Chapter 1

Introduction to Computational Chemistry and Overview of the Thesis

1.1 Introduction to Computational Chemistry

Theoretical basis of computational chemistry, focusing on the methods used in the thesis, is briefly described in this section followed by an overview of the new results discussed in the thesis. Molecular electronic structure theory is the application of the principles of quantum mechanics to calculate the structure and the properties of molecules. Evaluation of structure, energy and properties using `computer experiments’ provides insight into the chemical behavior and supplement experimental efforts in the structural elucidation of short-lived species, in the synthesis and design of materials with desired properties etc. [1]

The emergence of electronic structure theory as a successful field was made possible by the development in methodologies of quantum mechanics and powerful computers and efficient algorithms. Applying the principles of quantum mechanics to molecular problems is a challenging task
because we cannot solve the underlying equations exactly. [2] To solve them approximately, various theoretical models are developed. Understanding the strengths and weaknesses of each method helps to make the right choice of the method for the problem at hand. Some of the factors to be considered in choosing a model are, available computational resources, the size of the molecules, the accuracy needed for a reliable result, number of molecules to be computed. A theoretical model chemistry should ideally be able to give all observable properties of a molecular system. We discuss some of the theoretical models giving importance to the ones that are used in the thesis. The next four chapters detail the application of electronic structure theory to selected problems. A brief summary of these projects is also given in the next section.

The questions that are asked in the thesis are solved by solving the time-independent Schrödinger equation

$$H\Psi = E\Psi$$  \hspace{3cm} (1.1)

where $H$ is the Hamiltonian operator and $\Psi$ is the molecular wavefunction for a system of nuclei and electrons. [3] Since nuclei are much heavier than the electrons, they move much slowly. Hence to a good approximation (known as Born-Oppenheimer approximation) one can consider the electrons in a molecule to be moving in the field of fixed nuclei. [4] The resulting molecular electronic Hamiltonian (or total energy operator, sub-
ject to frozen nuclei), in atomic units, is

\[
H(r;R) = -\frac{1}{2} \sum_i^n \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) - \sum_i^n \sum_{\alpha} Z_{\alpha} \left| r_i - R_{\alpha} \right| + \\
\frac{1}{2} \sum_i^n \sum_j^n \frac{1}{|r_i - r_j|} + \frac{1}{2} \sum_{\alpha}^A \sum_{\beta}^A \frac{Z_{\alpha} Z_{\beta}}{|R_{\alpha} - R_{\beta}|}
\]  

(1.2)

where first term in the right hand side is the operator for the kinetic energy of the electrons; the second term is the coulomb attraction between electrons and nuclei; the third and fourth term represent the repulsion between electrons and between nuclei, respectively. Partial differential equations in 3n unknowns such as we have here are completely intractable to solve exactly, and therefore two important approximations are usually made.

As the first approximation, we reduce the exact function (equation 1.2) of 3n variables to n approximate functions of three variables each. That is, the wave function is approximated as a product of one electron wavefunctions (Molecular Orbitals) which are in turn, approximated by a Linear Combination of Atomic Orbitals (LCAO). The MO is represented as

\[
\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu i}
\]  

(1.3)

, where \( \psi_i \) is the i-th MO, \( c_{\mu i} \) are coefficients of linear combination, \( \phi_{\mu i} \) is the \( \mu \)-th atomic orbital and \( n \) is the number of atomic orbitals. Once an initial wavefunction is constructed, an electron is selected. The effect of all the other electrons is summed up, and used to generate a potential. (Thus the procedure is sometimes called a mean-field procedure.) This gives a single electron in a defined potential, for which the Schrödinger equation can be solved, giving a slightly different wavefunction for that
electron. This process is then repeated for each of the other electrons, which completes one step of the procedure. The whole procedure is then repeated, until the change from one step to the next is sufficiently small. This is called Hartree-Fock (HF) approximation, which is the foundation of much of modern molecular orbital theory. The procedure for solving the HF equation is often called self-consistent field (SCF) method.

