CHAPTER 1

Introduction to Computational Chemistry and Overview of the Thesis

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[1.1] Introduction

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be solvable...............” – P. A. M. Dirac

This famous statement by Dirac in the year 1929 regarding the laws of chemistry and physics referred mainly to the postulation of the Schrödinger equation. Over the years, several approximations have been emerged to solve the Schrödinger equation. Subsequently the application of quantum mechanics to solve problems in chemistry has been incorporated into efficient computer programs. These computational efforts received a critical boost when Hohenberg and Kohn, and Kohn and Sham, reformulated the Schrödinger equation into density functional theory (DFT), a theory based on the electron density. The increase in the applications of quantum chemistry has been facilitated by the development of faster computers and quantum chemistry softwares. This branch of chemistry that uses computers to assist in solving chemical problems is called computational chemistry.

In the beginning, the application of computational chemistry was limited to small molecules and for computing organic reaction mechanisms. The computational studies on transition-metal chemistry have lagged behind organic chemistry due to the requirement of more complicated quantitative wave functions. Currently, computational studies to predict the structure, bonding, reactivity and reaction mechanism of organometallic complexes have been proved to be an essential tool to complement the experimental research. This thesis deals with the
computational study of the structure, bonding and reactivity of transition metal organometallic complexes and clusters. Brief descriptions of the basis of the electronic structure methods used in this thesis are given in the following sections, followed by an overview of the remaining chapters.

[1.2] Electronic Structure Methods

Electronic structure methods are based upon the principles of quantum mechanics and employ a variety of mathematical techniques to solve the fundamental equations. This can usually be classified as ab initio, semi-empirical and density functional methods. The first method, ab initio, means “from the beginning” and uses only the fundamental constants to solve the Schrödinger equation. Semiempirical methods on the other hand simplify the computation either by approximating the different integrals using parameters derived from the experimental data of atoms and molecules or by neglecting some of them. In contrast to these wavefunction based methods, the density functional methods calculate the molecular electron probability density and calculate molecular electronic energy from density. The following sections provide an overview of the theory underlying ab initio and density functional theory methods.

[1.2.1] Ab initio Methods

Ab initio methods are based on the Schrödinger equation. The solution to Schrödinger equation gives the energy and wavefunction of atoms and molecules.
The wavefunction can be used to calculate the electronic distribution that can be further used to find the physical properties of the system.

[1.2.1.1] Schrödinger Equation and Hamiltonian

The Schrödinger equation describes the behaviour of electrons in atoms and molecules. The time-independent Schrödinger equation, in its succinct form, can be expressed as,

$$\hat{H}\Psi = E\Psi \quad (1.1)$$

where $\hat{H}$ is the Hamiltonian operator for a system of nuclei and electrons, $E$ is the total energy and $\Psi$ is the wave function which defines the system. The non-relativistic Hamiltonian operator $\hat{H}$ for any molecule having $M$ nuclei and $N$ electrons, assuming the nuclei and electrons to be point masses, is

$$\hat{H} = -\frac{\hbar^2}{2m_A} \sum_{A=1}^{M} \nabla_A^2 - \frac{\hbar^2}{2m_i} \sum_{i=1}^{N} \nabla_i^2 - \sum_{A=1}^{M} \sum_{i=1}^{N} \frac{Z_A e^2}{r_{Ai}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B e^2}{r_{AB}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{e^2}{r_{ij}} \quad (1.2)$$

where $A$ and $B$ refer to the nuclei and $i$ and $j$ to the electrons. Here, $m$ is the mass and $r$ is the position vector of the particles, $e$ is the electronic charge, $Z$ is the atomic number, $\hbar$ is represented by the Planck’s constant divided by $2\pi$ and $\nabla^2$ is the Laplacian Operator. The first and second terms are the nuclear and electronic kinetic energy operators. The third, fourth and fifth terms represent the potential energy for the nuclear-electron attraction, nuclear-nuclear repulsion and electron-electron repulsion respectively.
The energy and wave function of a molecule can be obtained by solving the Schrödinger equation. However, it is very difficult to solve the Schrödinger equation exactly for any system with more than one electron. Thus, various degrees of approximations using a finite wave function are used for solving the chemical problems. Some of the main approximations are briefly outlined here.

[1.2.1.2] Born-Oppenheimer Approximation

The Born-Oppenheimer approximation, which was introduced by Max Born and J. Robert Oppenheimer in 1927, separates the motion of the electrons in a molecule from the motion of the nuclei. The separation is based on the fact that the nuclei are much heavier than the electrons and move more slowly. Hence, to a good approximation, the electrons in a molecule can be considered moving in a field of fixed nuclei. Thus, the nuclear kinetic energy term can be neglected and the potential for the nuclear-nuclear repulsion can be considered to be a constant. This gives rise to the electronic Hamiltonian $\hat{H}_{\text{elec}}$, which describes the motion of $N$ electrons in the field of $M$ point charges.

$$\hat{H}_{\text{elec}} = -\frac{\hbar^2}{2m_i} \sum_{i=1}^{N} \nabla_i^2 - \sum_{A=1}^{M} \sum_{i=1}^{N} \frac{Z_A e^2}{r_{iA}} + \sum_{i=1}^{N} \sum_{j<i}^{N} \frac{e^2}{r_{ij}}$$  \hspace{1cm} (1.3)$$

