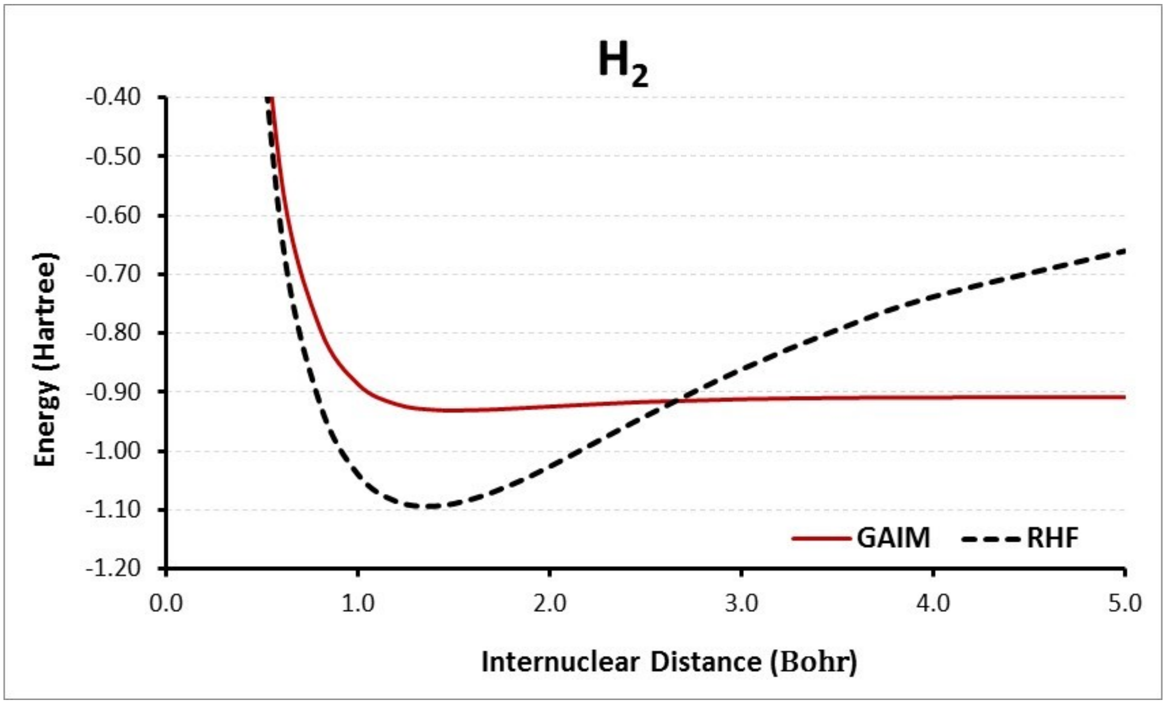

Figure 3.2: Potential energy curve for H_2 molecule, calculated using GAIM/STO-2G (solid curve) and RHF/STO-2G (dashed curve).

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Chapter 4

Solution of the GAIM Equations

4.1 Introduction

This chapter presents the SCF procedure that was used for solving the GAIM equations as well as the performance of GAIM. But before we proceed to discuss the solution of the GAIM equations, we consider the validity of the method that we have used in solving these equations. This method is based on the diagonalization of a single Fock matrix (for each atom) in AOs basis, which is constructed from α and β Fock matrices belonging to the same atom.

We investigated the validity of this method using HF theory before applying it to GAIM. This had been done by implementing the high-spin restricted open-shell Hartree-Fock (ROHF) method,[1] based on the diagonalization of a single Fock matrix in the MOs basis,[2–6] with the MUNgauss program.[7] Several open-shell systems were tested using this method. The calculated results were compared with the results obtained from the ROHF codes that are available in the MUNgauss and Gaussian 09[8] programs.

In the first section of this chapter, we will discuss the solution of the high-spin ROHF method based on diagonalizing a single Fock matrix. While in the other sections, we will discuss the solution of GAIM and its performance.

4.2 Solution of the High-Spin ROHF Method

The high-spin ROHF method based on the diagonalization of the single Fock matrix of equation (2.53) has been implemented using the MUNgauss program. MUNgauss implements several SCF methods such as RHF, UHF, ROHF, and GVB. The high-spin ROHF code is built from the UHF code, and called OSHF (Open-Shell HF). In this code, an initial guess for the coefficients matrix ($\mathbf{C}$) is given, and the density matrices $\mathbf{P}^{\alpha}$ and $\mathbf{P}^{\beta}$ are calculated. Fock matrices ($\mathbf{F}^{\alpha}_{\varphi}$ and $\mathbf{F}^{\beta}_{\varphi}$) over basis functions are obtained and transformed to $\mathbf{F}^{\alpha}_{\psi} = \mathbf{C}^{\dagger}\mathbf{F}^{\alpha}_{\varphi}\mathbf{C}$ and $\mathbf{F}^{\beta}_{\psi} = \mathbf{C}^{\dagger}\mathbf{F}^{\beta}_{\varphi}\mathbf{C}$. A Fock matrix ($\mathbf{F}^{hs}_{OSHF}$) in molecular orbital basis is built from $\mathbf{F}^{\alpha}_{\psi}$ and $\mathbf{F}^{\beta}_{\psi}$ using equation (2.53) with the Guest and Saunders diagonal canonicalization parameters set (see Table 2.1). Then $\mathbf{T}$ and ε are obtained by diagonalizing $\mathbf{F}^{hs}_{OSHF}$, i.e., $\mathbf{T}^{\dagger}\mathbf{F}^{hs}_{OSHF}\mathbf{T}$. A new $\mathbf{C} = \mathbf{C}_{old}\mathbf{T}$ is calculated and the procedure is iterated until the self-consistency is reached.

In order to test the validity of this method, the energies of following high-spin atoms (H, Li, B, N, Na, P) are calculated using the OSHF code which we have written within MUNgauss and the ROHF codes that are available in the MUNgauss and Gaussian 09 programs. A sample of the input files used with the OSHF code is available in appendix B. The calculated values are shown in Table 4.1. For all the atoms studied, the total energies calculated using OSHF code are identical to those calculated using the ROHF codes that are available in the MUNgauss and Gaussian 09 programs. Based

Table 4.1: Total energy in hartree for some high-spin atoms calculated with 6-31G basis set using the OSHF code in MUNgauss and the ROHF codes that are available in the MUNgauss and Gaussian 09 programs.

	OSHF	ROHF	
	MUNgauss	MUNgauss	Gaussian 09
H	-0.498233	-0.498233	-0.498233
Li	-7.431235	-7.431235	-7.431235
B	-24.519348	-24.519348	-24.519348
N	-54.382051	-54.382051	-54.382051
Na	-161.841392	-161.841392	-161.841392
P	-340.688937	-340.688937	-340.688937

on these results, the method of diagonalizing a single Fock matrix (for each atom) in AOs basis has been used to solve the GAIM equations.

4.3 Solution of GAIM Equations

The $\mathbf{F}^{\theta A}$ and $\mathbf{F}^{\theta B}$ depend on both $\mathbf{P}^{\theta A}$ and $\mathbf{P}^{\theta B}$ and also explicitly on each other through $\mathbf{P}^{\theta A}$ and $\mathbf{P}^{\theta B}$. Therefore, the GAIM equations (3.49 and 3.50) must be solved self-consistently and simultaneously. The solution of the GAIM equations has been implemented within the MUNgauss program. A code called mun.GAIMT.f90 was written within the framework of MUNgauss for solving the GAIM equations and the solution is carried out in the following steps:

1. Define input data that specify a molecule such as nuclear coordinate ($\mathbf{R}_{AB}$), atomic numbers (Z_A, Z_B), and basis set ($\{\varphi_i\}$).

2. Define input data that specify the atoms A and B in the molecule such as the number of electrons on each atom (N_A, N_B), the occupancy of each occupied atomic orbital of the two atoms, and the number of basis functions on each atom.

3. Calculate all required molecular integrals over the basis functions such as $S_{\mu\nu}$, $H_{\mu\nu}$, and $\{(\mu\nu|\lambda\sigma)\}$.

4. Obtain initial guesses for $\mathbf{C^A}$ and $\mathbf{C^B}$. In order to generate initial guesses for $\mathbf{C^A}$ and $\mathbf{C^B}$, two HF calculations should be done on the molecule A-B at some large internuclear distance. One is for calculating $E(A\cdots *)$ and the coefficient matrix is used as an initial guess for $\mathbf{C^A}$, while the other is for calculating $E(*\cdots B)$ and the coefficient matrix is used as an initial guess for $\mathbf{C^B}$ (see section 2.4). Then a GAIM calculation is performed at that distance and the resulting $\mathbf{C^A}$ and $\mathbf{C^B}$ are saved and then used as initial guesses for other shorter distances.

5. Calculate the density matrices $\mathbf{P}^{\theta A}$, $\mathbf{P}^{\theta B}$, $\mathbf{P}^{A}$, and $\mathbf{P}^{B}$ using equations 3.53 and 3.54.

6. Obtain the matrices $\mathbf{F}^{\theta A}$ and $\mathbf{F}^{\theta B}$ using equations 3.59 and 3.60.

7. Transform $\mathbf{F}^{\theta A}$ and $\mathbf{F}^{\theta B}$ in the AOs basis;

$$\mathbf{F}^{\theta A}_{\psi} = \mathbf{C}^{A\dagger}\mathbf{F}^{\theta A}\mathbf{C}^{A}, \qquad \mathbf{F}^{\theta B}_{\psi} = \mathbf{C}^{B\dagger}\mathbf{F}^{\theta B}\mathbf{C}^{B} \tag{4.1}$$

8. Construct a single $\mathbf{F}_{\psi}$ matrix for each atom with the Roothaan's diagonal canonicalization parameters set (see Table 2.1) as,

$$\mathbf{F}^{A}_{\psi} = \begin{array}{cc} \begin{array}{ccc} \quad\textit{closed}\quad & \quad\textit{open}\quad & \quad\textit{virtual}\quad \end{array} & \\ \left[\begin{array}{ccc} (3\mathbf{F}^{\beta A}_{\psi} - \mathbf{F}^{\alpha A}_{\psi})/2 & \mathbf{F}^{\beta A}_{\psi} & (\mathbf{F}^{\alpha A}_{\psi} + \mathbf{F}^{\beta A}_{\psi})/2 \\ \mathbf{F}^{\beta A}_{\psi} & (\mathbf{F}^{\alpha A}_{\psi} + \mathbf{F}^{\beta A}_{\psi})/2 & \mathbf{F}^{\alpha A}_{\psi} \\ (\mathbf{F}^{\alpha A}_{\psi} + \mathbf{F}^{\beta A}_{\psi})/2 & \mathbf{F}^{\alpha A}_{\psi} & (3\mathbf{F}^{\alpha A}_{\psi} - \mathbf{F}^{\beta A}_{\psi})/2 \end{array}\right] & \begin{array}{c} \textit{closed} \\ \textit{open} \\ \textit{virtual} \end{array} \end{array} \tag{4.2}$$

$$\mathbf{F}^{B}_{\psi} = \begin{array}{cc} \begin{array}{ccc} \quad\textit{closed}\quad & \quad\textit{open}\quad & \quad\textit{virtual}\quad \end{array} & \\ \left[\begin{array}{ccc} (3\mathbf{F}^{\alpha B}_{\psi} - \mathbf{F}^{\beta B}_{\psi})/2 & \mathbf{F}^{\alpha B}_{\psi} & (\mathbf{F}^{\beta B}_{\psi} + \mathbf{F}^{\alpha A}_{\psi})/2 \\ \mathbf{F}^{\alpha B}_{\psi} & (\mathbf{F}^{\beta B}_{\psi} + \mathbf{F}^{\alpha B}_{\psi})/2 & \mathbf{F}^{\beta B}_{\psi} \\ (\mathbf{F}^{\beta B}_{\psi} + \mathbf{F}^{\alpha B}_{\psi})/2 & \mathbf{F}^{\beta B}_{\psi} & (3\mathbf{F}^{\beta B}_{\psi} - \mathbf{F}^{\alpha B}_{\psi})/2 \end{array}\right] & \begin{array}{c} \textit{closed} \\ \textit{open} \\ \textit{virtual} \end{array} \end{array} \tag{4.3}$$

8. Diagonalize $\mathbf{F}^{A}_{\psi}$ and $\mathbf{F}^{B}_{\psi}$ to obtain $\mathbf{T}^{A}$ and $\mathbf{T}^{B}$.

9. Store $\mathbf{C}^{A}$ and $\mathbf{C}^{B}$.

10. Calculate new $\mathbf{C}^{A} = \mathbf{C}^{A}_{old}\mathbf{T}^{A}$, and new $\mathbf{C}^{B} = \mathbf{C}^{B}_{old}\mathbf{T}^{B}$.

11. Check whether $\mathbf{C}^{A}$ matches the stored $\mathbf{C}^{A}$, if not, reorder $\mathbf{C}^{\mathbf{A}}$. Similarly with $\mathbf{C}^{B}$.

12. Compute new density matrices; $\mathbf{P}^{\theta A}$, $\mathbf{P}^{\theta B}$, $\mathbf{P}^{A}$, and $\mathbf{P}^{B}$.

13. Calculate the electronic energy (E) using equation 3.66.

14. Calculate total energy; $E_{tot} = E + V_{NN}$, where V_{NN} is the nuclear repulsion energy.

15. Check for convergence: if $E_{i+1} - E_i \leqslant 1 \times 10^{-6}$ then save $\mathbf{C}^{A}$ and $\mathbf{C}^{B}$ and exit, otherwise return to step (6).

4.4 Computational Methodology

The energies of the molecules studied were calculated using GAIM/6-31G and RHF/6-31G. All calculations were performed using the MUNgauss program. The input and output files of LiH molecule used with the GAIM code are available in appendixes C and D.

4.5 Performance of GAIM

An initial testing of the performance of GAIM is given through calculation of the dissociation curves of H_2, LiH, Li_2, BH, HF, HCl, N_2, F_2, Cl_2 using both HF theory and GAIM with the 6-31G basis set. As discussed in section (3.2.1.3), we expect that GAIM energies will be close to HF energies at bond lengths close to equilibrium bond lengths. But unlike HF, molecules with GAIM have correct dissociation limit.

Figures (4.1-4.6) show the dissociation curves of H_2, LiH, Li_2, BH, HF, and HCl, respectively, calculated using both GAIM and HF theory. GAIM performs well with these cases. In each of the six cases above, GAIM energies at short distances and near the equilibrium bond length are identical to those of RHF theory. Unlike HF theory, GAIM behaves well at long internuclear distances and gives the correct dissociation limit for each of the six molecules. GAIM shows convergence problems with N_2, F_2, and Cl_2. This is due to difficulties in reordering the degenerate atomic orbitals p_x, p_y, and p_z in N, F, and Cl atoms. Future development in the GAIM code is required in order to solve this problem.

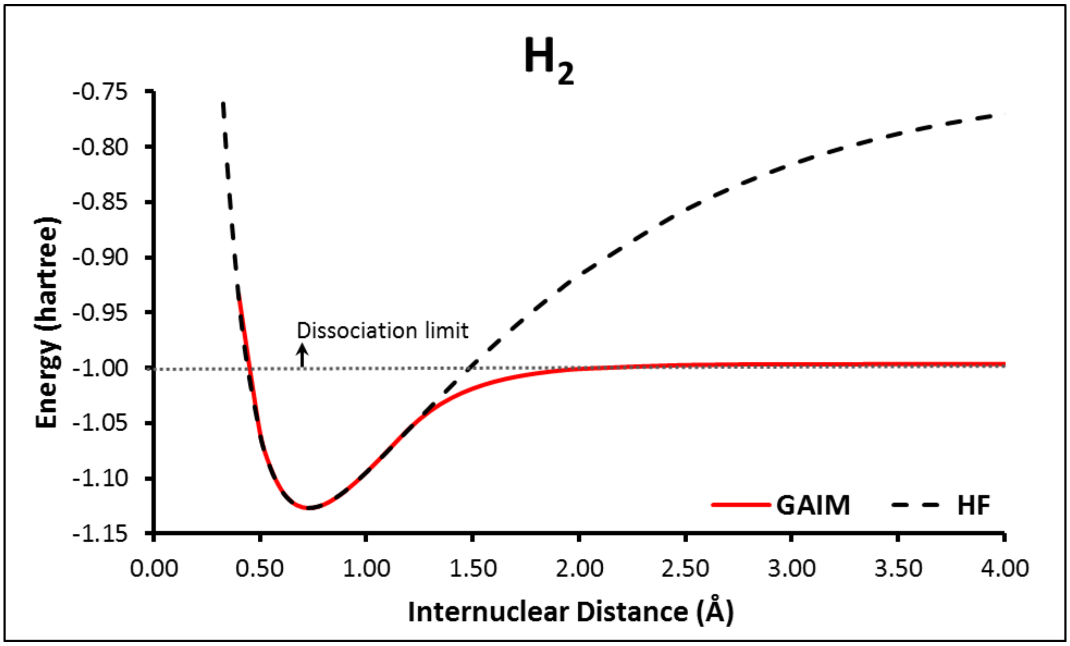

Figure 4.1: Dissociation curve for the H_2 molecule, calculated using GAIM/6-31G (solid curve) and RHF/6-31G (dashed curve).