The exact molecular orbital is an infinite set of differential equation. Applying the second approximation we replace the exact MO by a finite set of algebraic functions. These functions are usually called the atomic orbital (AO) basis, because they are atom-centered and resemble solutions to the HF problem for the constituent atoms of a molecule. The earliest computations were based on the use of Slater Type Orbitals (STO) as approximations to atomic orbitals. STO is represented as

$$\phi_i(\zeta, n, l, m; r, \theta, \phi) = N r^{n-\frac{1}{2}} e^{-\zeta r} Y_{lm}(\theta, \phi)$$ \hspace{1cm} (1.4)$$

where $N$ is a normalization constant, $\zeta$ is called exponent. The $r, \theta$ and $\phi$ are spherical coordinates and $Y_{lm}$ is the angular momentum part. The $n, l$ and $m$ are quantum numbers: principal, angular momentum and magnetic respectively. STO’s are computationally demanding and hence Gaussian Type Orbitals (GTO) were introduced. GTO’s, also called primitives is represented as:

$$g(\alpha, l, m; n; x, y, z) = N e^{-\alpha r^2} x^l y^m z^n$$ \hspace{1cm} (1.5)$$

where $N$ is a normalization constant, $\zeta$ is called exponent. The $x, y$ and $z$ are cartesian coordinates. In practical calculations, the basis function $\phi_\mu$
are chosen to be contracted Gaussian functions, that is, fixed linear combination of gaussian functions such as

\[ g_s(\alpha, r) = (2\alpha/\pi)^{3/4} e^{-\alpha r^2} \]  

(1.6)

\[ g_{px}(\alpha, r) = (128\alpha^5/\pi^3)^{1/4} x e^{-\alpha r^2} \]  

(1.7)

The smallest possible basis set is called the minimal basis set, and it contains one orbital for every atomic orbital of an atom (including unoccupied orbitals). The STO-3G basis is a well-known minimal basis set which contracts 3 Gaussian functions to approximate the more accurate Slater Type Orbitals. Although a contracted GTO might give a good approximation to an atomic orbital, it lacks any flexibility to expand or shrink in the presence of other atoms in a molecule. Hence, a minimal basis set such as STO-3G is not capable of giving highly accurate results.

The solution is to add extra basis functions beyond the minimum number required to describe each atom. The physical purpose of providing multiple basis functions per atomic orbital is to allow the size of orbitals to increase (for example, along a bond axis) or diminish (for example, perpendicular to a bond axis). Then, the Hartree-Fock procedure can weight each atomic orbital basis function individually to get a better description of the wave function. If we have twice as many basis functions as in a minimum basis, this is called a “double zeta” (DZ) basis set (the zeta, comes from the exponent in the GTO). Split-valance basis sets, which have only a single orbital for the core orbitals and two orbitals for valence orbitals are also widely used. Often additional flexibility is built in by adding higher-angular momentum basis functions. Since the highest angular momentum
orbital for carbon is a p orbital, the “polarization” of the atom can be described by adding a set of d functions on carbon. A set of 3 p functions are used for hydrogen atom as polarization functions. Polarization is added to describe small displacements of the orbitals from their atomic centers in the molecular environment and for the description of electron correlation. A double-zeta plus polarization basis set might be designated DZP. A commonly used example of a split-valence double-zeta plus polarization basis set is Pople’s so-called 6-31G* basis. Here the core orbitals are described by a contraction of 6 Gaussian orbitals, while the valence is described by two orbitals, one made of a contraction of 3 Gaussians, and one a single Gaussian function. The star (*) indicates polarization functions on non-hydrogen atoms. If polarization is added to hydrogen atoms also, this basis is labeled as 6-31G**. Finally, for anions and Rydberg excited states, additional diffuse functions are necessary. The 6-31+G basis set has 1 diffuse s-type and p-type gaussians added to the standard 6-31G basis set for heavy atom.

In the $i$-$jkG$ type basis set one $\phi$ function is used for inner shells and two sets for the valance shells. For a first row atom, there are nine $\phi$ functions per atom of the form

\[
\phi_{1s}(r) = \sum_{k=1}^{N_1} d_{1s,k} g_s(\alpha_1 k, r)
\]

\[
\phi_{2s'}(r) = \sum_{k=1}^{N_{2s'}} d_{2s,k} g_s(\alpha_2 k', r)
\]

\[
\phi_{2px'}(r) = \sum_{k=1}^{N_{2px'}} d_{2p,k} g_{px}(\alpha_2 k', r)
\]
and similar expressions for $2p_y$, $2p_y''$, $2p_z$ and $2p_z''$. The functions $\phi'$ and $\phi''$ represent inner and outer parts of the valence shell. For hydrogen, inner and outer $s$ functions are of the form

$$
\phi_{1s'}(r) = \sum_{k=1}^{N_1'} d_{k'1s} g_{s}(\alpha k'', r)
$$

$$
\phi_{1s''}(r) = \sum_{k=1}^{N_1''} d_{k''1s} g_{s}(\alpha k'', r)
$$

For 6-31G: For heavy atoms, $N_1 = 6$, $N_2' = 3$, $N_2'' = 1$. For hydrogen, $N_1' = 3$, $N_1'' = 1$.