Hence, Schrödinger equation for the electronic motion can be written in a compact form as,

$$\hat{H}_{\text{elec}} \Psi_{\text{elec}} = E_{\text{elec}} \Psi_{\text{elec}}$$  \hspace{1cm} (1.4)$$
The electronic energy $E_{elec}$ and the electronic wave function $\Psi_{elec}$ depend parametrically on the nuclear coordinates and explicitly on the electronic coordinates. The total energy of the system including the internuclear repulsion is

$$E_{\text{tot}} = E_{\text{elec}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B e^2}{r_{AB}}$$

(1.5)

The spectral studies support the Born-Oppenheimer approximation but it fails when nontrivial coupling of electronic and nuclear motion occurs in cases such as Jahn-Teller and Renner effects.\(^{3,4}\) Further approximations are required to get reliable information on the electronic structure for large molecules.

[1.2.1.3] LCAO-MO Approximation

The linear combination of atomic orbital (LCAO) approximation is commonly used to construct the trial wave function for a molecule.\(^{3,4}\) In this approximation, it is considered that near one nucleus the potential exerted by the other nuclei is negligible. Hence, the nature of the wave function near the nucleus must be analogous to the wave function of a hydrogen atom centered at that point. Thus, the molecular orbital ($\Psi$) can be considered as a combination of atomic orbitals ($\phi$) centered at each nucleus forming an orthonormal basis.

$$\Psi = \sum_{i=1}^{n} c_i \phi_i$$

(1.6)

where $c_i$ is the coefficient of each atomic orbitals $\phi_i$. 
**[1.2.1.4] Variation Theorem**

The set of molecular orbital (MO) expansion coefficients $c_i$ in LCAO approximation can be solved using the principles of variational theorem. According to variation theorem for a given system, the exact ground state wave function has the lowest expectation value for $\hat{H}$ and thus lowest energy $E_0$. In other words the energy calculated using a trial wave function is always greater than or equal to the exact ground state energy $E_0$.

$$E_\psi = \frac{\int \hat{H} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau} \geq E_0$$  \hspace{1cm} (1.7)

The wave function and ground state energy can be obtained by minimizing $E_\psi$ with respect to parameters that define the trial wave function $\Psi$. For getting good approximate ground state energy and wave function, many trial functions have to be tried and the lowest value of the variational integral gives the closest approximation to $E_0$ and ground state wave function.

**[1.2.1.5] Hartree-Fock Self Consistent Field Theory**

In the Hartree-Fock theory, each electron is assumed to be moving in the field of the nuclei and in the average field of other electrons. As a result, the motion of a given electron is considered independent of the actual position of the other electrons. It is to be noted that the Hamiltonian operator considering Born-Oppenheimer approximation (Eq. 1.3) is a sum of three terms. The first two terms depends only on the coordinates of one electron. This is nothing but a sum of one-
electron Hamiltonian operators $\sum_{i=1}^{N} \hat{h}^i_{elec}$. The one-electron operator $\hat{h}^i_{elec}$ includes kinetic energy of the electrons and the potential energy due to the attractive coulombic interaction between the nuclei and electrons.

$$\hat{h}^i_{elec} = -\frac{\hbar^2}{2m_j} \nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A e^2}{r_{iA}}$$  \hspace{1cm} (1.8)

The third term in the Hamiltonian is the sum of electron-electron repulsions, which depends upon the coordinates of two electrons. The Hamiltonian can thus be written as the sum of one- and two- electron terms.

$$\hat{H}_{elec} = \sum_{i=1}^{N} \hat{h}^i_{elec} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{e^2}{r_{ij}}$$  \hspace{1cm} (1.9)

The best approximate solution to the electronic Schrödinger equation is given by the variational principle (Eq. 1.7). It will try to find the wavefunction $\Psi_{elec}$ that give the lowest possible energy. Thus, the electronic energy of an approximate wave function $\Psi'_{elec}$ is given by

$$E_{elec} = \frac{\int \Psi'_{elec} \hat{H}_{elec} \Psi_{elec} d\tau}{\int \Psi'_{elec} \Psi_{elec} d\tau}$$  \hspace{1cm} (1.10)

Now, considering the normalization of the electronic wavefunction, the equation 1.10 becomes

$$E_{elec} = \int \Psi'_{elec} \hat{H}_{elec} \Psi_{elec} d\tau$$  \hspace{1cm} (1.11)

Substitution of the electronic Hamiltonian from equation 1.9 leads to
Integration of the first term leads to sum of the one-electron energies \( \varepsilon_i \) and is represented by \( 2 \sum_{i=1}^{N/2} \varepsilon_i \). The second integral can be expressed in terms of coulomb integral \( (J_{ij}) \) and exchange integral \( (K_{ij}) \) as

\[
\sum_{i=1}^{N/2} \sum_{j=1}^{N/2} 2J_{ij} - K_{ij}
\]

where,

\[
J_{ij} = \int \Psi_i^* (1) \Psi_j^* (1) \frac{1}{r_{12}} \Psi_j (2) \Psi_i (2) d\tau_1 d\tau_2 \quad (1.13)
\]

\[
K_{ij} = \int \Psi_i (1) \Psi_j (2) \frac{1}{r_{12}} \Psi_i^* (1) \Psi_j^* (2) d\tau_1 d\tau_2 \quad (1.14)
\]