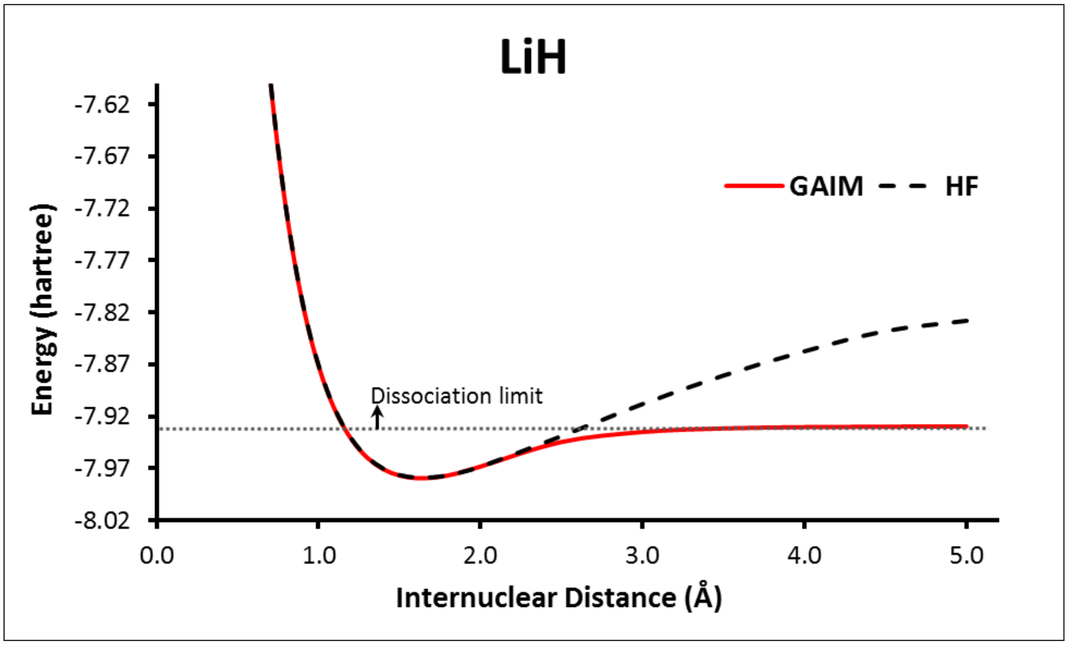

Figure 4.2: Dissociation curve for the LiH molecule, calculated using GAIM/6-31G (solid curve) and RHF/6-31G (dashed curve).

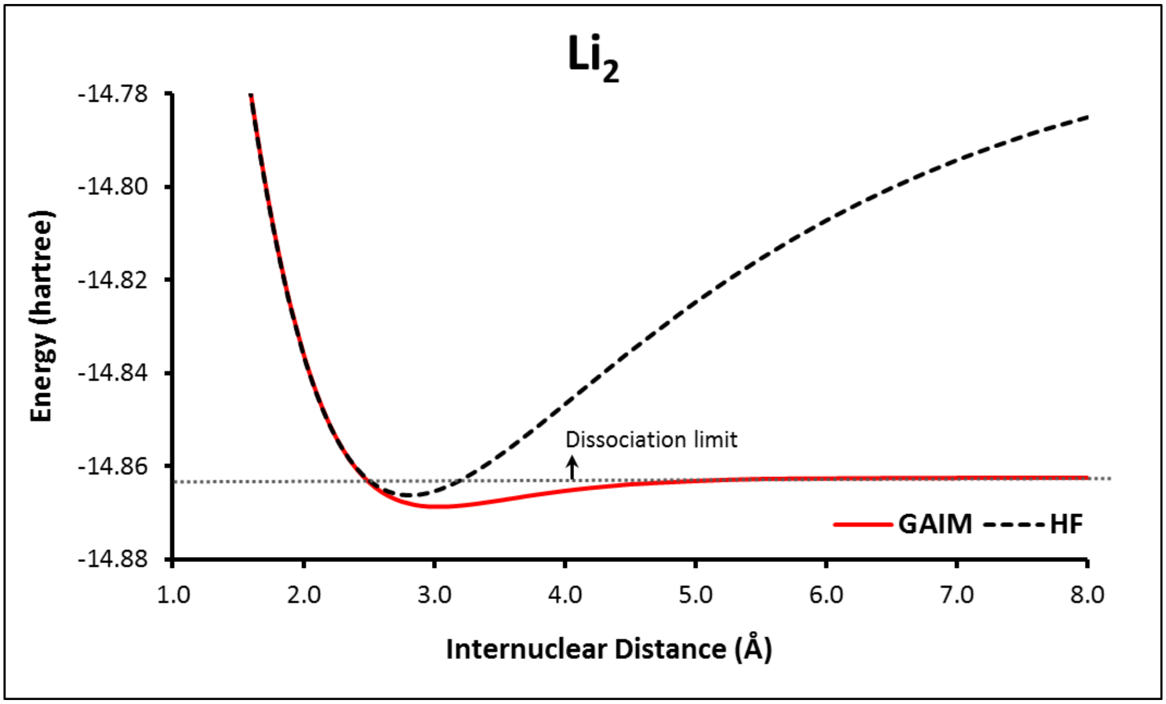

Figure 4.3: Dissociation curve for the Li_2 molecule, calculated using GAIM/6-31G (solid curve) and RHF/6-31G (dashed curve).

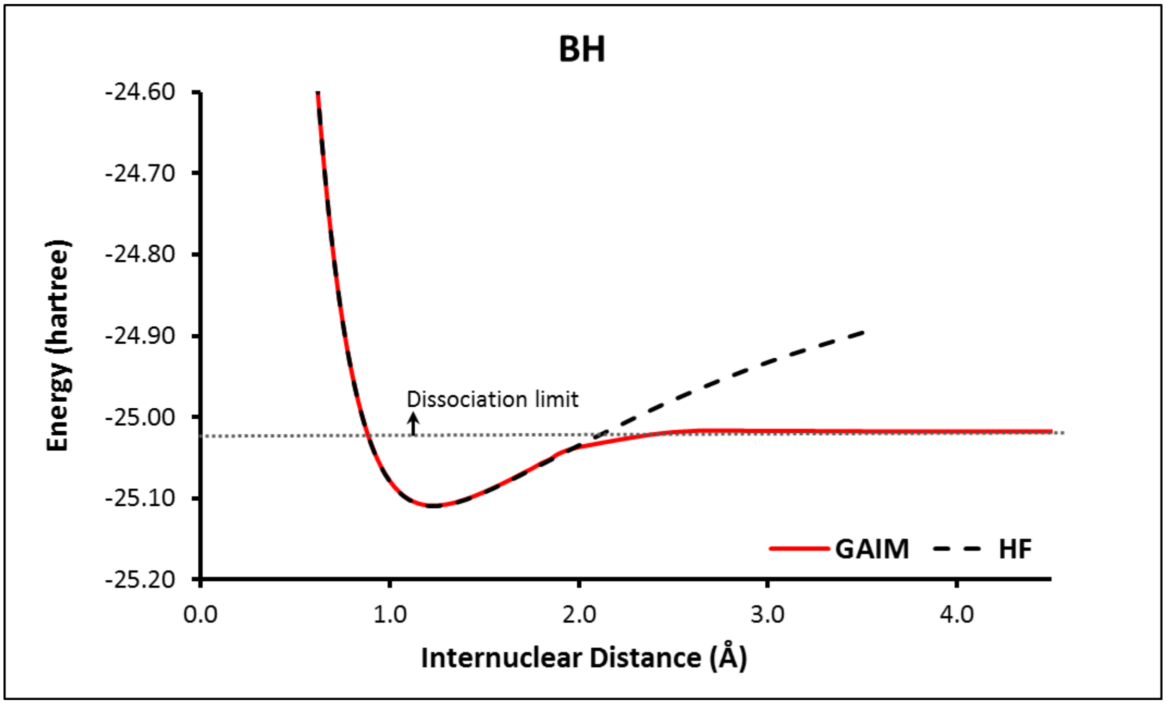

Figure 4.4: Dissociation curve for the BH molecule, calculated using GAIM/6-31G (solid curve) and RHF/6-31G (dashed curve).

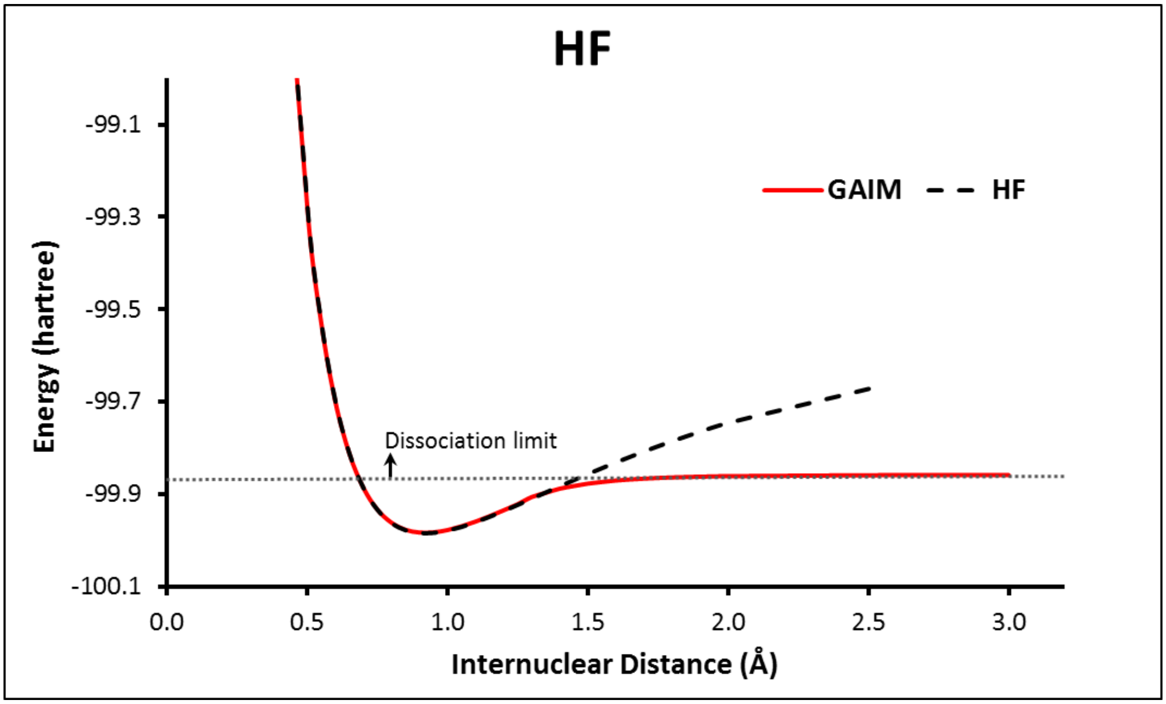

Figure 4.5: Dissociation curve for the HF molecule, calculated using GAIM/6-31G (solid curve) and RHF/6-31G (dashed curve).

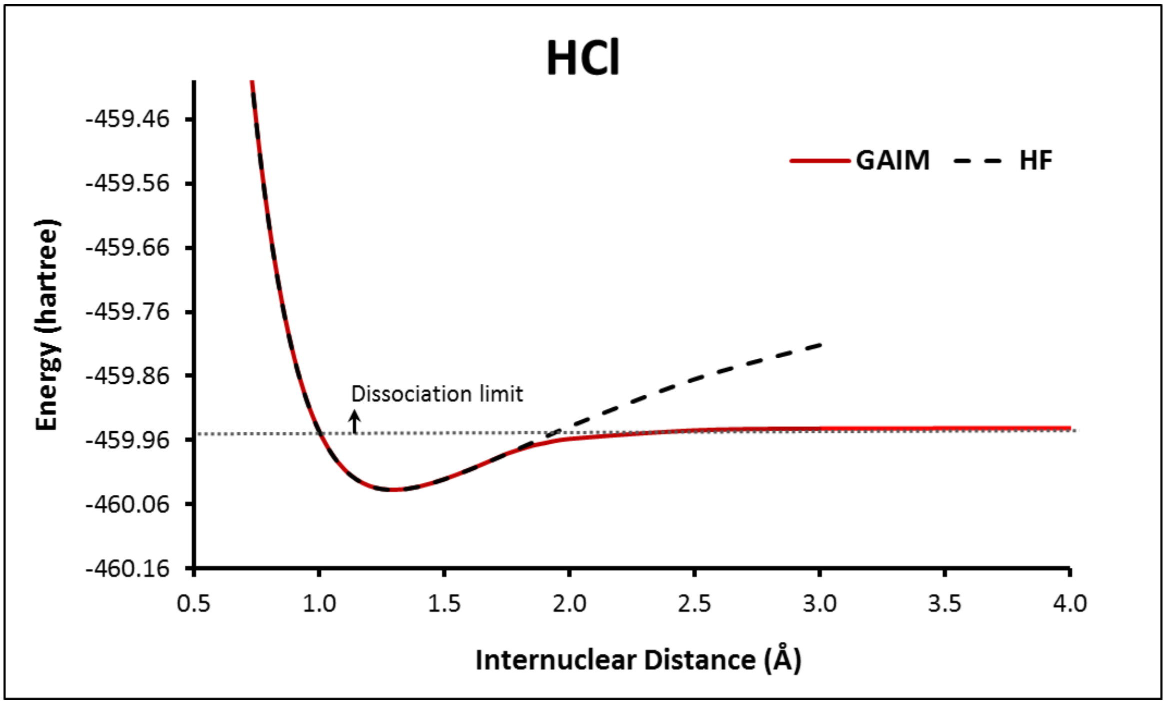

Figure 4.6: Dissociation curve for the HCl molecule, calculated using GAIM/6-31G (solid curve) and RHF/6-31G (dashed curve).

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Chapter 5

Conclusions and Future Work

We proposed a new approach for calculating the total energy of molecules called generalized atoms in molecules approach. This thesis presents the first version of GAIM in which: (i) the energy is formulated for diatomic molecules only, (ii) the correlation energy is considered to be zero, (iii) the exchange energy is expressed in the same way as in HF theory. In this approach, the energy is formulated as a sum of atomic energy contributions. An initial testing of the performance of GAIM is given through calculating the dissociation curves of H_2, LiH, Li_2, BH, HF, HCl, N_2, F_2, Cl_2 using both HF theory and GAIM with the 6-31G basis set. The numerical results show that GAIM performs very well with H_2, LiH, Li_2, BH, HF, and HCl. GAIM shows convergence problems with N_2, F_2, and Cl_2 due to difficulties in reordering the degenerate atomic orbitals p_x, p_y, and p_z in N, F, and Cl atoms. Further work for the development of GAIM is required.

Further future work includes:

1. Developing an algorithm to generate better initial guesses for $\mathbf{C}^A$ and $\mathbf{C}^B$.
2. Developing an algorithm to deal with degenerate orbitals.
3. Extending the GAIM approach to molecules that have more than two atoms.
4. Including electron correlation in the GAIM appoach.

5. Developing a density functional version of the GAIM approach.
6. Developing an efficient Fortran code for solving the GAIM equations within the framework of MUNgauss.[1]

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PART TWO

Computational Study on the Deamination Reaction of Adenine with OH^-/nH_2O (n=0, 1, 2, 3) and $3\,H_2O$

- This part is published as an article in the Canadian Journal of Chemistry. “Alrawashdeh, A. I.; Almatarneh, M. H.; Poirier, R. A. *Can. J. Chem.* **2013**, *91*, 518–526".
- Alrawashdeh, A. I. is the principal author and carried out most of the work under the supervision of R. A. Poirier.