Another approach is to consider the core (inner) electrons as an averaged potential, called Effective Core Potential (ECP), because the core orbitals in most cases are not affected by changes in chemical bonding. ECP’s reduce the number of electrons to be included in the calculations. This makes very efficient computation and incorporation of relativistic effects can be achieved effectively. LANL2DZ is one such basis set used widely for transition metals. [6]

The general form of ECP is $ECP(r) = \sum_{i=1}^{M} d_i r^{n_i} e^{-\zeta_i r}$ where $M$ is the number of terms in the expansion, $d_i$ is a coefficient for each term, $r$ denotes the distance from the nucleus, $n_i$ is a power of $r$ for the i-th term and $\zeta_i$ represents the exponent of the i-th term.
HF energy accounts for the bulk (~99%) of the exact energy and is successful in predicting equilibrium geometries and some properties. Bond making and bond breaking processes are not described well at this level. To a large extend the defects of HF method in estimating electron correlation may be compensated by isodesmic equations, where number of electron pairs are conserved. However, the energy that is left out could still be important in the chemical context. The difference between the Hartree-Fock (HF) energy and the exact nonrelativistic energy is usually termed the electron correlation energy, since it is due to detailed correlations between electrons which are averaged out in the HF approach. The errors in the HF approach are caused by the two major approximations that we make, i) use of approximate functions for exact functions and ii) use of finite set of basis functions for complete set. Electron correlation methods try to tackle this problem. [8] Post-HF electron correlation methods, use a linear combination of many configurations, instead of a single configuration in HF theory. The other configurations are generated by replacing occupied orbitals by virtual orbitals. One of the popular methods is Moller-Plesset (MP) or many-body perturbation theory, [7] where electron correlation is treated as a perturbation to the HF problem. In the MP scheme, wave-function and energy are expanded in a power series of the perturbation. In Configuration Interaction (CI), a linear combination of configurations (HF determinants) with all determinants formed by single and double orbital substitutions, with coefficients determined variationally. [9] In principle, by increasing the number of configurations included, the CI method is capable of providing arbitrarily accurate solutions to the exact wave function.
If all possible excited configurations are included, the method gives the exact solution within the space spanned by a given basis set and is referred to as full configuration interaction (FCI). Since FCI is computationally highly demanding, limited CI methods are used, and one popular method is CISD, where all single and double excitations are included. [9] Quadratic Configuration Interaction (QCI), [10] have size-consistency added to the CISD method. Coupled Cluster Theory (CC) uses the exponential form of the wave function $\Psi = e^{T} \Psi_0$, where $T = T_1 + T_2 + \ldots$. [11] The effect of higher excitations are included in the exponential term. The method in which all single and double excitations are included, i.e., $T = T_1 + T_2$, it is called CCSD. [12]

Another approach in electronic structure theory is Density Functional Theory. [13] DFT, unlike the wave function based methods, has electron density as the fundamental property. The exact ground state energy of a molecular system, as stated by first Hohenberg-Kohn theorem, is a functional only of the electron density and the fixed positions of the nuclei. [14] In other words, for a given nuclear coordinates, the electron density uniquely determines the energy and all properties of the ground state. Given the functional, Hohenberg and Kohn proved that the exact electron density function is the one which minimizes the energy (i.e., as a function of density) thereby providing a variational principle to find the density.

The total energy, deriving from the solution of the Schrodinger equation, can be decomposed in terms of kinetic energy, $T$, electron-nuclear attraction, $V_{en}$, and electron-electron interaction contributions (plus the nuclear-nuclear repulsion energy, which is constant at a given geometry).
The electron-electron interactions consist of the classical Coulomb repulsion, $J$, due to the electron density, plus nonclassical terms due to the correlations between electrons and exchange effects of Fermion statistics. Thus, we have

$$E(\rho) = T(\rho) + V_{en}(\rho) + J(\rho) + V_{xc}(\rho)$$  \hspace{1cm} (1.8)$$

Kohn-Sham formulation of DFT (KS-DFT) uses the kinetic energy of the noninteracting electrons, which can be solved exactly, and the kinetic energy difference between real and noninteracting systems is included in the exchange-correlation (XC) functional. [15] DFT is also an SCF method, in which Kohn-Sham orbitals are solved iteratively.