The coulomb integral \( J_{ij} \) represents the energy of the coulombic interaction between an electron in orbital \( \Psi_i \) with an electron in orbital \( \Psi_j \). This is a destabilization interaction between the electrons and always positive. The term exchange integral \( K_{ij} \) arises from the consideration of the electron spin in the antisymmetric wavefunction. Hence, the total energy can be represented as

\[
E_{\text{elec}} = 2 \sum_{i=1}^{N/2} \varepsilon_i + \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} 2J_{ij} - K_{ij} \quad (1.15)
\]

The corresponding operator for this energy expression is called the Fock operator \( \hat{F} \). The energy and wave function are determined by solving the following Hartree-Fock equation,

\[
\hat{F} \Psi_i = \varepsilon_i \Psi_i \quad i = 1, 2, 3, \ldots, N \quad (1.16)
\]
The simple approximate form for molecular wavefunction can be represented as linear combination of atomic orbital (LCAO).

\[ \Psi_i = \sum_{\nu=1}^{K} c_{\nu i} \phi_{\nu} \]  

(1.17)

Now, introducing the LCAO approximation into the Hartree-Fock equation (1.16) we get,

\[ \hat{F} \sum_{\nu=1}^{K} c_{\nu i} \phi_{\nu} = \varepsilon_i \sum_{\nu=1}^{K} c_{\nu i} \phi_{\nu} \]  

(1.18)

Multiplication of equation 1.18 by \( \phi_{\nu}^* \) and then integrating over all space leads to

\[ \sum_{\nu=1}^{K} c_{\nu i} \left( F_{\nu \nu} - \varepsilon_i S_{\nu \nu} \right) = 0 \]  

(1.19)

Here, \( F_{\nu \nu} \) and \( S_{\nu \nu} \) are defined as the following integrals

\[ F_{\nu \nu} = \int \phi_{\nu}^* \hat{F} \phi_{\nu} \, d\tau \]  

(1.20)

\[ S_{\nu \nu} = \int \phi_{\nu}^* \phi_{\nu} \, d\tau \]  

(1.21)

To obtain a nontrivial solution to equation 1.19 i.e. a solution for which the values of the coefficients \( c_{\nu i} \) are non zero, the term \( \sum_{\nu=1}^{K} (F_{\nu \nu} - \varepsilon_i S_{\nu \nu}) \) must be equal to zero. This leads to \( K \) equations known as Secular equations and the corresponding determinant is called Secular Determinant.
The solution of equation 1.22 gives a set of $K$ energy values, $\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots, \varepsilon_K$ and a set of $K$ wave functions, $\Psi_1, \Psi_2, \ldots, \Psi_K$. The equation is not linear and must be solved iteratively. The solution to the equation begins with the initial guess for the molecular wave function $\Psi_i$ (Eq. 1.17). This requires selection of a set of basis functions $\phi_\nu$ and a set of guesses for the initial values of the coefficients $c_\nu$. These are used to obtain a set of values for the $\varepsilon_i$. These values for the $\varepsilon_i$ are then substituted into the secular equation 1.22 and a new set of values for the coefficients $c_\nu$ are obtained. This iterative process is continued until the variations in the values of the $\varepsilon_i$ and the $c_\nu$ from one cycle to the next fall below a threshold. The resulting values for the $c_\nu$ are used to obtain the wave function $\Psi_i$ that minimize the value of energy $\varepsilon_i$. The procedure is called Self Consistent Field (SCF) method.

[1.2.1.6] Electron Correlation

The Hartree-Fock (HF) theory takes into account an average effect of electron repulsion, but not the explicit electron-electron interactions. This indicates that the probability of finding an electron at some location around an atom is determined by the distance from the nucleus but not the distance from the other electrons. However, in reality, the movement of electrons is influenced by the repulsion from individual electrons and it will affect the probability of finding one
electron at a particular region near other electrons. If we consider the effect of explicit electron-electron repulsions into the calculation, we can improve the energy and the wavefunction of a system. This is known as electron correlation.\textsuperscript{10} The HF energy can be improve with larger and more complete set of basis functions. However, the larger and complete basis sets can lower the HF energy to a limit called Hartree-Fock limit.\textsuperscript{3,4} The difference between the exact non-relativistic ground state energy $E_{\text{nonrel}}$ and the Hartree-Fock limit energy $E_{\text{HF}}$ is called the correlation energy ($E_{\text{corr}}$).

$$E_{\text{corr}} = E_{\text{nonrel}} - E_{\text{HF}}$$ \hfill (1.23)

The three common methods which incorporate electron correlation viz. Møller-Plesset Perturbation theory,\textsuperscript{11} Configuration Interaction,\textsuperscript{12} and Coupled Cluster Theory\textsuperscript{13} are discussed in the following sections. These calculations begin with a HF calculation and then correct for the correlation.

[1.2.1.6.1] Møller-Plesset Perturbation Theory

The electron correlation in Møller-Plesset Perturbation (MP) theory can be accounted for by treating the real molecule as a perturbed system. This method takes the sum of the one electron HF operator as the zeroth order unperturbed Hamiltonian $\hat{H}^{(0)}$ and is very close to the exact Hamiltonian $\hat{H}$. The energy and the wave functions of the Hamiltonian $\hat{H}^{(0)}$ can be systematically improved by a parameter $\lambda$ associated with the perturbating operator ($\hat{H}^{(1)}$). Within the limit of
perturbation theory the perturbation $\hat{H}^{(1)}$ is presumed to be relatively small compared to the unperturbed Hamiltonian.