Chapter 6

A Computational Study on the Deamination Reaction of Adenine with OH^-/nH_2O (n=0, 1, 2, 3) and $3\,H_2O$

6.1 Introduction

Extensive knowledge and understanding of genetic material and its physicochemical properties is one of the natural goals of science. One of the essential components of genetic material is adenine (Ade). Indeed, adenine is central to life functions in most, if not all, organisms.[1] It is one of the five nucleobases utilized in forming nucleotides of the nucleic acids.[2,3] Adenine has a diversity of vital roles including energy transfer, as a part of adenosine triphosphate (ATP), adenosine diphosphate (ADP), adenosine monophosphate (AMP) and the cofactors nicotinamide adenine dinucleotide (NAD) and flavin adenine dinucleotide (FAD), and protein synthesis, as a component of DNA and RNA.[2–4] The nucleobases play a specific role with their ability to establish hydrogen bonds responsible for the encoding and the expression of genetic information.[5]

Adenine is complementary to either thymine in DNA[6] or uracil in RNA,[7] and binds to each of them via two hydrogen bonds to assist in stabilizing the two nucleic acids.

Adenine as well as the other nucleobases can exist in more than one tautomeric form. Tautomerism may cause spontaneous mutations by altering the hydrogen bonding pattern of bases producing incorrect base pairing during DNA replication.[3,8] Numerous studies, both computational[8–15] and experimental[5,15,16] have been devoted to the tautomerism of adenine. These studies have provided reliable structures of adenine tautomers and their relative stabilities. Four possible tautomeric structures (9H, 7H, 3H, and 1H) have been found for adenine in its amino form. Geometries of these tautomers are shown in Figure 6.1. In the gas phase, the relative stabilities in the ground-state are 9H $>$ 7H $>$ 3H $>$ 1H,[5,10,15] whereas for the lowest singlet excited state, this order is found to be different: 3H $>$ 1H $>$ 9H $>$ 7H. It should be noted here that the tautomers with N−H fragments in the five-membered ring of adenine are more stable in the ground state, while the tautomers with N−H fragments in the six-membered ring of adenine are more stable in the excited state.[10] In solution adenine exists as a mixture of 9 H and 7 H tautomers and as the 7 H tautomeric form in the crystalline state.[15] Among the different tautomers, 9 H is the dominant form in both aqueous solution and the gas phase.[8,10,15]

Mutations can be caused by deamination where a nucleobase converts to a base containing a keto group instead of the original amino group. The deamination of adenine produces hypoxanthine (HPX) which pairs with cytosine instead of thymine which, if not repaired by hypoxanthine-DNA glycosylase, results in a post-replicative A·T → G·C transition mutation. The deamination of nucleobases has been investigated extensively.[17–31] Deamination events at adenine residues occur slowly in DNA[17,18] and the rate of deamination is known to increase in the presence of various reagents such as NO,[19] HNO_2,[20] and bisulfite.[3,21] The rate constant for deamination of adenine in single-stranded DNA is $4 \times 10^{-8} s^{-1}$ at pH=7.6 and 110°C.[17] Under the same conditions the rate of deamination of cytosine to uracil is 40 times faster.[22]

Karan et al. proposed that “adenine deamination is one of several forms of hydrolytic damage that may occur as spontaneous premutagenic lesions in DNA in vivo”.[17] Barlow et al.[18] investigated the hydrolytic deamination of 1-(2-hydroxy-1-phenylethyl) adenosine in [^{18}O] water and analyzed the reaction products by electrospray mass spectroscopy. They found that deamination takes place by direct attack of H_2O on C6 of adenine with displacement of the exocyclic amino group.

The hydrolytic deamination of adenine has been studied at the B3LYP/6-31G(d,p) level by Zhang et al.[24] They found that the reaction of adenine with H_2O is very slow both in gas phase and in water. Their accepted mechanism is that a tetrahedral intermediate is formed first, followed by hydrogen transfer from the hydroxyl group to the amino group. More recently, Wang et al.[25] employed B3LYP/6-311G(d,p) to study the proton-catalyzed hydrolytic deamination of adenine. Four pathways initiated from four different protonation sites of adenine have been investigated in their study. They have found that the preferred pathway is for the N1-protonated adenine. In this pathway, nucleophilic attack results in a tetrahedral intermediate, followed by a water mediated transfer of a hydrogen atom to the amino group. Their reported activation energy is 140 kJ mol^{-1}.

No computational studies of the deamination reaction of adenine with OH^- have been reported. This chapter provides a detailed computational study of the deamination reaction of adenine with OH^-/nH_2O, (n = 0, 1, 2, 3) and $3\,H_2O$. Our previous studies on deamination of formamidine,[26] cytosine,[28,29] guanine,[31] and 8-oxoguanine[32] were useful for this work. One of the main aims of this study is to determine the most likely mechanism for the deamination reaction of adenine with OH^-/nH_2O. In order to achieve this goal, the effect of explicit H_2O molecules on the mechanism and energetics has been explored for four different pathways. In addition, we explored the role of solvent using the polarized continuum model (PCM). Our group has recently found that the overall activation energy for the deamination of cytosine with $3\,H_2O$ is in excellent agreement with the experimental value.[33] For this reason, the deamination of adenine with $3\,H_2O$ has also been investigated.

6.2 Computational Methodology

The Gaussian 09[34] package was used to perform all the computations. The geometries of all reactants, transition states, intermediates, and products were fully optimized at the HF/6-31G(d), B3LYP/6-31G(d), B3LYP/6-31+G(d), and MP2/6-31G(d) levels of theory. Thermodynamic properties (ΔE, ΔH, and ΔG), activation energies, enthalpies, and Gibbs energies of activation were calculated for each reaction pathway at the G3MP2B3[35] and CBS-QB3[36] levels. G4MP2[37] and G3B3[38] calculations were also performed for the deamination with OH^- (pathway A). These Gaussian-n theories agree within 8 kJ mol^{-1} (see Tables 6.1 and 6.2), which is within the reported error of the Gaussian-n theories. All structures for the deamination with $OH^-/3\,H_2O$ and $3\,H_2O$ were further calculated at G3MP2B3 level using the polarizable continuum model (PCM).[39] Intrinsic reaction coordinate (IRC) analysis was performed to ensure that each transition state is connected to the appropriate minima (reactant, product or intermediate). The last IRC structures in both directions were then further optimized. Frequency calculations were performed to confirm whether the structures are minima with all real frequencies or transition states with only one imaginary frequency.

6.3 Results and Discussion

Only one adenine tautomer (9H) has been considered in this study due to its dominance in both aqueous solution and the gas phase. The deamination reaction of adenine with OH^-/nH_2O, (n = 0, 1, 2, 3) and $3\,H_2O$ are shown in Figure 6.2. For the deamination of adenine with OH^-/nH_2O, the hypoxanthine anion (HPX^-) is the favored product (compared to OH^- or NH_2^-) due to significant negative charge delocalization in the purine ring. Figure 6.3 outlines the four pathways denoted as pathways A

⟶ D for the deamination of adenine with OH^-/nH_2O, for n=0, 1, 2, 3, respectively. Figure 6.4 outlines pathway E for the deamination of adenine with $3\,H_2O$. Since the N10-C6-N1-C2 side of adenine is normally hydrogen bonded to thymine or uracil, H_2O molecules have been added to the N10-C6-C5-N7 side of adenine to generate possible hydrogen-bonded complexes with H_2O molecules.

The activation energies and Gibbs energies of activation for the deamination of adenine at the different levels of theory for all pathways are given in Tables 6.1 to 6.5. Thermodynamic properties for the deamination reaction of adenine at the different levels of theory are listed in Table 6.6. The geometries and relative energies for the reactant, intermediates, transition states, and product involved in all pathways are shown in Figures 6.5 to 6.14. Unless otherwise stated, all values in the text are for the G3MP2B3 level of theory.

6.3.1 Pathway A: Deamination of Adenine with OH^-

The optimized structures and the relative energies for pathway A are shown in Figures 6.5 and 6.6, respectively and outlined schematically in Figure 6.3. The activation energies and Gibbs energies of activation computed at different levels of theory for pathway A are given in Table 6.1.

Initially, a deprotonation at the amino group of adenine leads to the formation of a highly resonance-stabilized adenine anion$-H_2O$ complex (**RA**), as shown in Figures 6.3, 6.5 and 6.6. We have not considered deprotonation at N9 since the sugar moiety binds at this position. Nucleophilic addition of H_2O to C6 with a simultaneous hydrogen transfer from H_2O to the imine nitrogen (**TS1A**) generates a tetrahedral intermediate (**IA**). This step is the rate-determining step. Finally, a hydrogen-transfer from the hydroxyl group to the amino group through the four-centered transition state (**TS2A**) results in a hydrogen-bonded complex of a hypoxanthine anion and ammonia (**PA**). **PA** is 35 kJ mol^{-1} more stable than the individual products. The mechanism for deamination of adenine is similar to that for the deamination of formamidine,[26] cytosine,[28,29] guanine,[31] and 8-oxoguanine[32] with OH^-. The activation energy of the rate-determining step is 190 kJ mol^{-1} compared to 148 and 155 kJ mol^{-1} for cytosine[28] and guanine,[31] respectively. The Gaussian-n values differ by no more than 9 kJ mol^{-1}, and the results of B3LYP are in good agreement with the Gaussian-n theories (see Table 6.1).

6.3.2 Pathways B $\longrightarrow$ D: Deamination of Adenine with OH^-/nH_2O (n=1, 2, 3)

The optimized structures for pathways B, C, and D are shown in Figures 6.7, 6.9, and 6.11, respectively. The relative energies for pathways B, C, and D are shown in Figures 6.8, 6.10, and 6.12, respectively. They are all outlined schematically in Figure 6.3. The activation energies and Gibbs energies of activation computed at different levels of theory for pathways B, C, and D are given in Tables 6.2, 6.3, and 6.4, respectively.

The deamination of adenine is initiated by deprotonation at the amino group of adenine to form complexes **RB**, **RC** and **RD** for pathways B, C, and D, respectively as shown in Figures 6.3, 6.7, 6.9, and 6.11. The next step in these pathways is similar to pathway A, where tetrahedral intermediates **IB**, **IC** and **ID** form via four-centered transition states **TS1B**, **TS1C** and **TS1D** with activation energies of 122, 111, and 105 kJ mol^{-1} for pathways B, C, and D, respectively. In the last step, the intermediates **IB** and **ID** convert to products **PB** and **PD** by single water mediated 1,3-hydrogen shifts from the hydroxyl group to the amine nitrogen atom via six-centered transition states **TS2B** and **TS2D** with activation energies of 88 and 68 kJ mol^{-1} for pathways B and D, respectively. Pathway C branches into two different pathways, C_A and C_B. For pathway C_A, deamination occurs by a 1,3-hydrogen shift assisted by single water molecule via a six-centered transition state (**TS2C$_A$**) with an activation energy of 65 kJ mol^{-1}. While for pathway C_B, deamination occurs by a 1,3-hydrogen shift assisted by two water molecules via an eight-centered transition state (**TS2C$_\mathbf{B}$**) with an activation energy of 73 kJ mol^{-1}. The three water-mediated transition state does not appear to exist and the deamination favors the single water-mediated mechanism.

The overall activation energies are 176, 163, 155, and 145 kJ mol^{-1} for pathways B, C_B, C_A, and D, respectively. Addition of water molecules decreased the overall activation energy for the deamination of adenine with OH^-, but the effect becomes smaller with each additional water molecule. This effect can be explained by considering the role of water molecules in the reaction. Water molecules can act not only as solvent but also as a catalyst to promote hydrogen transfer. The first water molecule has a major effect on the activation energy as it mediates the 1,3-hydrogen shift, while the effect of the second and third water molecules is significantly less as they simply act as solvent. Using PCM, the overall activation energy for pathway D is 139 kJ mol^{-1}, lower by only 6 kJ mol^{-1} compared with the result of the gas phase.

6.3.3 Pathway E: Deamination of Adenine with $3\,H_2O$

In order to determine if hydroxide ion is essential for the deamination of adenine we have investigated a mechanism with $3\,H_2O$, pathway E. The optimized structures and the relative energies for pathway E are shown in Figures 6.13 and 6.14, respectively. Pathway E is outlined schematically in Figure 6.4. The activation energies and Gibbs energies of activation computed at different levels of theory for pathway E are given in Table 6.5.

Pathway E is a three-step reaction mechanism. In the first step, a hydrogen-bonded complex of the amine 9H-tautomer of adenine (**RE**) forms the imine tautomer of adenine (**I1E**) via transition state (**TS1E**) as shown in Figures 6.4 and 6.13. The gas-phase activation energy for this step is 77 kJ mol^{-1}, which is higher compared to that found for cytosine (72.6 kJ mol^{-1})[28] and lower compared to that found for guanine

(85 kJ mol^{-1}).[31] This gas-phase activation energy is lowered by 3 kJ mol^{-1} using the PCM solvation model. In the second step, which is rate-determining, nucleophilic addition of a water molecule to C6 and simultaneous hydrogen transfer from H_2O to the exocyclic imine nitrogen results in the formation of a tetrahedral intermediate (**I2E**) via transition state (**TS2E**). Finally, the hypoxanthine-ammonia-water complex (**PE**) is formed via the six-centered transition state (**TS3E**), which involves a 1,3-hydrogen transfer of the hydroxyl hydrogen to the amino group. We should note that for **TS3E**, we have also investigated a 1,3-hydrogen shift mediated by two and three water molecules. Our calculations have revealed that the single water-mediated transition state is more energetically favored than the two water-mediated transition state, while the three water-mediated mechanism does not appear to exist for **TS3F**. This finding agrees with our previous work on the 1,3-hydrogen shift in formamidine decomposition.[40]

The gas-phase activation energies are 85 kJ mol^{-1} and 70 kJ mol^{-1} for the rate-determining and final steps, respectively, resulting in an overall gas-phase activation energy of 139 kJ mol^{-1}. The predicted overall gas-phase activation energy is higher by 2 kJ mol^{-1} while the gas-phase activation energy for rate-determining step is lower by 15 kJ mol^{-1} compared with the results using PCM. The overall activation energies at CBS-QB3, B3LYP/6-31G(d) and B3LYP/6-31+G(d) are in excellent agreement with the G3MP2B3 value, differing by no more than 3 kJ mol^{-1}.

6.4 Thermodynamic Properties for the Deamination Reaction of Adenine

The thermodynamic properties for the deamination of adenine with OH^-/nH_2O, (n = 0, 1, 2, 3) and $3\,H_2O$ are listed in Table 6.6. The deamination reactions of adenine with OH^-/nH_2O, (n = 0, 1, 2, 3) are exothermic and exergonic at all levels of theory for the separated species or for complex to complex in all pathways. This is in contrast to the deamination of adenine with $3\,H_2O$ which is endothermic and endergonic at G3MP2B3 and CBS-QB3 levels. The B3LYP/6-31+G(d) results are in better agreement with G3MP2B3 results than HF, B3LYP, and MP2 using the 6-31G(d) basis set. As shown in Table 6.6, the addition of diffuse functions is important.

6.5 Conclusion

The deamination of adenine with OH^-/nH_2O, (n = 0, 1, 2, 3) and $3\,H_2O$ has been studied using ab initio calculations. Five pathways have been investigated in order to obtain the most plausible mechanism for the deamination reaction of adenine. The deprotonation of adenine by OH^- is a very exothermic process due to the formation of a highly resonance-stabilized anion. Adding water molecules decreased the overall activation energy for the deamination reaction of adenine with OH^-, but the effect becomes smaller with each additional water molecule. Our results support the single water-mediated transition state mechanism rather than two water-mediated mechanism. The overall activation energy for the deamination of adenine with $OH^-/3\,H_2O$, pathway **D**, is 145 kJ mol^{-1} in the gas phase and 139 kJ mol^{-1} with PCM. The most plausible mechanism is the deamination of adenine with $3\,H_2O$, pathway **E**, that is initiated by tautomerization of adenine, followed by formation of a tetrahedral intermediate which dissociates to products via a 1,3-hydrogen shift. The overall activation energy of pathway **E** is lower than that for pathway **D** by 6 and 2 kJ mol^{-1} for gas phase and PCM, respectively. The use of PCM does not significantly affect the mechanism or the activation energy compared to the gas phase. The B3LYP results are in better agreement with G3MP2B3 results than HF, and MP2.

6.6 Acknowledgement

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6.7 Supporting Information Available

Full geometries and energies of all structures for all pathways investigated at all levels of theory discussed in the present paper. This information is available free of charge via the internet at http://pubs.acs.org.

Table 6.1: Activation energies and Gibbs energies of activation (kJ mol^{-1}) at 298.15 K for deamination of adenine with OH^- (pathway A).