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, approximations exist which permit the calculation of certain physical quantities quite accurately. The most widely used approximation is the local density approximation (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated. Generalized gradient approximations (GGA) are still local but also take into account the gradient of the density at the same coordinate. [16] Using the latter (GGA) very good results for molecular geometries and ground state energies have been achieved. The combination of gradient-corrected correlation functionals with the Becke exchange functional has been shown to yield significantly more accurate relative energies than the earlier LDA-based forms for KS-DFT.

Accuracy achieved by the DFT calculations are comparable to that of MP2, but the computational requirement of DFT is comparable to HF
methods. As there is no explicit construction of the molecular wave function, the basis set requirements for DFT are far more modest than those needed to obtain reliable results via the MP2 method (or any other correlation method). Perhaps the best DFT results to date have been obtained by mixing a small part of the exact exchange interactions (as modeled in the HF method) with gradient-corrected exchange functionals.

The discussion till now was on the evaluation of energy on fixed nuclear positions, thereby getting a Potential Energy Surface (PES) of the different nuclear coordinates. Geometry Optimization is the technique of arriving at the minimum on the PES. When we are interested in the reaction path, it is necessary to compute the Transition States and higher order Saddle Points along the reaction coordinate. Vibrational frequency analysis helps in characterizing the nature of the stationary points as minima or TS (zero and one imaginary frequency respectively).

There are several state-of-the-art computational chemistry packages available such as, Gaussian 03, GAMESS, ADF, DMol etc. Visualization packages, such as GaussView, Molden, Molekel, helps in the visualization of the structure, orbitals, electron density, laplacian, animation of frequencies or reaction path etc. Calculations in this thesis is carried out using Gaussian 94/03 program packages. The theoretical models used in the thesis are the following. Hybrid Hartree Fock-DFT - B3LYP method which uses a combination of the three-parameter Becke exchange functional with the Lee-Yang-Parr nonlocal correlation functionals is used in all the projects. The basis sets employed in the calculations are: 6-311G(d) (Chapter 2), 6-31G* and 6-311+g* (Chapter 3), LANL2DZ (Chapters 4 and 5). Specific
details of the computational methods are described in the methods section of each chapter.

1.2 Overview of the Thesis

1.2.1 Nonplanarity at Tri-coordinated Aluminum and Gallium: Cyclic Structures for $X_3H_{m}^n$ ($X = B, Al, Ga$)

Cyclopentadienyl cation, $C_3H_4^+$, the smallest $2\pi$-aromatic system, and all the three-membered boron ring clusters are studied both theoretically and experimentally. However very little is known about the heavier analogs of boron, the alanes and galanes. In view of the known differences between the hydrocarbons and the heavier analogs, it is interesting to see the differences between boranes, alanes and galanes. Structures and energies of $X_3H_2^2^-, X_3H_4^-, X_3H_5$, and $X_3H_6^+$ ($X = B, Al$ and $Ga$) were investigated theoretically at B3LYP/6-311G(d) level. The global minimum structures of $B$ are not found to be global minima for $Al$ and $Ga$. The hydrides of the heavier elements $Al$ and $Ga$ have shown a total of seven, six and eight minima for $X_3H_2^2^-$, $X_3H_4^-$, and $X_3H_5$, respectively. However, $X_3H_6^+$ has three and four minima for $Al$ and $Ga$, respectively. The nonplanar arrangements of hydrogens with respect to $X_3$ ring is found to be very common for $Al$ and $Ga$ species. Similarly, species with lone pairs on heavy atoms dominate the potential energy surfaces of $Al$ and $Ga$ three-ring systems. The first example of a structure with tri-coordinate pyramidal arrangement at $Al$ and $Ga$ is found in $X_3H_4^-$ (2g), contrary to the conventional wisdom of $C_3H_4$, $B_3H_4^-$, etc. The influence of $\pi$-delocalization in stabilizing the
structures decreases from $X_3H_3^{2-}$ to $X_3H_6^+$ for heavier elements Al and Ga. In general, minimum energy structures of $X_3H_4^-$, $X_3H_5$, and $X_3H_6^+$ may be arrived at by protonating the minimum energy structures sequentially starting from $X_3H_3^{2-}$. The resonance stabilization energy (RSE) for the global minimum structures (or nearest structures to global minimum which contains $\pi$-delocalization) is computed using isodesmic equations.