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}$$  \hfill (1.24)

In this method, the perturbed wave function and perturbed energy are expressed as a power series in $\lambda$.

$$\Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \ldots$$  \hfill (1.25)

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots$$  \hfill (1.26)

The energy correction in MP theory can be taken as various orders like 1\textsuperscript{st} order (MP1), 2\textsuperscript{nd} order (MP2), 3\textsuperscript{rd} order (MP3) and so on. The 1\textsuperscript{st} order energy correction is nothing but HF energy.\textsuperscript{11}

[1.2.1.6.2] Configuration Interaction Method

A configuration interaction (CI) wave function is constructed from the HF wave function and adding new determinants that represent promotion of electrons from the occupied to virtual orbitals. The actual wave function of the system is a linear combination of these Slater determinants that corresponds to different electronic configurations.

Configuration interaction methods are classified by the number of excitations used to create each determinant. If only one electron has been excited for each determinant, it is called a configuration interaction single-excitation (CIS) calculation. CIS calculations give an approximation to the excited states of the
molecule, but do not change the ground state energy. Single and double excitation (CISD) calculations yield a ground state energy that has been corrected for correlation. The configuration interaction calculation with all possible excitations is called full CI. The full CI calculation using an infinitely large basis set will give an exact quantum mechanical energy. However, full CI calculations are possible only for small molecules.

[1.2.1.6.3] Coupled Cluster Theory

Here, the correlated wave function is expressed as a sum of the HF ground state determinant and determinants representing the promotion of electrons from this state to the virtual MOs. However, unlike CI, this sum of the determinant is constructed by operating a series of excitation operators ($\hat{T}$) on the HF wave function.

$$\Psi = e^{\hat{T}_1} \Psi_{HF}$$

(1.27)

where $\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots$

The operators $\hat{T}_1, \hat{T}_2, \cdots$ represent promotion of one, two, ... number of electrons into virtual orbitals. The different coupled cluster methods are named as coupled cluster doubles (CCD), coupled cluster singles and doubles (CCSD), etc depending upon how many terms are included in constructing the excitation operator.
[1.2.2] Basis Set

For performing any quantum mechanical calculation the molecular orbitals $\psi_i$ are considered as the linear combination of a given set of functions $\phi_i$, called basis sets$^{3,4}$

$$\psi_i = \sum_{i=1}^{N} C_i \phi_i$$  \hspace{1cm} (1.28)

These basis functions $\phi_i$ contain a radial $R_{nl}(r)$ and angular part $Y_{lm}(\theta \phi)$. The angular function $Y_{lm}(\theta \phi)$ commonly known as the spherical harmonics, which contains all the angular information needed to describe the wave function. The different types of basis functions differ in the radial function $R_{nl}(r)$.

One such basis functions is the Slater Type Orbitals (STO)$^{14}$ The atomic orbitals (AO) can be always represented by Slater type functions which have exponential radial parts. The radial part of a STO with principal quantum number $n$ can be represented in the form

$$R_{nl}(r) \propto r^{n-1}e^{-\xi r}$$  \hspace{1cm} (1.29)

where, $\xi$ is the orbital exponent. STOs can be used as basis functions for more accurate solutions for small atoms and molecules. Sometimes two or more numbers of STOs are used to improve the accuracy. The many-centre two-electron integrals involving STOs are rather difficult to evaluate which require numerical integration techniques and are very computational time consuming. This problem can be overcome to some extent by the use of Gaussian type functions introduced by
Boys. These gives easily integrable poly electronic functions. The very commonly used Gaussian Type Orbital (GTO) has the radial function in the form

\[ R_{nl}(r) \propto r^{n-1}e^{-\alpha r^2} \]  \hspace{1cm} (1.30)

The main disadvantage of the Gaussian function is that it does not adequately describe the form of real atomic orbitals. In particular, the Gaussian function lacks a cusp at the nucleus and hence the region near the nucleus is described rather poorly. In practice, more number of GTOs with different orbital exponents are used to fit the atomic orbitals. Depending upon the number of Gaussian functions used to describe an orbital, the basis set can be termed as minimal basis set, double zeta (DZ), triple zeta (TZ) basis set and so on. Since mainly valence orbitals are involved in chemical bonding, the efficiency can be enhanced without excessive computing time by increasing the number of GTOs only for the valence orbitals. This results in split valence basis sets.

However, to maintain the same degree of accuracy with less computational cost the Gaussian functions can be contracted to form contracted Gaussian type orbitals. In this procedure, the number of GTOs remains the same but the number of variational coefficients reduces drastically. These GTOs are then referred as primitives and the resulting functions as the contracted Gaussians functions. The contraction can be expressed as follows

\[ \phi_i = \sum_{p=1}^{Q} D_{ip} \phi_p \]  \hspace{1cm} (1.31)
where, \( D_{lp} \) are the coefficients within a given basis set and \( g_p \) are the primitive GTOs.