	TS1A		TS2A		Overall
Theory/Basis Set	E_a	$\Delta G^{\#}$	E_a	$\Delta G^{\#}$	E_a
HF/6-31G(d)	213	219	141	139	250
B3LPY/6-31G(d)	187	193	92	90	203
B3LYP/6-31+G(d)	183	186	89	88	201
MP2/6-31G(d)	201	208	123	121	223
G3MP2B3	190	194	108	107	206
G4MP2	189	197	112	112	207
G3B3	187	191	108	107	206
CBS-QB3	196	199	111	109	208

Table 6.2: Activation energies and Gibbs energies of activation (kJ mol^{-1}) at 298.15 K for deamination of adenine with OH^-/H_2O (pathway B).

	TS1B		TS2B		Overall
Theory/Basis Set	E_a	$\Delta G^{\#}$	E_a	$\Delta G^{\#}$	E_a
HF/6-31G(d)	168	180	126	132	228
B3LYP/6-31G(d)	122	126	71	74	171
B3LYP/6-31+G(d)	121	132	65	71	167
MP2/6-31G(d)	136	149	97	99	183
G3MP2B3	122	134	88	92	176
CBS-QB3	121	129	90	91	177

Table 6.3: Activation energies and Gibbs energies of activation (kJ mol^{-1}) at 298.15 K for deamination of adenine with $OH^-/2\,H_2O$ (pathway C).

	TS1C		TS2C$_A$		TS2C$_B$		Overall ΔE$_a$	
Theory/Basis Set	E$_a$	ΔG$^\#$	E$_a$	ΔG$^\#$	E$_a$	ΔG$^\#$	C$_A$	C$_B$
HF/6-31G(d)	149	158	108	112	116	124	212	219
B3LYP/6-31G(d)	117	125	64	68	65	71	156	170
B3LYP/6-31+G(d)	115	120	51	55	59	65	152	160
MP2/6-31G(d)	130	138	81	84	83	87	179	180
G3MP2B3	111	124	65	76	73	79	155	163
CBS-QB3	116	125	60	67	65	72	161	167

Table 6.4: Activation energies and Gibbs energies of activation (kJ mol^{-1}) at 298.15 K for deamination of adenine with $OH^-/3\,H_2O$ (pathway D).

	TS1D		TS2D		Overall
Theory/Basis Set	E$_a$	ΔG$^\#$	E$_a$	ΔG$^\#$	E$_a$
HF/6-31G(d)	132	143	107	110	194
B3LYP/6-31G(d)	109	124	61	64	145
B3LYP/6-31+G(d)	111	113	52	54	141
MP2/6-31G(d)	113	130	67	74	150
G3MP2B3	105	120	68	71	145
CBS-QB3	101	114	68	71	140
G3MP2B3 (PCM)	110	121	58	59	139

Table 6.5: Activation energies and Gibbs energies of activation (kJ mol^{-1}) at 298.15 K for deamination of adenine with $3\,H_2O$ (pathway E).

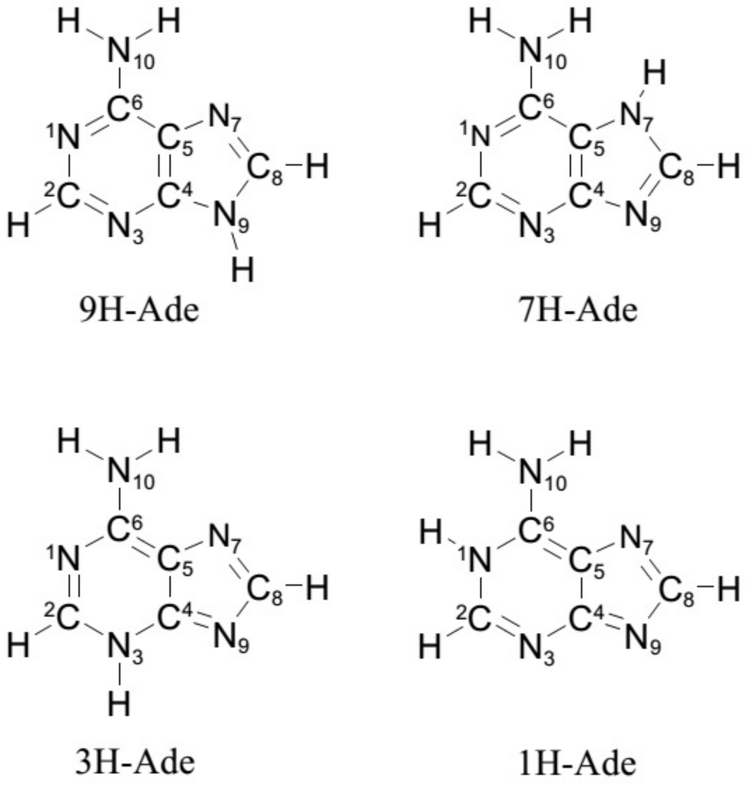
	TS1E		TS2E		TS3E		Overall
	E$_a$	ΔG$^\#$	E$_a$	ΔG$^\#$	E$_a$	ΔG$^\#$	E$_a$
HF/6-31G(d)	133	142	145	164	116	127	197
B3LYP/6-31G(d)	76	84	83	101	50	59	137
B3LYP/6-31+G(d)	74	85	87	101	53	62	136
G3MP2B3	77	95	85	105	70	79	139
CBS-QB3	75	83	97	115	69	77	141
G3MP2B3 (PCM)	74	84	100	118	46	60	137

Table 6.6: Thermodynamic properties (kJ mol^{-1}) at 298.15 K for deamination of adenine with OH^-/nH_2O and $3\,H_2O$ (all pathways).

	HF/ 6-31G(d)	B3LYP/ 6-31G(d)	B3LYP/ 631+G(d)	G3MP2B3	CBS-QB3
Ad + OH^- → HPX^- + NH_3					
ΔH	-302	-332	-208	-204	-204
ΔG	-306	-336	-211	-208	-208
Ad + $3H_2O$ → HPX + NH_3 + $2H_2O$					
ΔH	-4	-14	-3	17	16
ΔG	-3	-14	-1	18	18
RA → PA[a]					
ΔH	-50	-41	-28	-9	-13
ΔG	-59	-49	-39	-17	-21
RB → PB[a]					
ΔH	-57	-43	-38	-22	-24
ΔG	-68	-54	-49	-33	-35
RC → PC[a]					
ΔH	-54	-34	-24	-12	-10
ΔG	-67	-45	-39	-18	-15
RD → PD[a]					
ΔH	-65	-33	-40	-22	-19
ΔG	-77	-43	-56	-33	-31
RE → PE[b]					
ΔH	-26	-23	-21	-1	-1
ΔG	-29	-28	-26	-9	-7

[a] Structures of these complexes are shown in Figure 6.3.

[b] Structures of these complexes are shown in Figure 6.4.



9H-Ade 7H-Ade

3H-Ade 1H-Ade

Figure 6.1: Structures and atom numbering for adenine tautomers.

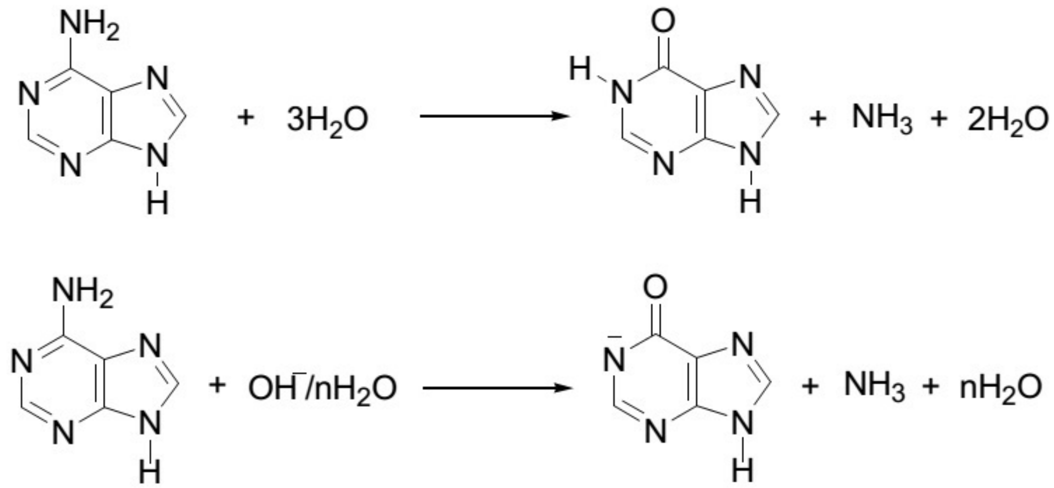


Figure 6.2: Deamination of adenine with OH^-/nH_2O and $3\,H_2O$.

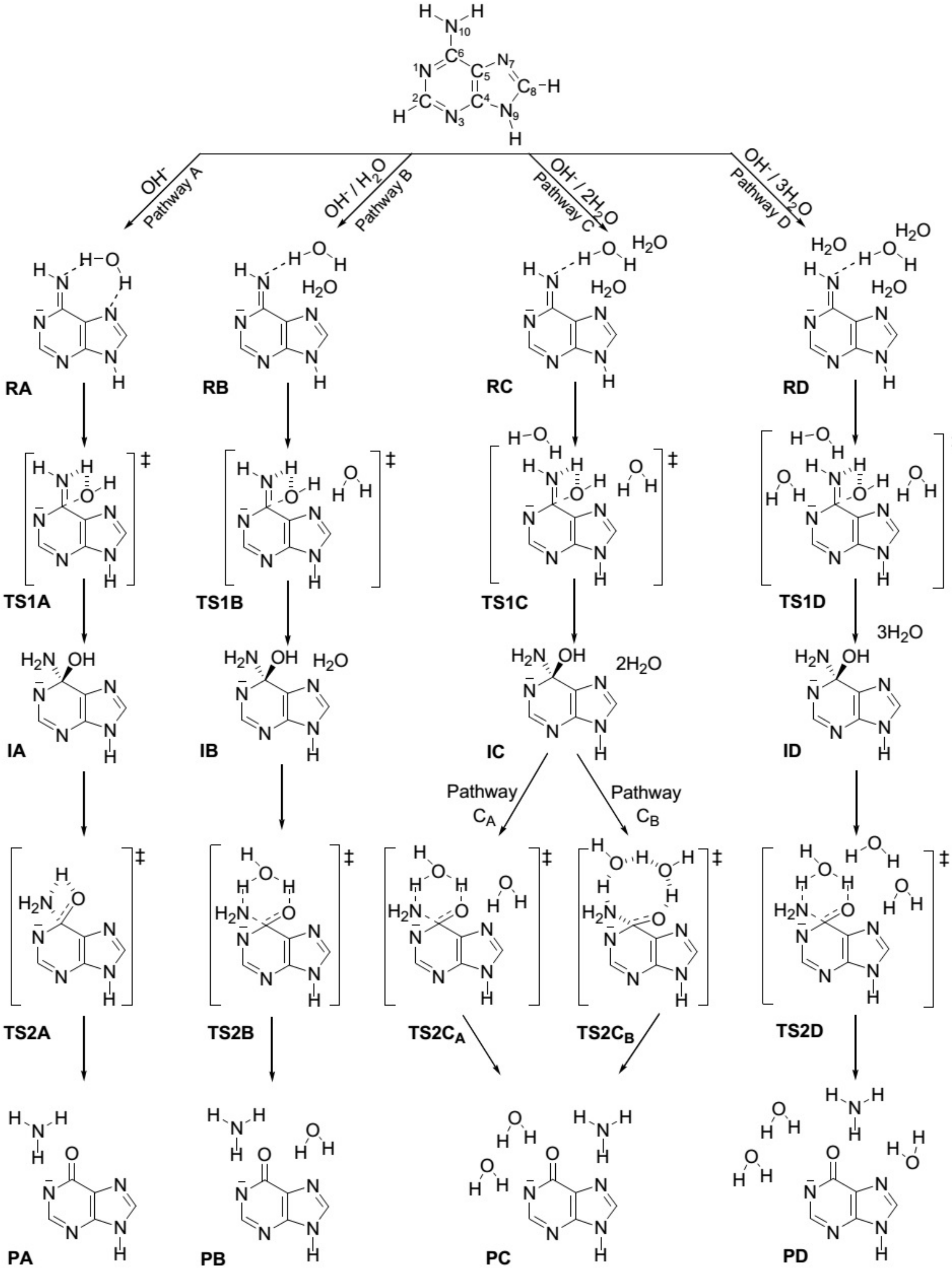


Figure 6.3: Schematic outline of pathways A, B, C, and D for the deamination of adenine with OH^-/nH_2O, (n = 0, 1, 2, 3).

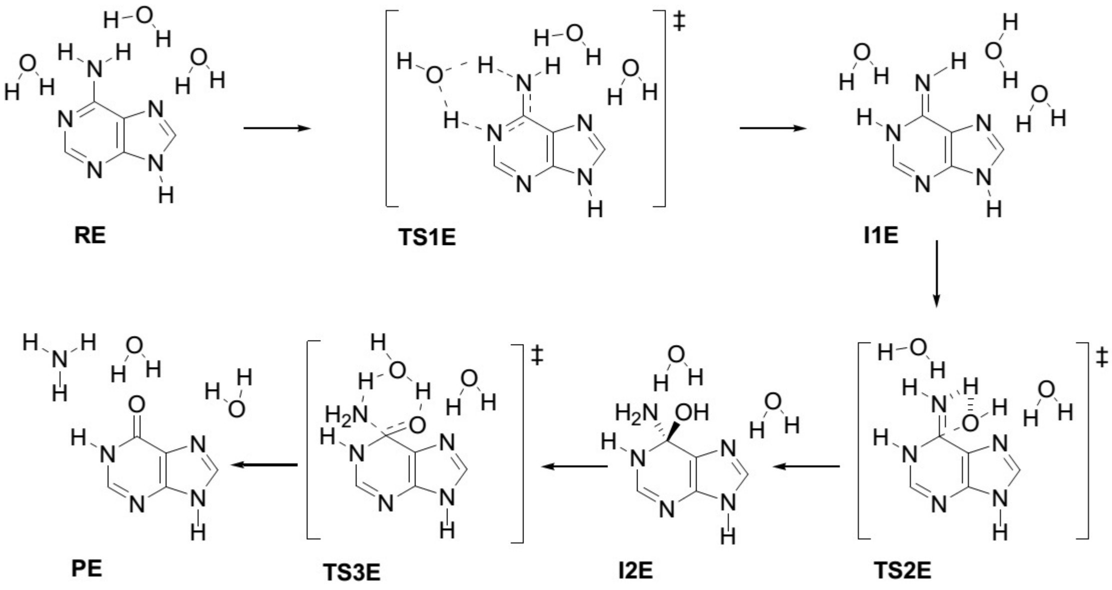


Figure 6.4: Schematic outline of pathway E for the deamination of adenine with 3 H_2O.

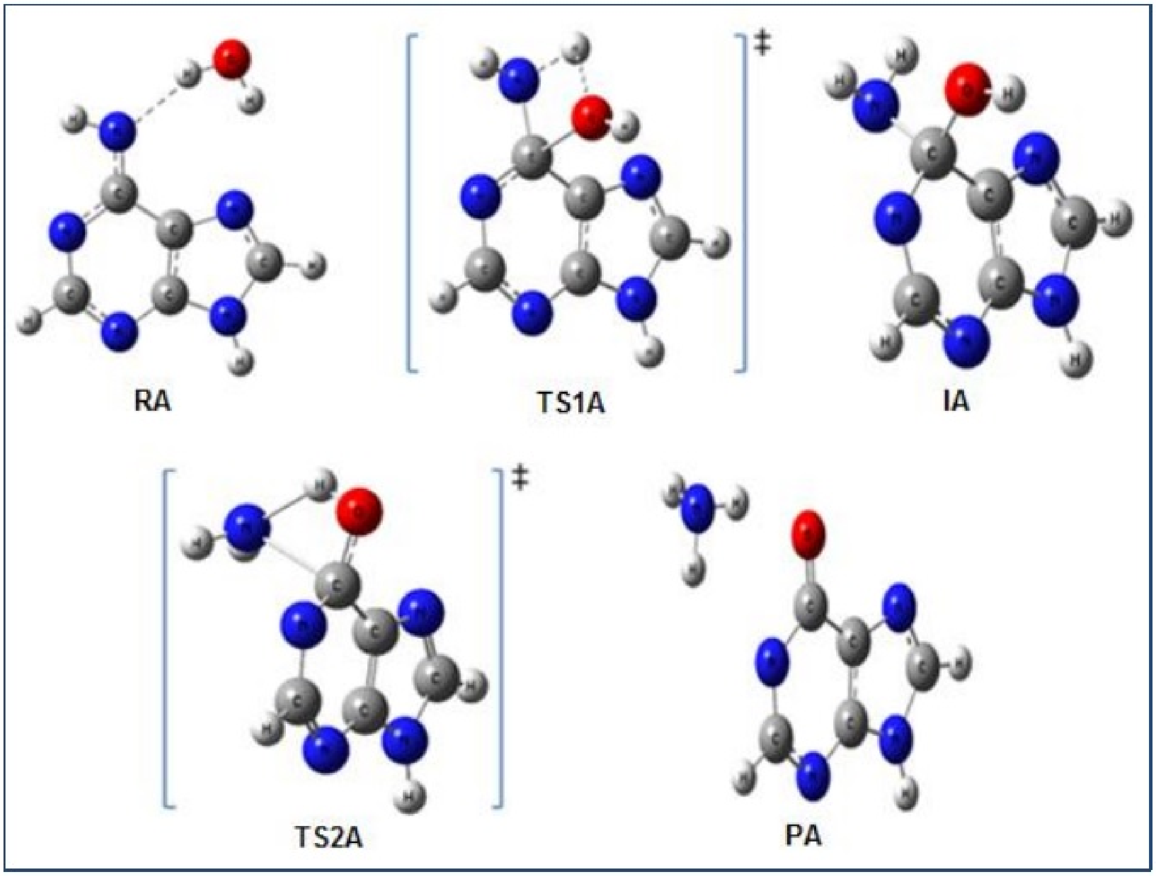


Figure 6.5: Optimized geometries along pathway A for the deamination of adenine with OH^- at HF/6-31G(d) level of theory.