1.2.2 Dehydrogeno closo-Carboranes and closo-Silaboranes: A Theoretical Study of Structure and Reactivity

In this chapter, we compare larger clusters, carborane and silaborane and their dehydrogeno derivatives. 1,2-Carboranes, 1,2-silaboranes ($C_2B_nH_{n+2}$, and $Si_2B_nH_{n+2}$, $n = 4,5,8$ and 10) and their dehydrogeno derivatives are studied using Density Functional Theory (B3LYP/6-311+G*). 1,2-Dehydrogeno-$\sigma$-dicarbadodecaborane is comparable in reactivity to benzyne. Several isomers of dehydrogenocarboranes, 1,2-$C_2B_{10}H_{10}$ (8a), 2,3- and 2,6-$C_2B_8H_8$ (10a and 11a), and 2,3-$C_2B_5H_5$(13a), were found to be more $\pi$-stabilized than benzyne, indicating the possibility of their synthesis. The 2,3-$C_2B_5H_5$ (13a) is estimated to be more favorable than the experimentally available 1,2-$C_2B_{10}H_{10}$ (8a) by 21.5 kcal/mol. This arises from the extra stabilization gained from the better overlap of the $C_2B_3H_3$ rings with the 2 BH caps. These could be ideal dienophiles in pericyclic reactions, according to Frontier Molecular Orbital Analysis. Silaboranes have similar structural features as carboranes with modifications resulting from the larger size of Si. Dehydrogenosilaboranes differ considerably in structure and bonding from the carbon analogs so as to avoid Si-Si multiple
bond. One of the Si atoms moves away from the surface in Si$_2$B$_{10}$H$_{10}$ (15), Si$_2$B$_8$H$_8$ (16,17 and 18), and 1,2-Si$_2$B$_5$H$_5$ (19). One Si atom forms a bridge to a trigonal surface in 2,3-Si$_2$B$_5$H$_5$ (20) and 1,2-Si$_2$B$_4$H$_4$ (21). Symmetrical structures based on icosahedron and octahedron are found to be more stable compared to the other structures. Three-dimensional aromaticity estimated using NICS calculations follow the trend in stability; symmetrical structures have more negative NICS values.

1.2.3 Theoretical Study on the double Insertion of Acetylene to the Nickel Complexes of Benzyne and Carborynes.

Carborynes, didehydrogenodicarbaboranes, as showed in Chapter 3 has similarity with benzynes in their reactions. In this chapter we explore the possibility of transition metal complexes of carbonye and their reactivity in comparison to that of benzyne. The carborynes, C$_2$B$_{10}$H$_{10}$ and C$_2$B$_5$H$_5$, which are theoretically estimated to be the best among the carborynes, are chosen for the study. The reactivity of the complexes of these two carborynes along with the benzyne nickel complex are studied for the double insertion reaction of acetylene. The stationary points and transition states involved in the reaction mechanism are optimized under B3LYP/LANL2DZ level of theory. These studies would encourage experimental investigations in the area leading to many functionalization pathways of carboranes.

1.2.4 Transition Metal Catalyzed Activation of $\beta$-C-H bond

In the previous chapters we have seen the application of electronic structure theory to the problems ranging from small molecules to the clusters and
transition metal complexes. In this chapter we concentrate on a transition metal catalyzed reaction. The activation of CH bond is central to chemistry since they provide a solution to the industrial preparation of hydrocarbon derivatives from the naturally available saturated hydrocarbons occurring in the petroleum and natural gas. \( \beta \)-hydride elimination reaction which is a crucial intermediate in many useful reactions are studied with the first row transition metal as the catalyst. The free energy of reaction as a function of varying metals is computed. The structure and the stability of the \( \beta \)-agostic complex, the property of which determines the course of the reaction, is studied in detail. The metal-ligand combinations across the whole range of first row transition metals is analyzed to understand factors that control the reaction.
Bibliography


   http://www.ccl.net/cca/documents/basis-sets/basis.html