Further improvement of the basis set could be made by including polarization and diffusion functions. The basis sets, which add basis functions whose angular quantum number is greater than the maximum angular quantum number of the valence shell of the ground state atom is called polarized basis set. For anions, compounds with lone pairs and H-bonded dimers where electron density has a significant value at a large distance from nuclei, highly diffuse function with very small orbital exponent are used for better agreement with experiment.

Computations involving heavier atoms are relatively difficult than those involving first and second row atoms of the periodic table. This is because of the increasing number of two electron integrals to be evaluated. This can be overcome by the use of pseudo potentials. Since the core orbitals are not affected by the changes in chemical bonding, one can treat them by an average potential. The valence electrons can be described by appropriate basis functions. A commonly used pseudo potential is the Effective Core Potential (ECP)\(^{16}\) and is of the general form,

\[
ECP (r) = \sum_{i}^{k} C_i r^{n_i} e^{-\alpha_i r^2}
\]  

(1.32)

where, \( k \) is the number of terms in the expansion, \( C_i \) is a coefficient of each term, \( r \) is the distance from the nucleus \( n_i \) and \( \alpha_i \) is an exponent for \( i^{th} \) term. The use of ECP is found to be computationally very efficient, particularly for transition metals,
because it reduces the number of basis functions. ECP also makes room for the incorporation of relativistic effects.

[1.2.3] Density Functional Theory

Density Functional Theory (DFT) simplifies the many body problem in wavefunction based methods by using with the electronic charge density \( \rho \) as fundamental variable rather than the wavefunction. Thus, for N electrons system the basic variable \( \rho \) depends only on the three spatial coordinates rather than the intractable \( 3N \) spatial coordinates and \( N \) spin coordinates required to describe the many-body electronic wave function. Here, the many-body problem of calculating electron-electron interaction energy is transformed into single-body problem, without explicitly calculating the electron-electron interaction energy. This is done by using ground state density \( \rho_0 \) and the single particle wave function.

Hohenberg and Kohn established the connection between the electron density and the many-electron Schrödinger equation. They (HK-I theorem) showed that all the properties of a molecular system can in principle be deduced from the electronic density function of the system. The ground state energy is thus a functional of ground state electron probability density \( \rho_0 \).

\[
E_0 = \mathcal{E}[\rho_0(r)]
\]  \hspace{1cm} (1.33)

Similarly, the ground-state wave function (\( \Psi_0 \)) for a system is a functional of the ground state electron density \( \rho_0 \).
Thus, the number of electrons, \( N \) can be determined from the ground state electron density \( \rho_0 \) as

\[
N = \int \rho_0(r) d^3r \quad \text{(1.35)}
\]

The HK-II theorem\(^5\) states that for every trial density function \( \rho(r) \) that satisfies the equation 1.35 for total number of electrons and \( \rho(r) \geq 0 \) for all \( r \), the following inequality holds.

\[
E_0 \leq E[\rho(r)] \quad \text{(1.36)}
\]

In other words, if some density represents the correct number of electrons of the system, the total energy calculated from this density cannot be lower than the true energy of the ground state.

Kohn and Sham proposed a method for minimization of energy functional, \( E[\rho(r)] \) known as Kohn-Sham (KS) method.\(^6\) According to this, the total-energy functional can be written in terms of electron density as

\[
E[\rho(r)] = T[\rho(r)] + U[\rho(r)] + V[\rho(r)] \quad \text{(1.37)}
\]

where \( T[\rho(r)] \), \( U[\rho(r)] \) and \( V[\rho(r)] \) are the functionals for the electronic kinetic energy, electron-electron interaction energy and potential energy for interaction between electron and nuclei, called as external potential \( \nu(r) \). The potential energy in the given potential \( \nu(r) \) is given by,
The minimization of the energy functional $E[\rho(r)]$ with respect to $\rho(r)$ in principle will lead to the ground state energy of the system.

The KS method considers a reference system of non-interacting electrons to approximate the kinetic energy $T[\rho(r)]$ and electron-electron interaction $U[\rho(r)]$ functionals. According to this assumption, the kinetic energy $T_s[\rho(r)]$ and electron-electron interaction $U_s[\rho(r)]$ for the reference system are exactly known. Therefore, the kinetic energy $T[\rho(r)]$ and electron-electron interaction $U[\rho(r)]$ functionals can be expressed as,

\[
T[\rho(r)] = T_s[\rho(r)] + \Delta T[\rho(r)] \quad (1.39)
\]
\[
U[\rho(r)] = U_s[\rho(r)] + \Delta U[\rho(r)] \quad (1.40)
\]

where $\Delta T[\rho(r)]$ and $\Delta U[\rho(r)]$ are the difference in average electronic kinetic energy and electron-electron repulsion terms in comparison to the non-interacting reference system. Thus, substituting $V[\rho(r)]$, $T[\rho(r)]$ and $U[\rho(r)]$ from Eq. 1.38, 1.39 and 1.40, to the total-energy functional in Eq. 1.37 gives

\[
E[\rho(r)] = T_s[\rho(r)] + \Delta T[\rho(r)] + U_s[\rho(r)] + \Delta U[\rho(r)] + \int v(r)\rho(r)d^3r \quad (1.41)
\]

Here, the unknown terms are $\Delta T[\rho(r)]$ and $\Delta U[\rho(r)]$ and the sum of these terms is called the exchange-correlation functional, $E_{xc}[\rho(r)]$.

\[
E_{xc}[\rho(r)] = \Delta T[\rho(r)] + \Delta U[\rho(r)] \quad (1.42)
\]
It can also be written as sum of the exchange and correlation functionals.

\[ E_{xc}[\rho(r)] = E_x[\rho(r)] + E_c[\rho(r)] \]  

(1.43)

where \( E_x[\rho(r)] \) is due to the Pauli principle (exchange energy) and \( E_c[\rho(r)] \) is due to correlations. The accuracy of Kohn-Sham (KS) method depends on the quality of this exchange-correlation functional, \( E_{xc}[\rho(r)] \).