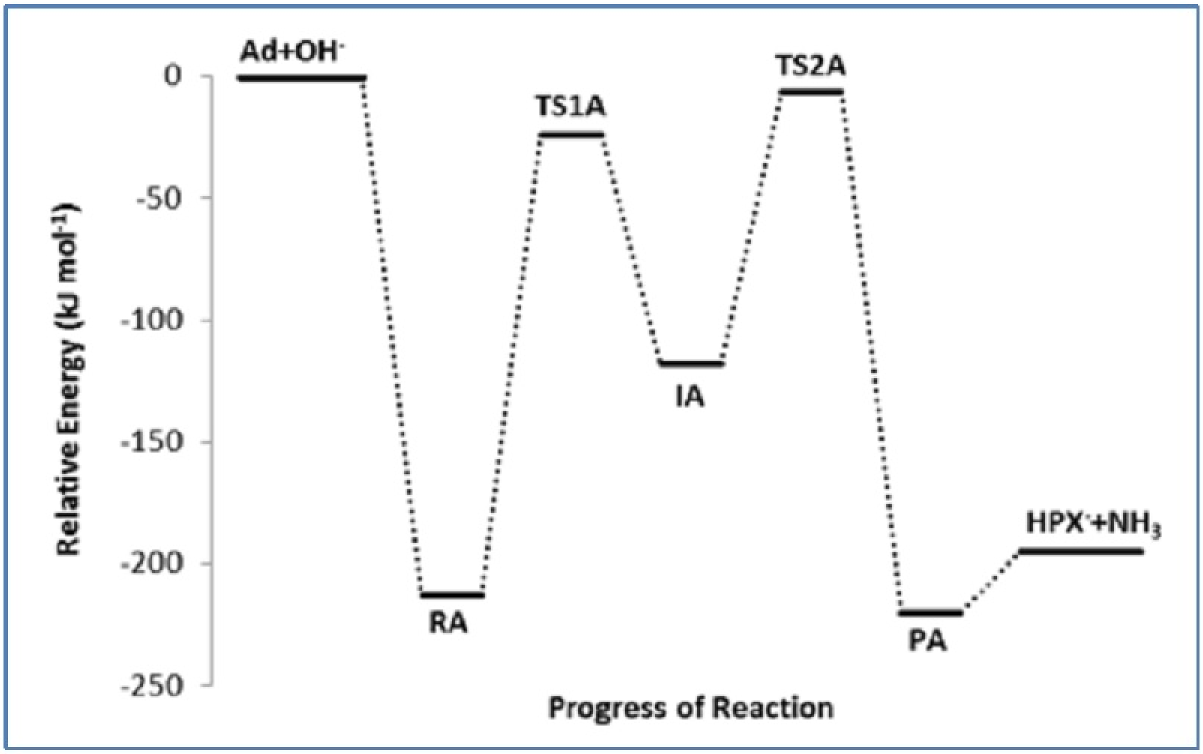


Figure 6.6: Pathway A for the deamination of adenine with OH^-. Relative energies at G3MP2B3 level of theory in the gas phase.

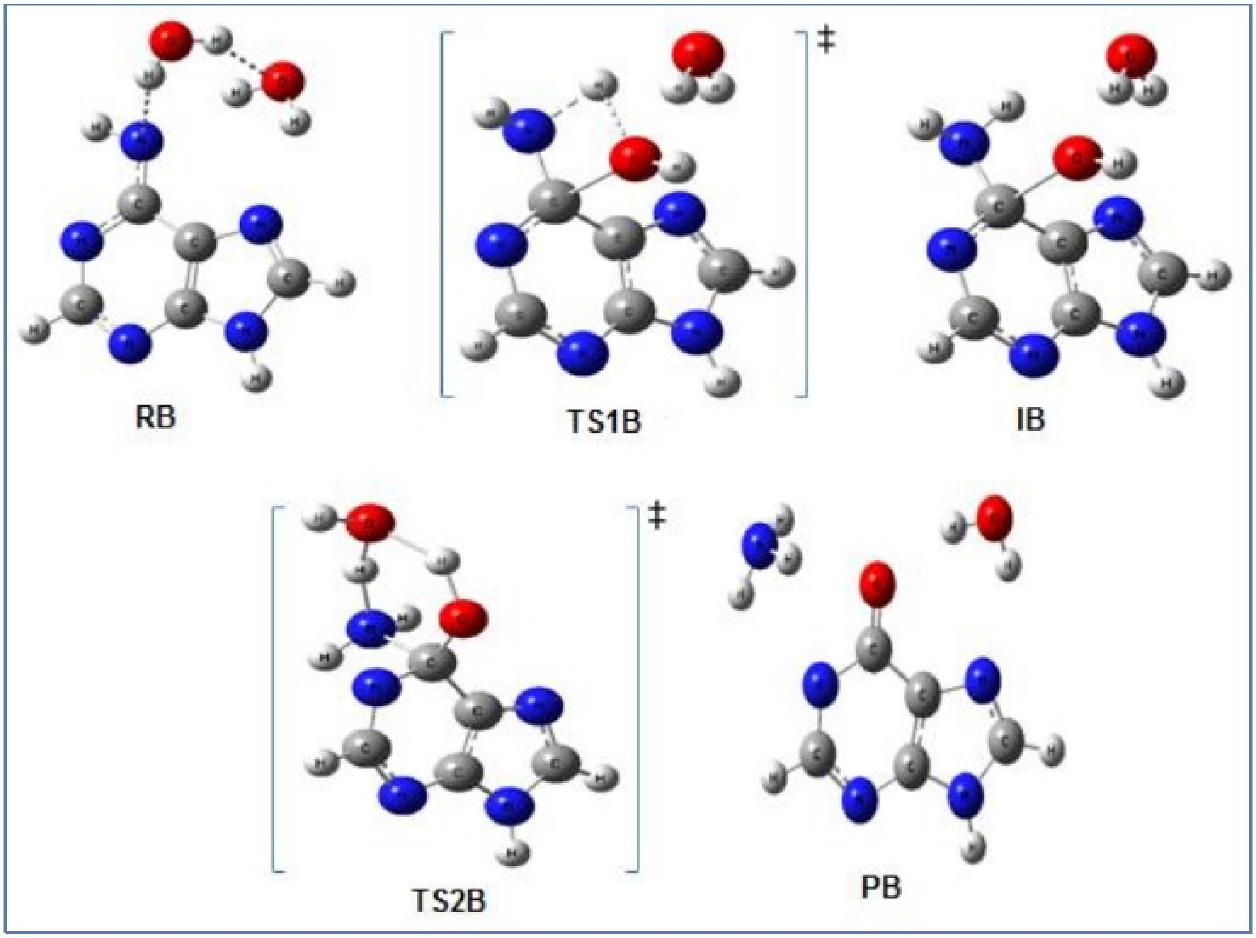


Figure 6.7: Optimized geometries along pathway B for the deamination of adenine with OH^-/H_2O at HF/6-31G(d) level of theory.

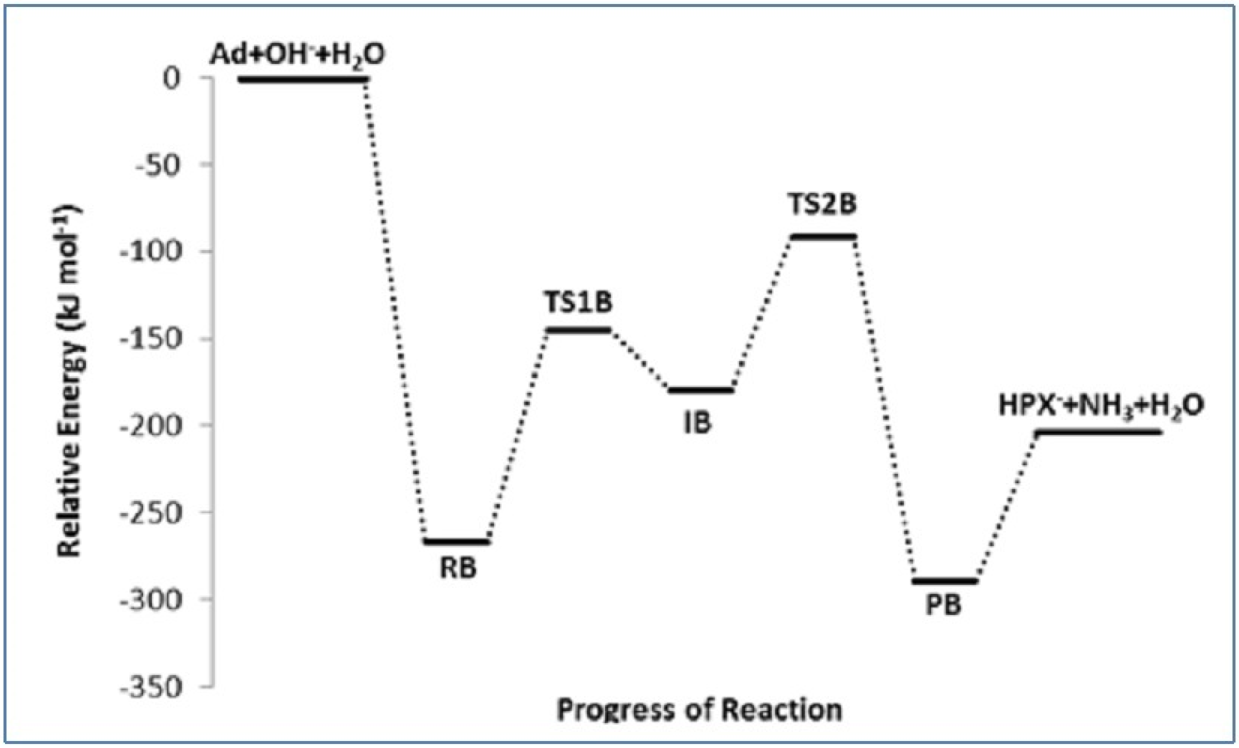


Figure 6.8: Pathway B for the deamination of adenine with OH^-/H_2O. Relative energies at G3MP2B3 level of theory in the gas phase.

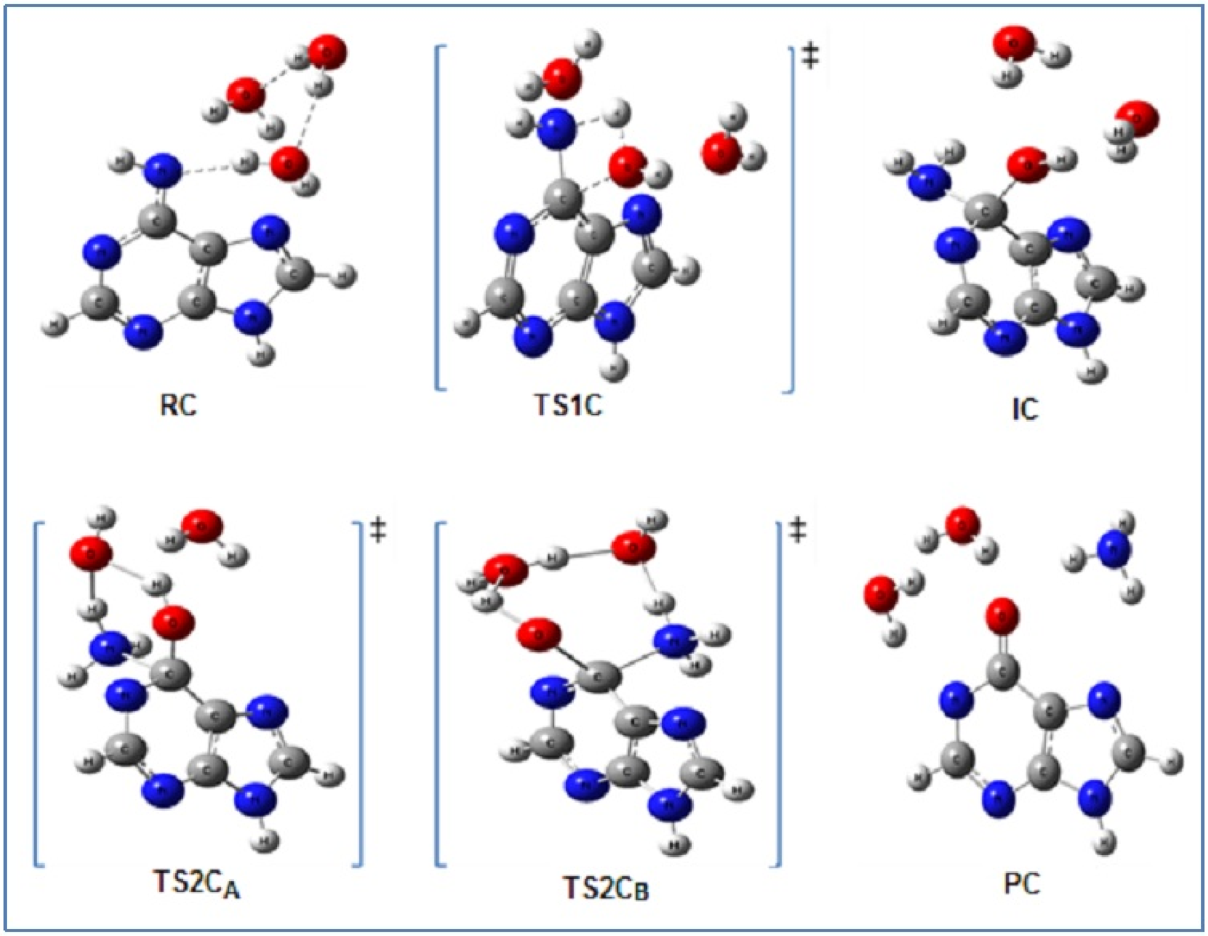


Figure 6.9: Optimized geometries along pathway C for the deamination of adenine with $OH^-/2\,H_2O$ at HF/6-31G(d) level of theory.