DFT in principle gives a good description of ground state properties but the practical applications are based on approximations for the exchange-correlation functional, \( E_{xc}[\rho(r)] \). Solving the exact exchange-correlation would solve the many-body problem exactly, which is not feasible in practice and thus require approximation. Some of the popular approximations are described below.

**[1.2.3.1] Local Density Approximation (LDA)**

In LDA, the contribution of each volume element to the total exchange correlation energy is taken to be that of the homogenous electron gas density at that point. When the density \( \rho \) varies with position extremely slowly then the energy functional \( E_{xc}^{LDA}[\rho(r)] \) can be expressed as,

\[ E_{xc}^{LDA}[\rho(r)] = \int \varepsilon_{xc}^{LDA}[\rho(r)] d^3r \]  

(1.44)

\( \varepsilon_{xc}^{LDA}[\rho(r)] \) is the exchange-correlation energy density of homogenous electron gas with electron density \( \rho \).
[1.2.3.2] Local Spin-Density Approximation (LSDA)

Unlike LDA, LSDA allows electrons with different spins to occupy different spatial orbitals. Hence, for open-shell molecules and molecular geometries near dissociation LSDA works better than LDA. Here, the exchange correlation energy is given by

\[ E^{\text{LSDA}}_{\text{xc}} [\rho^\alpha(r), \rho^\beta(r)] = \int E^{\text{LSDA}}_{\text{xc}} [\rho^\alpha(r), \rho^\beta(r)] d^3r \]  \hspace{1cm} (1.45)

[1.2.3.3] Generalized Gradient Approximation (GGA)

The LDA and LSDA use the exchange-correlation energy for the uniform electron gas at every point in the system regardless of the real charge density. For a system of non-uniform charge density the exchange-correlation energy can deviate significantly from the uniform result. This deviation can be expressed in terms of the gradient and higher spatial derivatives of the total charge density. The GGA estimates the contribution of each volume element based on the magnitude and gradient of the electron density within that element. This can be achieved by expressing the energy functional with more general functions of \( \rho(r) \) and \( \nabla \rho(r) \). Such energy functionals are of the general form

\[ E^{\text{GGA}}_{\text{xc}} [\rho^\alpha(r), \rho^\beta(r)] = \int E^{\text{GGA}}_{\text{xc}} [\rho^\alpha(r), \rho^\beta(r), \nabla \rho^\alpha(r), \nabla \rho^\beta(r)] d^3r \]  \hspace{1cm} (1.46)

Different GGAs differ in the choice of the functions \( \rho \) and \( \nabla \rho \).
[1.2.3.4] Hybrid Functional

The hybrids functional are constructed by mixing the certain percentage of Hartree-Fock exchange with exchange and correlation from DFT exchange-correlation functional. Different hybrid functionals are available based on the approximations to the exchange and correlation functionals. The commonly used functional in this thesis is the hybrid functional B3LYP.\textsuperscript{17a-c} This is a combination of the Lee-Yang-Parr GGA for correlation and Becke’s three-parameter hybrid functional B3 for exchange. The hybrid functional B3 is a linear combination of a fraction of Hartree-Fock exchange and the DFT exchange functional.

\[
E_{\text{xc}}^{\text{B3LYP}} = E_{\text{xc}}^{\text{LDA}} + a_0 (E_x^{\text{HF}} - E_x^{\text{LDA}}) + a_x (E_x^{\text{GGA}} - E_x^{\text{LDA}}) + a_c (E_c^{\text{GGA}} - E_c^{\text{LDA}})
\]

where \(a_0 = 0.20\), \(a_x = 0.72\) and \(a_c = 0.81\) are the three empirical parameters determined by fitting the predicted values to a set of atomization energies, ionization potentials, proton affinities and total atomic energies.

[1.3] Theoretical Methods Used in the Thesis

The level of theory used in this thesis for computations is the hybrid HF-DFT method, B3LYP\textsuperscript{17a-c} and LANL2DZ\textsuperscript{17d-f} basis set with the effective core potentials of Hay and Wadt. Frequency calculations were carried out at the same level of theory to characterize the nature of the optimized structures. Gaussian 03 program package is used for the calculations.\textsuperscript{18} In some cases, single point energy calculation at higher level is performed for verification. These cases are mentioned in detail in the appropriate chapters.
Chapter 1

[1.4] Overview of the Thesis

The remaining four chapters of the thesis are organized as follows. In the second and third chapters of thesis, the reactivity of the cationic Fe-borylene complex toward metathesis, β-hydride transfer and insertion reactions are described. The structure and bonding of mono and dinuclear metallacycles of Cp2Ti and Cp2Zr with C2-cumulenes (HNCCNH and OCCO) are studied in the fourth chapter. In the last chapter, a total valence electron count for the condensed transition metal clusters has been proposed which establishes the missing link between the electron count for condensed boranes (mno rule), and transition metal clusters (Mingos’ rule).