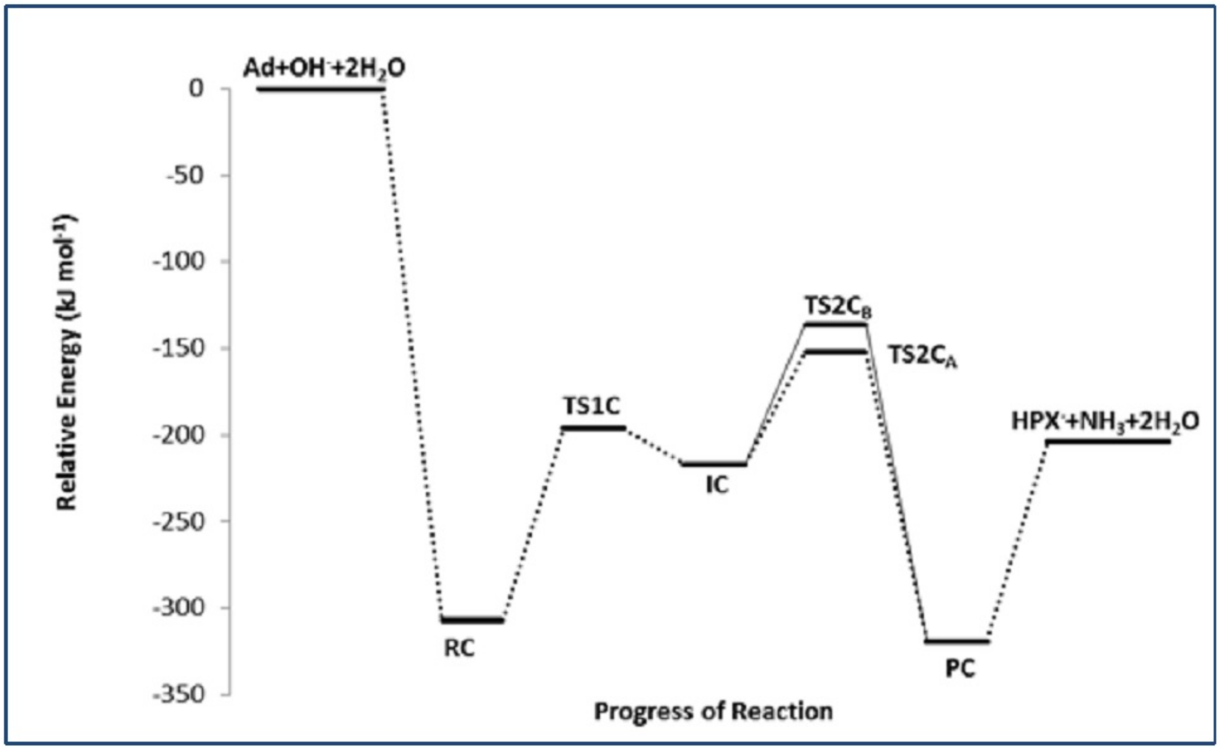


Figure 6.10: Pathway C for the deamination of adenine with $OH^-/2\,H_2O$. Relative energies at G3MP2B3 level of theory in the gas phase.

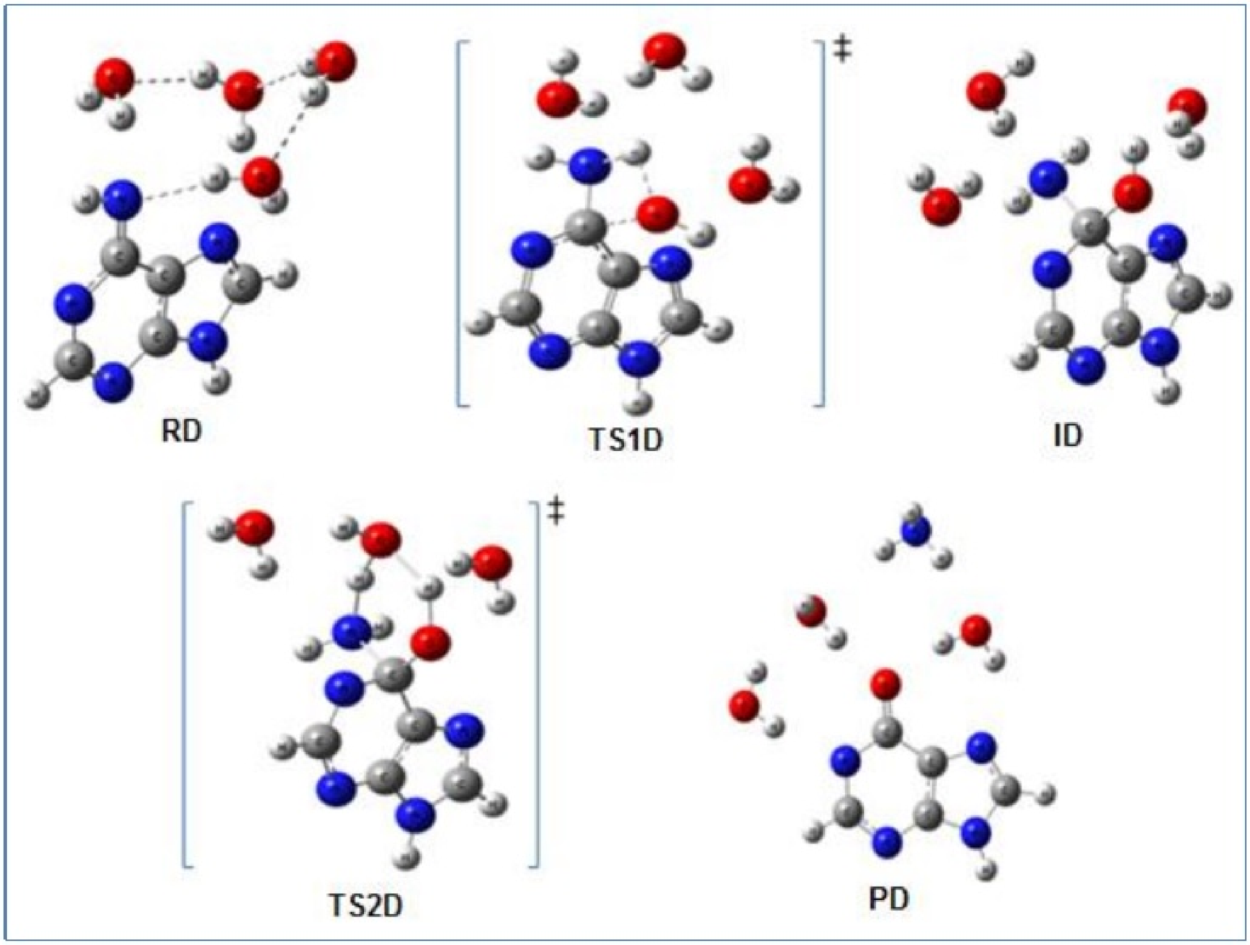


Figure 6.11: Optimized geometries along pathway D for the deamination of adenine with $OH^-/3\,H_2O$ at HF/6-31G(d) level of theory.

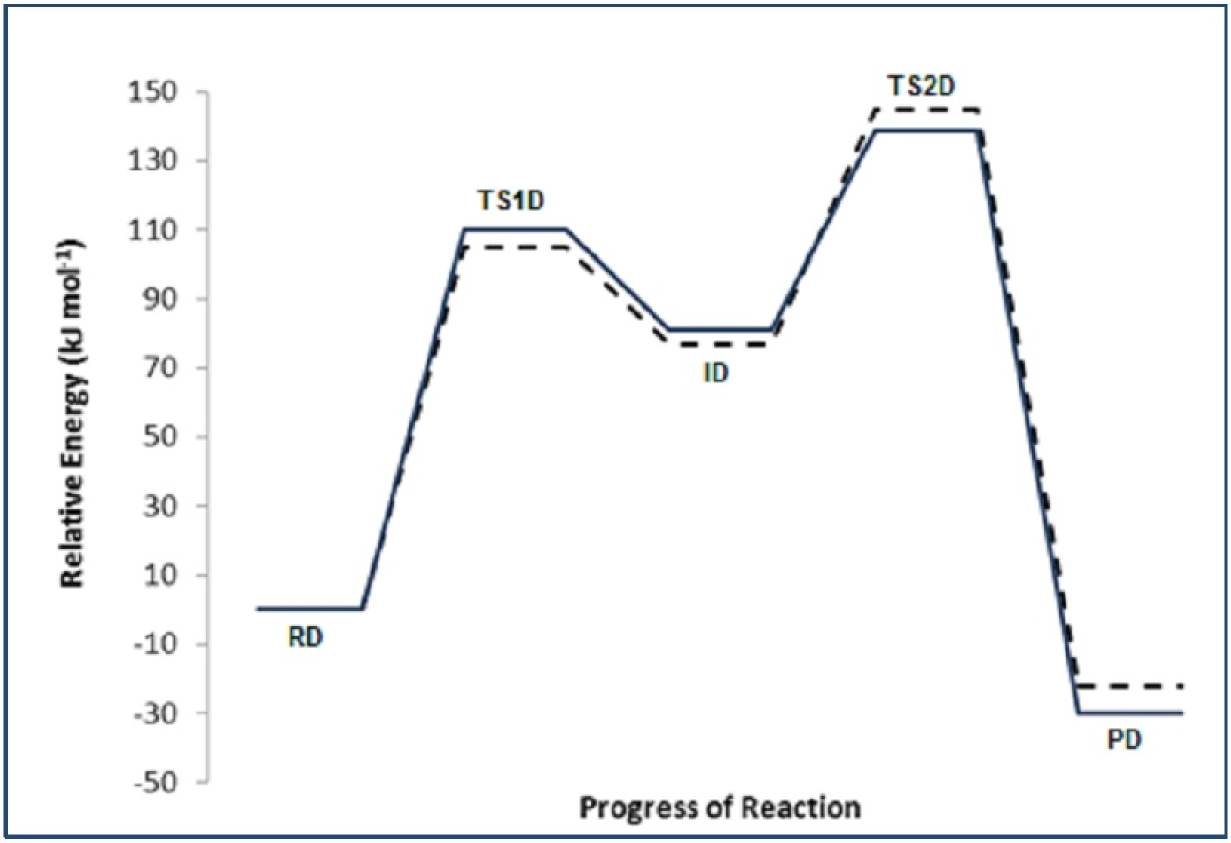


Figure 6.12: Pathway D for the adenine deamination with $OH^-/3\,H_2O$ for the gas phase (dashed line), PCM (solid line). Relative energies at G3MP2B3 level of theory.

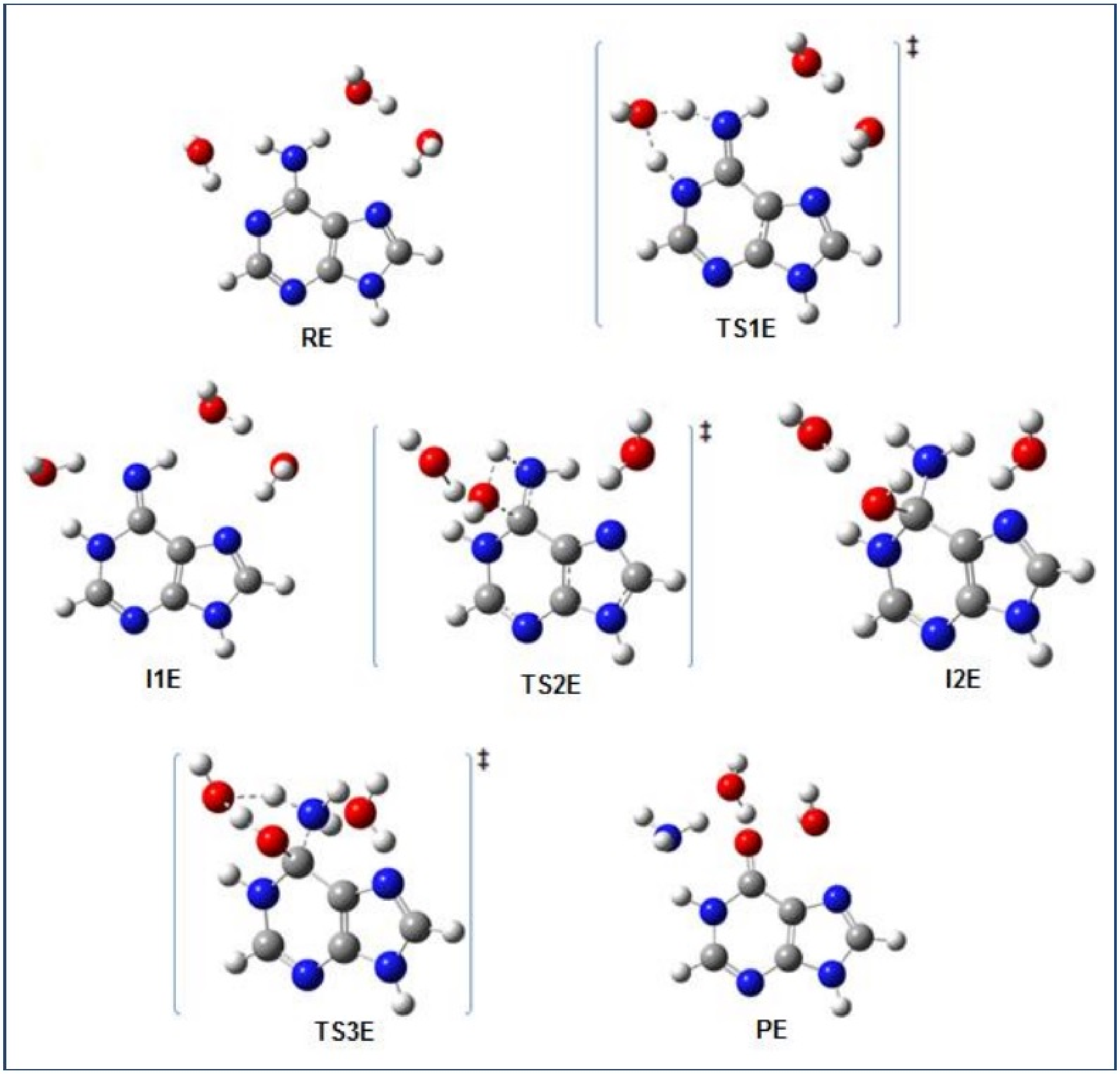


Figure 6.13: Optimized geometries along pathway E for the deamination of adenine with $3\,H_2O$ at B3LYP/6-31G(d) level of theory.

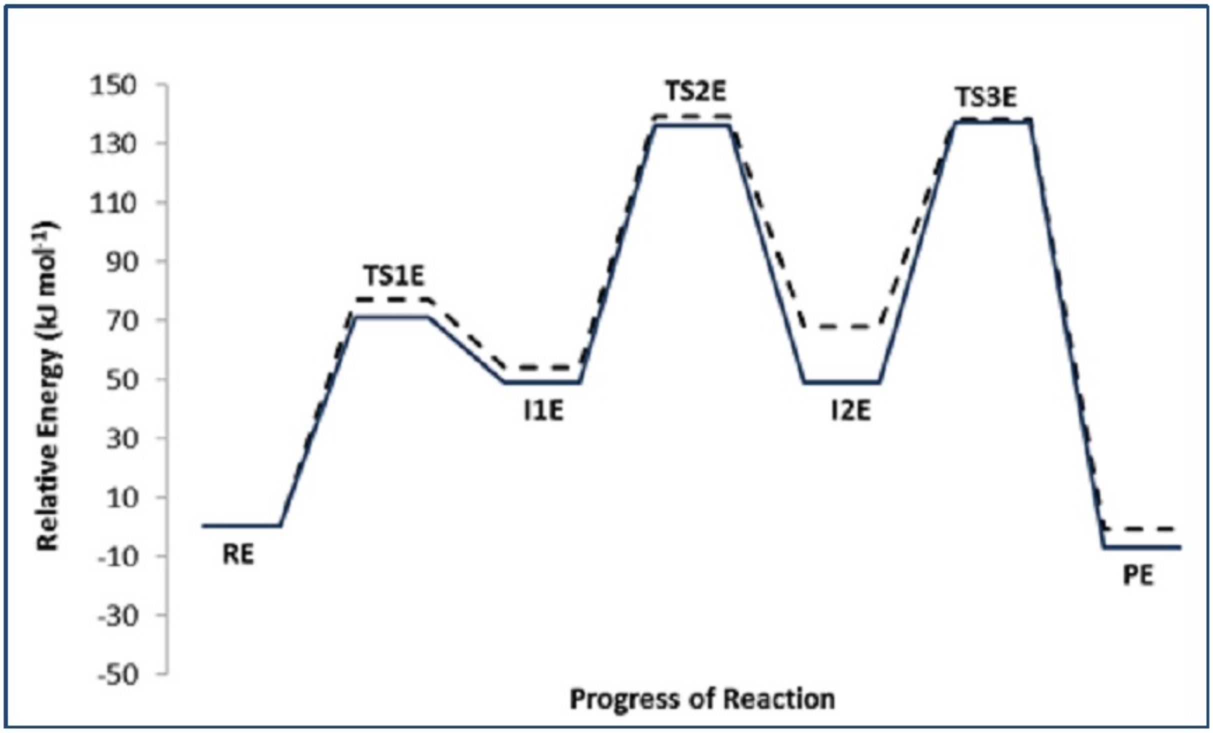


Figure 6.14: Pathway E for the adenine deamination with 3 H_2O for the gas phase (dashed line), PCM (solid line). Relative energies at G3MP2B3 level of theory.

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Appendix A

Integral of Gaussian Functions

In molecular calculations, MOs or AOs are expanded as linear combinations of basis functions φ_μ, whereas basis functions are constructed as linear combinations of P primitive Gaussian functions. The following is an example for basis functions constructed from $1s$ primitive Gaussians,[1]

$$\varphi_\mu(\mathbf{r}_1) = \sum_{p=1}^{P} d_{p\mu} \left(\frac{2\alpha_{p\mu}}{\pi}\right)^{3/4} e^{-\alpha_{p\mu}|\mathbf{r}_1 - \mathbf{R}_\mu|^2} \tag{A.1}$$

where, $\mathbf{r}_1$ is the coordinates of electron one, $\mathbf{R}_\mu$ is the point where φ_μ is centered, $d_{p\mu}$ and $\alpha_{p\mu}$ are the contraction coefficients and the exponents, respectively, that are defined for a given basis set. The computational advantage of using Gaussian functions is that the product of two Gaussian functions is another Gaussian. This appendix contains the formulae needed for evaluating overlap, kinetic energy, nuclear-electron attraction, and two-electron repulsion integrals over basis functions that use $1s$ primitive Gaussian functions.

Overlap Integral

The elements of the overlap integral over basis functions that use 1s primitive Gaussians can be evaluated as follows,[1]

$$\begin{aligned} S_{\mu\nu} &= \int \varphi_\mu^*(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)d\mathbf{r}_1 \\ &= \sum_{p=1}^{P}\sum_{q=1}^{Q} d_{p\mu}d_{q\nu}\left(\frac{\pi}{\alpha_{p\mu}+\alpha_{q\nu}}\right)^{3/2} e^{-\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}}R_{\mu\nu}^2} \end{aligned} \tag{A.2}$$

where $R_{\mu\nu}$ is the distance between the two points where the φ_μ and φ_ν are centered.

Kinetic Energy Integral

The elements of the kinetic energy integral over basis functions that use 1s primitive Gaussians can be evaluated as,[1]

$$\begin{aligned} T_{\mu\nu} &= -\frac{1}{2}\int \varphi_\mu^*(\mathbf{r}_1)\nabla_1^2\varphi_\nu(\mathbf{r}_1)d\mathbf{r}_1 \\ &= \sum_{p=1}^{P}\sum_{q=1}^{Q} d_{p\mu}d_{q\nu}\left(\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}}\right)\left(3-\frac{2\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}}R_{\mu\nu}^2\right)\left(\frac{\pi}{\alpha_{p\mu}+\alpha_{q\nu}}\right)^{3/2} e^{-\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}}R_{\mu\nu}^2} \end{aligned} \tag{A.3}$$

Nuclear-Electron Attraction Integral

The elements of the nuclear-electron attraction integral over basis functions that use 1s primitive Gaussians can be evaluated as follows,[1]

$$\begin{aligned} V_{\mu\nu} &= -\sum_{A=1}^{M} Z_A \int \frac{\varphi_\mu^*(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)}{r_{1A}}d\mathbf{r}_1 \\ &= -\sum_{A=1}^{M}\sum_{p=1}^{P}\sum_{q=1}^{Q} d_{p\mu}d_{q\nu}\left(\frac{\pi Z_A}{\alpha_{p\mu}+\alpha_{q\nu}}\right) e^{-\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}}R_{\mu\nu}^2}\left(\frac{\pi}{\left(\alpha_{p\mu}+\alpha_{q\nu}\right)R_{\mu\rho}^2}\right)^{1/2} erf\left(R_{\mu\rho}\sqrt{\alpha_{p\mu}+\alpha_{q\nu}}\right) \end{aligned} \tag{A.4}$$

where, Z_A is the charge of nucleus A, "erf" is the error function, and $\mathbf{R}_{\mu p}$ is the distance between the point where the φ_μ is centered and the center ρ which is defined by

$$\mathbf{R}_\rho = \frac{\alpha_{p\mu}\mathbf{R}_\mu + \alpha_{q\nu}\mathbf{R}_\nu}{\alpha_{p\mu} + \alpha_{q\nu}} \tag{A.5}$$

Two-Electron Repulsion Integral

The elements of the two-electron repulsion integral over basis functions that use $1s$ primitive Gaussians can be evaluated as follows,[1]

$$\begin{aligned}(\mu\nu|\sigma\lambda) &= \int\int \frac{\varphi_\mu^*(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1)\varphi_\mu^*(\mathbf{r}_2)\varphi_\nu(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \sum_{p=1}^{P}\sum_{q=1}^{Q}\sum_{r=1}^{R}\sum_{s=1}^{S} \Bigg\{ d_{p\mu}d_{q\nu}d_{r\sigma}d_{s\lambda} \frac{\pi^{5/3}}{\left(\alpha_{p\mu}+\alpha_{q\nu}\right)\left(\alpha_{r\sigma}+\alpha_{s\lambda}\right)\sqrt{\alpha_{p\mu}+\alpha_{q\nu}+\alpha_{r\sigma}+\alpha_{s\lambda}}} \\ &\qquad \times \left(e^{-\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}}R_{\mu\nu}^2-\frac{\alpha_{r\sigma}\alpha_{s\lambda}}{\alpha_{r\sigma}+\alpha_{s\lambda}}R_{\sigma\lambda}^2}\right) R_{\rho\theta} \sqrt{\frac{\pi\left(\alpha_{p\mu}+\alpha_{q\nu}+\alpha_{r\sigma}+\alpha_{s\lambda}\right)}{\left(\alpha_{p\mu}+\alpha_{q\nu}\right)\left(\alpha_{r\sigma}+\alpha_{s\lambda}\right)}} \\ &\qquad \times erf\left(R_{\rho\theta}\sqrt{\frac{\left(\alpha_{p\mu}+\alpha_{q\nu}\right)\left(\alpha_{r\sigma}+\alpha_{s\lambda}\right)}{\left(\alpha_{p\mu}+\alpha_{q\nu}+\alpha_{r\sigma}+\alpha_{s\lambda}\right)}}\right)\Bigg\}\end{aligned} \tag{A.6}$$

where $\mathbf{R}_{\rho\theta}$ is the distance between the point $\mathbf{R}_\rho$ and the point $\mathbf{R}_\theta$ which is defined by

$$\mathbf{R}_\theta = \frac{\alpha_{r\sigma}\mathbf{R}_\sigma + \alpha_{s\lambda}\mathbf{R}_\lambda}{\alpha_{r\sigma} + \alpha_{s\lambda}} \tag{A.7}$$

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Appendix B

Input File of OSHF Code

Input File for Li Atom

```
MOLECULE CHARGE = 0 MULTIPLICITY = 2
Title="Li"
FREEZ
Li
end
END ! molecule
BASIS
name = 6-31G
END
!OUTput OBject=QM:CMO%ROHF end
OUTput OBject=QM:CMO%OSHF end
stop
G03: SCF Done: E(ROHF) = -7.43123499367
```

Appendix C

Input File of GAIM Code

Input File for LiH Molecule

```
molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 8.0 end
END
basis name=6-31G print end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 5.0 end
```

```
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 4.5 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 4.0 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
```

```
END
DEFine LiH= 3.5 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 3.0 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 2.5 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
```

```
Li
H Li LiH
END
DEFine LiH= 2.0 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.9 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.85 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end
```

```
molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.8 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.75 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.7 end
END
basis name=6-31G end
```

```
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.65 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.6 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.55 end
```

```
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.50 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.45 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
```

```
END
DEFine LiH= 1.4 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.35 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.3 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
```

```
Li
H Li LiH
END
DEFine LiH= 1.25 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.2 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.15 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end
```

```
molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.1 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.05 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 1.0 end
END
basis name=6-31G end
```

```
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 0.95 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 0.9 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 0.85 end
```

```
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 0.8 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 0.75 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
```

```
END
DEFine LiH= 0.70 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 0.65 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 0.6 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
```

```
Li
H Li LiH
END
DEFine LiH= 0.55 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

molecule
FREEZmatrix
Li
H Li LiH
END
DEFine LiH= 0.50 end
END
basis name=6-31G end
OUTPUT OBJ=QM:CMO%GAIMT end

stop
```