[1.4.1] Chapter 2: Reactivity of Cationic Terminal Fe-Borylene Complex: Mechanism for Boron Metathesis

Transition metal borylene complexes have received significant attention in the recent years, which is partially attributed to the similarities with classical organometallic ligand systems such as Fischer carbenes and vinylidenes. Recently metathesis reactions of the transition metal aminoborylene complex [Cp(CO)2FeBN(i-Pr)2](BAr4)− (Ar4f = 3,5-(CF3)2C6H3) (1a) with AX (2), where A = Ph3P, Ph3As; X = O, S, were reported by Aldridge and co-workers (Scheme 1.1a). It led to the isolation of [Cp(CO)2Fe(A)](BAr4)− (3) and (i-Pr)2NBX (4). The reaction of Ph2CO with 1a, however, does not follow the metathesis pathway; the ligand transformation process, Meerwein–Ponndorf β-hydride transfer from an isopropyl substituent of the aminoborylene ligand to the coordinated ketone, takes place instead (Scheme 1.1b).
Obviously, not all unsaturated substrates are suitable to undergo metathesis with the borylene complex. This raises many interesting questions about the details of the reaction, the characteristics of the metal-borylene complex, and the unsaturated substrates likely to undergo boron metathesis. The analysis\(^2\) shows that boron metathesis proceeds via the initial attack of the substrates at the positively charged boron atom of the metal-borylene complex and forms the more preferable acyclic intermediate. On the contrary, the attack of the olefin takes place at the metal end of the M=C bond of the metal-carbene complex in olefin metathesis and proceeds via [2+2] cyclo-addition. The energetics of boron metathesis and olefin metathesis reactions are comparable. Substrates which are polar and have low-lying \(\sigma^*\)-MO (weak \(\sigma\)-bond) prefer boron metathesis reaction. The relative stability of the metathesis products is controlled by the strength of the M-E and B-X bonds of the products (Scheme 1.1a). The \(\beta\)-hydride transfer (Scheme 1.1b) is a competitive reaction to boron metathesis for the substrates having low-lying \(\pi^*\)-MO. The metathesis reactions of the Fe-borylene complex with various substrates indicate the role of polarity in tuning the reaction in a preferred direction.
Chapter 3: Reactivity of Cationic Terminal Fe-Borylene Complex toward Carbodiimide and Isocyanate: Insertion versus Metathesis Reactions

In contrast to boron metathesis, the reaction of the borylene complex 1a, or its dicyclohexylamino counterpart \([\text{CpFe(CO)}_2(\text{BNCy}_2)]^+\) (1b) with dicyclohexylcarbodiimide (CyNCNCy) gives an insertion product, in which two equivalents of carbodiimide are assimilated, one into each of the Fe=B and B=N double bonds to form the spirocyclic complexes 5a,b (Scheme 1.2a).

On the other hand, the reaction of isocyanates (R'NCO; R' = Ph, 2,6-Xyl, Cy) with 1b gives an entirely different type of product i.e. \([\text{CpFe(CO)}_2(\text{CNR}')]^+\) (6) via a net oxygen abstraction process from the heteroallene precursor (Scheme 1.2b). To rationalize the difference in the reactivity of 1a and 1b toward carbodiimide and isocyanates, mechanistic study has been carried out.

**Scheme 1.2:** Schematic Representation of the Reactions of 1a,b (a) Insertion Reaction with CyNCNCy and (b) Oxygen atom abstraction Reaction with R'NCO.

It has been shown that both carbodiimide and isocyanate substrates prefer insertion into the Fe=B bond rather than the B=N bond of the borylene complex. In case of isocyanates, the net metathesis reaction is a competitive pathway to...
insertion. The metathesis pathway is facile for isocyanate substrates if initial coordination at the boron atom occurs via the oxygen atom (kinetically favored). Insertion chemistry is feasible when the isocyanate attacks initially via the nitrogen atom. However, further reaction of the mono-insertion product so formed with excess isocyanate offers a number of facile (low energetic barrier) routes to $[\text{CpFe(CO)}_2(\text{CNR}')]^+$ (6) rather than to the formation of the bis-insertion product $[\text{CpFe(CO)}_2\text{C(NR')(O)B(NR')(O)CNR}_2]^+$ ($R' = \text{Ph, } 2,6\text{-Xyl, Cy}$) (i.e. the direct analogue of the observed products (5a,b) from the carbodiimide reaction). Moreover, the presence of a number of facile competing reaction pathways for the formation of the final isonitrile products (6) indicate that the product distribution is better explained in terms of competing pathways, rather than differing extents of reaction along similar trajectories.

[1.4.3] Chapter 4: Structure and Bonding in Mono and Dinuclear Metallacycles of Cp$_2$M (M = Ti, Zr) with C2-Cumulenic Ligands XCCX (X = O, NH): Comparison with Metallacycles of 1,2,3-Butatriene and 1,3-Butadiyne

The unstable 14-electron titanocene Cp$_2$Ti and zirconocene Cp$_2$Zr have been playing a vital role in the synthetic organometallic chemistry, olefin polymerization, organometallic chemical vapour deposition, C-C coupling and cleavage reactions. The carbene-type frontier orbitals of Cp$_2$M (M = Ti, Zr) help in the reaction with unsaturated compounds such as 1,3-butadiynes and 1,2,3-butatrienes to form several mono and binuclear metallacycles. The structure and reactivity of these complexes are well studied both experimentally and theoretically. However, similar three and five membered 2,5-dihetero-substituted metallacycles are not reported yet. On the other hand, binuclear complexes of 2,5-dihetero
substituted metallacycles have been reported in the literature. The structure and bonding in the mono and binuclear metallacycles of \( \text{Cp}_2\text{M} \) (\( \text{M} = \text{Ti}, \text{Zr} \)) with \( \text{C}_2\)-cumulenes \( \text{XCCX} \) (\( \text{X} = \text{O}, \text{NH} \)) is investigated in this chapter (Scheme 1.3).

\[ \text{Scheme 1.3:}\ ]\text{ Schematic representation of the mono and dinuclear complexes of } \text{Cp}_2\text{M} \text{ (M = Ti, Zr)} \text{ with XCCX (X = O, NH, CH, CH}_2\text{). } [\text{M}] \text{ represents Cp}_2\text{M fragment.}\]

The bonding analysis on the \( \text{C}_2\)-cumulene ligands indicates that the ligand OCCO can be described as dianion of 1,3-butadiyne and the ligand HNCCNH as similar to 1,2,3-butatriene, where terminal CH\(_2\) groups are replaced by isolobal NH groups having lone pair. The number of filled in plane \( \pi \) MOs are same in all these four \( \text{C}_2\)-cumulenic ligands, but the two hetero-cumulenic ligands have two additional electrons in the perpendicular \( \pi \) MO. The ligands \( \text{H}_2\text{CCCCH}_2 \) and HNCCNH can interact with the \( \text{Cp}_2\text{M} \) fragment through the terminal C-X (\( \text{X} = \text{CH}_2, \text{NH} \)) as well as central C-C \( \pi \) bond to form three membered metallacycles 1MX and 2MX (Scheme 1.3). On the other hand, three membered metallacyle 2MX are not the stationary points on the potential energy surface for the ligands OCCO and HCCCCH. The interaction of the in-plane \( \pi \) MOs in 3ZrO and 3MNH is similar to that of the metallacyclocumulene and metallacyclopentyne. However, the antibonding interaction in the third filled perpendicular \( \pi \) MO results in distortion of the
five membered ring of 3ZrO and 3MNH. The relative stability of the five membered metallacycle 3MX as compared to three-membered metallacycle 1MX increases when X changes from O to CH₂. This trend is more pronounced in Zr complexes due to the bigger size of Zr. All the cis- binuclear complexes except 4MCH are non-planar and the bending of the metallocene fragments from the plane of XCCX are larger for X = NH and O. The rehybridization of the in-plane and perpendicular π MO probably results in the bending of the two metallocene fragments in 4MX with respect to XCCX plane. Unlike the cis-dimetallabicycles, the two Cp₂M fragments in 5MX are in the same plane with respect to XCCX ligand.

[1.4.4] Chapter 5: mno Rule for Condensed Boranes versus Mingos’ Rule for Condensed Transition Metal Clusters: The missing link

In this chapter, the topographic and electronic similarities between the poly-condensed transition metal clusters and polyhedral borane clusters are investigated with the help of electron-counting rules. The correlation between the electron count for the polyhedral boranes (Wade’s n + 1 rule) and for the transition metal clusters (PSEPT, 7n + 1 rule) can be understood from the isolobal analogy between BH and transition metal fragments. The relationship between the electron count of poly-condensed polyhedral boranes (mno rule) and poly-condensed transition metal clusters (Mingos’ rule) is not straightforward. The mno rule for condensed boranes and Mingos’ rule for transition metal clusters are based on different sets of parameters and thus one to one correspondence between these two rules is missing. In this chapter, a total valence electron count for the condensed transition metal
clusters is proposed which establishes the missing link between the electron count for condensed boranes (mno rule), and transition metal clusters (Mingos’ rule). According to this rule, \( m + n + o + 6n - 3(m - 1) = 7n - 2m + o + 3 \) \((n = \text{number of vertices}, m = \text{number of polyhedra}, o = \text{number of single vertex sharing})\) number of electron pairs are necessary for the stability of closo polycondensed transition metal clusters. The additional electron pairs required for nido and arachno polyhedra, one and two respectively, are to be added separately. Comparison of this electron count with Mingos’ rule gives a relation between \( n_s \) (number of shared vertices), \( y_b \) (number of bonds between the shared atoms) and \( m \) (number of polyhedra) as \( y_b = 2n_s - 3(m - 1) + o \). The rule is also extended as \( m + n + o + p + 6x - x_s/n_s\{3(m - 1)\} \), (where \( x = \text{number of transition metals}, x_s = \text{number of shared transition metals and} \ n_s = \text{number of shared atoms} \) to the incorporate the electron counts of the metallaboranes. This rule converts to mno rule (where \( x = x_s = 0 \)) for condensed boranes and \( 7n - 2m + o + 3 \) rule (where \( x = n, x_s = n_s \)) for condensed transition metal clusters.
[1.5] References


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