Appendix D

Output File of GAIM Code

Output File for LiH Molecule

```
Welcome to MUNgauss - August 12, 2014 Version

 N_molecules:  1
 Molecule is a symmetric top.
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 8.00000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   8.000000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     8.00000000               0.00000000     0.00000000    15.11780791
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.198441468

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
The basis set has now been re-ordered FDPS
Basis set (normalized) for this calculation (exponents are scaled:) 6-31G (6D/10F)
```

```
 ***************************************************************************************
              ATOMIC ORBITAL                       GAUSSIAN FUNCTIONS
 ***************************************************************************************
 ATOM       NO.    TYPE            SCALE FACTOR    EXPONENT        COEFF
 ***************************************************************************************
 LITHIUM
                  Shell     1
         1-    3  2P                 1.03000
                                                2.3249183E+00  8.9415080E-03
                                                6.3243032E-01  1.4100946E-01
                                                7.9053430E-02  9.4536370E-01
                  Shell     2
         4-    6  3P                 1.12000
                                                3.5961972E-02  1.0000000E+00
 ---------------------------------------------------------------------------------------
 HYDROGEN
                  Shell     3
         7        1S                 1.20000
                                                1.8731138E+01  3.3494604E-02
                                                2.8253946E+00  2.3472695E-01
                                                6.4012174E-01  8.1375733E-01
                  Shell     4
         8        2S                 1.15000
                                                1.6127775E-01  1.0000000E+00
 ---------------------------------------------------------------------------------------
 LITHIUM
                  Shell     5  CORE
         9        1S                 1.00000
                                                6.4241892E+02  2.1426078E-03
                                                9.6798515E+01  1.6208872E-02
                                                2.2091120E+01  7.7315572E-02
                                                6.2010702E+00  2.4578605E-01
                                                1.9351177E+00  4.7018900E-01
                                                6.3673579E-01  3.4547084E-01
                  Shell     6
        10        2S                 1.03000
                                                2.3249183E+00 -3.5091746E-02
                                                6.3243032E-01 -1.9123284E-01
                                                7.9053430E-02  1.0839878E+00
                  Shell     7
        11        3S                 1.12000
                                                3.5961972E-02  1.0000000E+00
 ***************************************************************************************
Total number of basis functions:         11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.198441468 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        439 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         56 IJKJ:        105 IJJL:         46 IIKK:         95
 IJJJ:         13 IIIL:         13 IIII:         11 IJKL:        100
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         32 IJKJCN:         69
IIKLCN:         38 IJKLCN:         54
```

```
 TOTAL OF        439 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


The basis set has now been re-ordered FDPS
Projecting extended Huckel matrix (STO-3G)  to 6-31G
 BLD_GUESS_MO_UHF> Generate UHF guess
UHF Open Shell (Doublet ) SCF, Nuclear Repulsion Energy:       0.000000000 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
    1         -6.454936050        -6.454936050
    2         -7.429740824        -7.429740824   8.11727E-02
    3         -7.430658963        -7.430658963   3.73081E-03
    4         -7.430951857        -7.430951857   2.13552E-03
    5         -7.431093629        -7.431093629   1.41228E-03
    6         -7.431307908        -7.431307908                     4-POINT
    7         -7.431235840        -7.431235840   3.35048E-03
    8         -7.431235847        -7.431235847   2.03337E-05
    9         -7.431235848        -7.431235848   9.23247E-06
At Termination Total Energy is        -7.431236  Hartrees

S = 0.500 ( 0.500 EXPECTED),   S(S+1) =  0.7500 (  0.7500 EXPECTED)
UHF Open Shell (Doublet ) SCF, Nuclear Repulsion Energy:       0.000000000 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
    1          9.551901474         9.551901474
    2         -0.221923977        -0.221923977   3.87480E-01
    3         -0.300601691        -0.300601691   1.45691E-01
    4         -0.307875866        -0.307875866   5.90208E-02
    5         -0.314956105        -0.314956105                     4-POINT
    6         -0.312915484        -0.312915484   7.46663E-02
    7         -0.312952722        -0.312952722   3.44320E-03
    8         -0.312966489        -0.312966489   1.71293E-03
    9         -0.312990516        -0.312990516                     4-POINT
   10         -0.312980394        -0.312980394   3.45510E-03
   11         -0.312980404        -0.312980404   3.03843E-05
   12         -0.312980409        -0.312980409   2.41686E-05
   13         -0.312980423        -0.312980423                     4-POINT
   14         -0.312980414        -0.312980414   7.01995E-05
At Termination Total Energy is        -0.312980  Hartrees

S = 0.500 ( 0.500 EXPECTED),   S(S+1) =  0.7500 (  0.7500 EXPECTED)

 GAIM's Electronic and Total Energies:
 Cycle    1         -8.106970913        -7.908529444
 Cycle    2         -8.127538029        -7.929096561
 Cycle    3         -8.127829971        -7.929388502
 Cycle    4         -8.127852020        -7.929410551

At Termination Total_Energy is        -7.929411  Hartrees
               --------------------------------

 N_molecules:  2
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 5.00000000
```

```
Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                 Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   5.000000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

-------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
-------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     5.00000000               0.00000000     0.00000000     9.44862994
-------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.317506349

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.317506349 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        624 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         77 IJKJ:        159 IJJL:         65 IIKK:        106
 IJJJ:         16 IIIL:         16 IIII:         11 IJKL:        174
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         85
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        624 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.247049231        -7.929542882
 Cycle    2         -8.247131400        -7.929625051

At Termination Total_Energy is        -7.929625  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 4.50000000

Z MATRIX FOR: HLi, (C(inf)v)
```

```
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   4.500000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

--------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                         COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
--------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     4.50000000               0.00000000     0.00000000     8.50376695
--------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.352784833

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.352784833 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        637 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         79 IJKJ:        165 IJJL:         67 IIKK:        108
 IJJJ:         16 IIIL:         16 IIII:         11 IJKL:        175
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        637 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.282559412       -7.929774580
 Cycle    2         -8.282606179       -7.929821346

At Termination Total_Energy is        -7.929821  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 4.00000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
```

```
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   4.000000    (   1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     4.00000000               0.00000000     0.00000000     7.55890395
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.396882937

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.396882937 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        642 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         79 IJKJ:        165 IJJL:         67 IIKK:        108
 IJJJ:         16 IIIL:         16 IIII:         11 IJKL:        180
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        642 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.327052897        -7.930169960
 Cycle    2         -8.327138742        -7.930255806

At Termination Total_Energy is        -7.930256  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 3.50000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
```

```
   2    1    1   3.500000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     3.50000000               0.00000000     0.00000000     6.61404096
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.453580499

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.453580499 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        643 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         79 IJKJ:        165 IJJL:        67 IIKK:        109
 IJJJ:         16 IIIL:         16 IIII:         11 IJKL:        180
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        643 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.384736015       -7.931155516
 Cycle    2         -8.384953738       -7.931373239
 Cycle    3         -8.385042919       -7.931462420

At Termination Total_Energy is        -7.931462  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 3.00000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                 Z3     BETA                 Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   3.000000   (  1)
```

```
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     3.00000000               0.00000000     0.00000000     5.66917797
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.529177249

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.529177249 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        674 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         82 IJKJ:        174 IJJL:         72 IIKK:        109
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        674 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.463002443       -7.933825194
 Cycle    2         -8.463530785       -7.934353536
 Cycle    3         -8.463803234       -7.934625985
 Cycle    4         -8.463963107       -7.934785858
 Cycle    5         -8.464057540       -7.934880291

At Termination Total_Energy is        -7.934880  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 2.50000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
```

```
   2    1    1   2.500000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL       AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     2.50000000               0.00000000     0.00000000     4.72431497
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.635012699

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.635012699 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        676 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        109
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        676 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.576038607        -7.941025909
 Cycle    2         -8.577112823        -7.942100124
 Cycle    3         -8.577905222        -7.942892523
 Cycle    4         -8.578449151        -7.943436452
 Cycle    5         -8.578828432        -7.943815733
 Cycle    6         -8.579095666        -7.944082967
 Cycle    7         -8.579285712        -7.944273013
 Cycle    8         -8.579422016        -7.944409318
 Cycle    9         -8.579520533        -7.944507834

At Termination Total_Energy is        -7.944508  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 2.00000000
```

```
Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   2.000000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                        COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000             0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     2.00000000             0.00000000     0.00000000     3.77945198
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.793765874

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.793765874 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.752790147       -7.959024274
 Cycle    2         -8.753482161       -7.959716287
 Cycle    3         -8.755207808       -7.961441935
 Cycle    4         -8.756525623       -7.962759750
 Cycle    5         -8.757562399       -7.963796525
 Cycle    6         -8.758389258       -7.964623384
 Cycle    7         -8.759056286       -7.965290412
 Cycle    8         -8.759599901       -7.965834028
 Cycle    9         -8.760047038       -7.966281164
 Cycle   10         -8.760417884       -7.966652011
 Cycle   11         -8.760727760       -7.966961887
 Cycle   12         -8.760988423       -7.967222550
 Cycle   13         -8.761208998       -7.967443124
 Cycle   14         -8.761396640       -7.967630766
 Cycle   15         -8.761557019       -7.967791146
 Cycle   16         -8.761694669       -7.967928796
 Cycle   17         -8.761813249       -7.968047375
 Cycle   18         -8.761915734       -7.968149860
```

```
 Cycle   19         -8.762004566        -7.968238693

At Termination Total_Energy is        -7.968239  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.90000000

Z MATRIX FOR: HLi, (C(inf)v)
-------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                 Z2    ALPHA                Z3     BETA                Z4
-------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.900000   (  1)
-------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.90000000               0.00000000     0.00000000     3.59047938
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.835543025

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.835543025 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM’s Electronic and Total Energies:
 Cycle    1         -8.808237240        -7.972694215
 Cycle    2         -8.808302409        -7.972759385
```

```
At Termination Total_Energy is        -7.972759  Hartrees
               -------------------------------


 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.85000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA               Z3     BETA               Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.850000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                  COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000              0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.85000000              0.00000000     0.00000000     3.49599308
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.858125269

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.858125269 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.832859503        -7.974734235
 Cycle    2         -8.832960786        -7.974835518
 Cycle    3         -8.833057195        -7.974931927

At Termination Total_Energy is        -7.974932  Hartrees
```

```
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.80000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1      BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.800000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                  COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.80000000               0.00000000     0.00000000     3.40150678
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.881962082

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.881962082 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.858580012        -7.976617930
 Cycle    2         -8.858634036        -7.976671954

At Termination Total_Energy is        -7.976672  Hartrees
               --------------------------------
```

```
 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.75000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.750000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000             0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.75000000             0.00000000     0.00000000     3.30702048
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.907160998

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.907160998 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.885173641        -7.978012642
 Cycle    2         -8.885207426        -7.978046428

At Termination Total_Energy is        -7.978046  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
```

```
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.70000000

Z MATRIX FOR: HLi, (C(inf)v)
-----------------------------------------------------------------------------------------------
   I   AN   Z1     BL                 Z2    ALPHA                Z3     BETA                Z4
-----------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.700000   (  1)
-----------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

-----------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                  COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
-----------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000              0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.70000000              0.00000000     0.00000000     3.21253418
-----------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.933842204

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.933842204 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.912817682        -7.978975478
 Cycle    2         -8.912829683        -7.978987479

At Termination Total_Energy is        -7.978987  Hartrees
              --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
```

```
Li
H        Li       LIH

VARIABLES:
LIH = 1.65000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.650000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000                0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.65000000                0.00000000     0.00000000     3.11804788
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.962140453

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.962140453 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.941572324        -7.979431871
 Cycle    2         -8.941564671        -7.979424218

At Termination Total_Energy is        -7.979424  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH
```

```
VARIABLES:
LIH = 1.60000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                 Z2    ALPHA               Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.600000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.60000000               0.00000000     0.00000000     3.02356158
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       0.992207342

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       0.992207342 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:       174 IJJL:        72 IIKK:        110
 IJJJ:         17 IIIL:        17 IIII:        11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -8.971509305        -7.979301963
 Cycle    2         -8.971484550        -7.979277208

At Termination Total_Energy is        -7.979277  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
```

```
LIH = 1.55000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA               Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.550000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

-------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                      COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
-------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.55000000               0.00000000     0.00000000     2.92907528
-------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.024214030

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.024214030 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.002707808        -7.978493778
 Cycle    2         -9.002667818        -7.978453788

At Termination Total_Energy is        -7.978454  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.50000000
```

```
Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.500000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

-------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
-------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.50000000               0.00000000     0.00000000     2.83458898
-------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.058354498

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.058354498 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.035253043        -7.976898545
 Cycle    2         -9.035198519        -7.976844021

At Termination Total_Energy is        -7.976844  Hartrees
               -------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.45000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
```

```
   I   AN   Z1     BL                  Z2    ALPHA               Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.450000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000              0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.45000000              0.00000000     0.00000000     2.74010268
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.094849481

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.094849481 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

       677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:        84 IJKJ:       174 IJJL:        72 IIKK:       110
 IJJJ:        17 IIIL:        17 IIII:        11 IJKL:       192
Number of integrals in INCORE buffers:
IIKKCN:        55 IJJLCN:        36 IJKJCN:        87
IIKLCN:        42 IJKLCN:        64
 TOTAL OF       677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.069236038        -7.974386558
 Cycle    2         -9.069166406        -7.974316925

At Termination Total_Energy is        -7.974317  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.40000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA               Z3     BETA                Z4
------------------------------------------------------------------------------------------------
```

```
   1    3
   2    1    1   1.400000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.40000000               0.00000000     0.00000000     2.64561638
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.133951248

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.133951248 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.104754208        -7.970802960
 Cycle    2         -9.104667677        -7.970716430

At Termination Total_Energy is        -7.970716  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.35000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                 Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.350000   (  1)
```

```
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                COORDINATES IN BOHR
   I EL        AN        X             Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.35000000               0.00000000     0.00000000     2.55113008
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.175949442

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.175949442 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM’s Electronic and Total Energies:
 Cycle    1         -9.141912498        -7.965963056
 Cycle    2         -9.141806160        -7.965856718
 Cycle    3         -9.141810762        -7.965861320

At Termination Total_Energy is        -7.965861  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.30000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                   Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.300000   (  1)
------------------------------------------------------------------------------------------------
```

```
Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.30000000               0.00000000     0.00000000     2.45664379
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.221178267

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.221178267 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:         174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:          17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.180830946        -7.959652679
 Cycle    2         -9.180695719        -7.959517452
 Cycle    3         -9.180699772        -7.959521505

At Termination Total_Energy is        -7.959522  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.25000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.250000   (  1)
------------------------------------------------------------------------------------------------
```

```
Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                        COORDINATES IN BOHR
   I EL        AN        X              Y              Z                      X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.25000000               0.00000000     0.00000000     2.36215749
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.270025398

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.270025398 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.221622557       -7.951597160
 Cycle    2         -9.221457982       -7.951432585
 Cycle    3         -9.221462258       -7.951436860

At Termination Total_Energy is        -7.951437  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H       Li       LIH

VARIABLES:
LIH = 1.20000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                 Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.200000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)
```

```
----------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                        COORDINATES IN BOHR
   I EL        AN        X              Y              Z                       X              Y              Z
----------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000              0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.20000000              0.00000000     0.00000000     2.26767119
----------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.322943123

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.322943123 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.264430268        -7.941487146
 Cycle    2         -9.264230474        -7.941287352
 Cycle    3         -9.264235107        -7.941291985

At Termination Total_Energy is        -7.941292  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H       Li       LIH

VARIABLES:
LIH = 1.15000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                 Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.150000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)
```

```
------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.15000000               0.00000000     0.00000000     2.17318489
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.380462389

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.380462389 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:       174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF       677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM’s Electronic and Total Energies:
 Cycle    1         -9.309408464       -7.928946075
 Cycle    2         -9.309166574       -7.928704186
 Cycle    3         -9.309171608       -7.928709219

At Termination Total_Energy is        -7.928709  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H       Li       LIH

VARIABLES:
LIH = 1.10000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                 Z2    ALPHA               Z3     BETA               Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.100000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
```

```
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.10000000               0.00000000     0.00000000     2.07869859
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.443210679

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.443210679 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.356733249       -7.913522570
 Cycle    2         -9.356441871       -7.913231192
 Cycle    3         -9.356447312       -7.913236633

At Termination Total_Energy is        -7.913237  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 1.05000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.050000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
```

```
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.05000000               0.00000000     0.00000000     1.98421229
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.511934997

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.511934997 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.406610893       -7.894675895
 Cycle    2         -9.406262704       -7.894327706
 Cycle    3         -9.406268533       -7.894333536

At Termination Total_Energy is        -7.894334  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H       Li       LIH

VARIABLES:
LIH = 1.00000000

Z MATRIX FOR: HLi, (C(inf)v)
-----------------------------------------------------------------------------------------------
   I   AN   Z1     BL                 Z2    ALPHA               Z3     BETA               Z4
-----------------------------------------------------------------------------------------------
   1    3
   2    1    1   1.000000   (  1)
-----------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
```

```
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     1.00000000               0.00000000     0.00000000     1.88972599
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.587531747

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.587531747 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy        Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.459290916       -7.871759169
 Cycle    2         -9.458879684       -7.871347937
 Cycle    3         -9.458885864       -7.871354117

At Termination Total_Energy is        -7.871354  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 0.95000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                 Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   0.950000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
```

```
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     0.95000000               0.00000000     0.00000000     1.79523969
---------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.671086049

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.671086049 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1        -9.515086300       -7.844000251
 Cycle    2        -9.514608490       -7.843522441
 Cycle    3        -9.514614976       -7.843528927

At Termination Total_Energy is        -7.843529  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 0.90000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                 Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   0.900000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

---------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
---------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
```

```
   2 H          1   0.00000000     0.00000000     0.90000000               0.00000000     0.00000000     1.70075339
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.763924163

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.763924163 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.574404298       -7.810480135
 Cycle    2         -9.573861492       -7.809937328
 Cycle    3         -9.573868269       -7.809944106

At Termination Total_Energy is        -7.809944  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 0.85000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1   3
   2   1    1   0.850000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     0.85000000               0.00000000     0.00000000     1.60626709
```

```
-----------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       1.867684408

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.867684408 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.637793034        -7.770108626
 Cycle    2         -9.637195372        -7.769510964
 Cycle    3         -9.637202541        -7.769518133

At Termination Total_Energy is        -7.769518  Hartrees
               ------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 0.80000000

Z MATRIX FOR: HLi, (C(inf)v)
-----------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
-----------------------------------------------------------------------------------------------
   1    3
   2    1    1   0.800000   (  1)
-----------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

-----------------------------------------------------------------------------------------------------------------
                            COORDINATES IN ANGSTROMS                                   COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
-----------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     0.80000000               0.00000000     0.00000000     1.51178079
-----------------------------------------------------------------------------------------------------------------
```

```
Nuclear repulsion energy:       1.984414684

Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       1.984414684 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:       174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.706010340        -7.721595657
 Cycle    2         -9.705381228        -7.720966545
 Cycle    3         -9.705389211        -7.720974527

At Termination Total_Energy is        -7.720975  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 0.75000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   0.750000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                            COORDINATES IN ANGSTROMS                                COORDINATES IN BOHR
   I EL        AN        X              Y              Z                       X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000             0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     0.75000000             0.00000000     0.00000000     1.41729449
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       2.116708996
```

```
Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       2.116708996 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.780123116        -7.663414120
 Cycle    2         -9.779505412        -7.662796416
 Cycle    3         -9.779515434        -7.662806438

At Termination Total_Energy is        -7.662806  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 0.70000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   0.700000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000               0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     0.70000000               0.00000000     0.00000000     1.32280819
------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       2.267902496
```

```
 WARNING: Distance between atoms    2 and    1 is  1.3228
                      Check the geometry
Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       2.267902496 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:       174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.861645700       -7.593743204
 Cycle    2         -9.861109704       -7.593207208
 Cycle    3         -9.861125009       -7.593222514

At Termination Total_Energy is        -7.593223  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 0.65000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   0.650000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

--------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                      COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
--------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000              0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     0.65000000              0.00000000     0.00000000     1.22832189
--------------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       2.442356534
```

```
 WARNING: Distance between atoms    2 and    1 is  1.2283
                      Check the geometry
Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       2.442356534 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1         -9.952726556        -7.510370022
 Cycle    2         -9.952380741        -7.510024207
 Cycle    3         -9.952409670        -7.510053137

At Termination Total_Energy is        -7.510053  Hartrees
               -------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 0.60000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                   Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   0.600000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

--------------------------------------------------------------------------------------------------------------------
                            COORDINATES IN ANGSTROMS                                         COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
--------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000              0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     0.60000000              0.00000000     0.00000000     1.13383559
--------------------------------------------------------------------------------------------------------------------
```

```
Nuclear repulsion energy:       2.645886245

 WARNING: Distance between atoms    2 and    1 is  1.1338
                       Check the geometry
Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       2.645886245 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1       -10.056394910       -7.410508665
 Cycle    2       -10.056401988       -7.410515743

At Termination Total_Energy is        -7.410516  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 0.55000000

Z MATRIX FOR: HLi, (C(inf)v)
-------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
-------------------------------------------------------------------------------------------------
   1    3
   2    1    1   0.550000   (  1)
-------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

-----------------------------------------------------------------------------------------------------------------
                            COORDINATES IN ANGSTROMS                                 COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
-----------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000             0.00000000     0.00000000     0.00000000
   2 H          1   0.00000000     0.00000000     0.55000000             0.00000000     0.00000000     1.03934929
-----------------------------------------------------------------------------------------------------------------
```

```
Nuclear repulsion energy:       2.886421358

 WARNING: Distance between atoms    2 and    1 is  1.0393
                       Check the geometry
Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       2.886421358 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1        -10.176761090       -7.290339732
 Cycle    2        -10.177454555       -7.291033197
 Cycle    3        -10.177627997       -7.291206638
 Cycle    4        -10.177688793       -7.291267435

At Termination Total_Energy is        -7.291267  Hartrees
               --------------------------------

 N_molecules:  1
 Molecule is a symmetric top.
The program objects/defaults have been reset
Free format Z-Matrix for: HLi, (C(inf)v)
Li
H        Li       LIH

VARIABLES:
LIH = 0.50000000

Z MATRIX FOR: HLi, (C(inf)v)
------------------------------------------------------------------------------------------------
   I   AN   Z1     BL                  Z2    ALPHA                Z3     BETA                Z4
------------------------------------------------------------------------------------------------
   1    3
   2    1    1   0.500000   (  1)
------------------------------------------------------------------------------------------------

Cartesian coordinates for: HLi, (C(inf)v)

------------------------------------------------------------------------------------------------------------------
                             COORDINATES IN ANGSTROMS                                COORDINATES IN BOHR
   I EL        AN        X              Y              Z                        X              Y              Z
------------------------------------------------------------------------------------------------------------------
   1 Li         3   0.00000000     0.00000000     0.00000000                0.00000000     0.00000000     0.00000000
```

```
   2 H         1   0.00000000     0.00000000     0.50000000             0.00000000     0.00000000     0.94486299
---------------------------------------------------------------------------------------------------------------
Nuclear repulsion energy:       3.175063494

 WARNING: Distance between atoms    2 and    1 is  0.9449
                       Check the geometry
Charge=    0, Number of electrons=    4

The basis set has now been re-ordered FDPS
6-31G Basis Set - Total number of basis functions:       11

GAIMT Open Shell (Singlet ) SCF, Nuclear Repulsion Energy:       3.175063494 Hartrees
Convergence on Density Matrix Required is   5.0000E-06
Cycle    Electronic Energy       Total Energy    Convergence   Extrapolation
All integrals will be kept INCORE
NOTE: INTEGRALS .LE.  1.00E-07 (I2EACC) WERE NOT KEPT
Exponent cutoff used:  2.00E+01 PQCUT2 cutoff used:  1.00E-16

        677 TWO-ELECTRON INTEGRALS CALCULATED IN ISPCLC (RAW)
 TOTAL NUMBER OF EACH OF THE 8 TYPES OF INTEGRALS SAVED:
 IIKL:         84 IJKJ:        174 IJJL:         72 IIKK:        110
 IJJJ:         17 IIIL:         17 IIII:         11 IJKL:        192
Number of integrals in INCORE buffers:
IIKKCN:         55 IJJLCN:         36 IJKJCN:         87
IIKLCN:         42 IJKLCN:         64
 TOTAL OF        677 TWO-ELECTRON INTEGRALS CALCULATED (RAW)


 GAIM's Electronic and Total Energies:
 Cycle    1       -10.320202536       -7.145139042
 Cycle    2       -10.321702792       -7.146639298
 Cycle    3       -10.322037436       -7.146973942
 Cycle    4       -10.322168990       -7.147105496
 Cycle    5       -10.322227464       -7.147163970

At Termination Total_Energy is        -7.147164  Hartrees
               --------------------------------


         PROGRAM> end of inputs


Program terminated normally


Job: RUN ended on :30-Oct-15 at 15:18:20
User: aalrawas
Cpu     time:  00h00m00s15c on clhead
Elapsed time:  00h00m00s00c
```